



Time-Resolved EPR Study on Origins of Photoinduced Functionalities by Excited Triplet States in π -Conjugated Systems

江間, 文俊

(Degree)

博士 (学術)

(Date of Degree)

2019-03-25

(Date of Publication)

2021-03-25

(Resource Type)

doctoral thesis

(Report Number)

甲第7443号

(URL)

<https://hdl.handle.net/20.500.14094/D1007443>

※ 当コンテンツは神戸大学の学術成果です。無断複製・不正使用等を禁じます。著作権法で認められている範囲内で、適切にご利用ください。



Doctoral Dissertation

(博 士 論 文)

**Time-Resolved EPR Study on Origins of
Photoinduced Functionalities by Excited Triplet
States in π -Conjugated Systems**

(パイ共役系励起三重項状態による
光機能性の解明)

January 2019

(平成 31 年 1 月)

Graduate School of Science, Kobe University

(神戸大学大学院理学研究科)

Fumitoshi Ema

(江間 文俊)

Contents.....	2
----------------------	----------

Chapter 1

General Introduction	7
-----------------------------------	----------

1.1 Photo-Functional π -Conjugated Organic Materials	7
1.2 Transition Processes between Ground and Excited States	8
1.3 Room Temperature Phosphorescent Organic Crystals	9
1.4 Electron Spin Resonance (ESR) / Electron Paramagnetic Resonance (EPR).....	10
1.5 Goal and Outline of This Study	12
References	15

Chapter 2

Theory.....	25
--------------------	-----------

2.1 Electron Spin Resonance (ESR)	25
2.2 Spin Polarization.....	30
2.3 Excited Triplet State	31
2.4 Spin-Orbit Coupling (SOC) and Intersystem Crossing (ISC).....	35
2.5 Zero-Field Splitting (ZFS) Parameter	42
2.6 Energy Splitting As a Function of Magnetic Field	45
2.7 Zero-Field Splitting (ZFS) and Electronic Structure	49
2.8 EPR Spectrum of Excited Triplet State	51

2.9 Magnetophotoselection	57
2.10 Spin-Spin Dipolar Coupling	61
2.11 Transition Pathway	64
2.12 Electronic Coupling	68
References	70

Chapter 3

Experimental.....	73
3.1 Materials	73
3.2 UV-vis Absorption Measurements	73
3.3 Emission Spectra Measurements	74
3.4 Electro Chemical Measurements	74
3.5 Time-resolved EPR Measurements.....	74
3.6 Theoretical Calculations	75
References	77

Chapter 4

Electronic Structure of Möbius Antiaromatic Excited Triple State of Twisted [28]Hexaphyrin	79
4.1 Chapter Introduction	79
4.2 Materials and Methods.....	82

4.2.1 Materials and Sample Preparations	82
4.2.2 UV-vis Absorption Measurements.....	83
4.2.3 Time-resolved EPR Measurements.....	83
4.2.4 Theoretical Calculations.....	84
4.3 Results.....	86
4.3.1 UV-vis Absorption Measurements for the [26]Hex and [28]Hex.....	86
4.3.2 Time-resolved EPR Measurements for the [26]Hex and [28]Hex.....	86
4.3.3 Molecular Orbital Calculations for the [26]Hex and [28]Hex	87
4.4 Discussion	88
4.4.1 Identification of the ZFS Tensor	88
4.4.2 The Orientation of the Principal D-Tensor Axes	90
4.4.3 Deactivation of the Triplet State of [28]Hex.....	91
4.5 Conclusion	96
Figures.....	98
Tables	111
References.....	121

Chapter 5

Electronic Structure of Room Temperature Phosphorescent Organic

Inclusion Crystals..... 133

5.1 Chapter Introduction	133
--------------------------------	-----

5.2 Materials and Methods.....	135
5.2.1 Materials and Sample Preparations.....	135
5.2.2 Emission Spectra Measurements.....	138
5.2.3 Time-resolved EPR Measurements.....	138
5.2.4 Electrochemical Measurements	139
5.2.5 Theoretical Calculations.....	139
5.2.6 X-ray Crystal Structural Analysis	140
5.3 Results.....	140
5.3.1 Emission Properties of Organic Inclusion Crystals	140
5.3.2 Time-resolved EPR Experiments for the Organic Inclusion Crystals	141
5.4 Discussion	142
5.4.1 Excited Triplet State of the Organic Inclusion Crystals Observed by TREPR Method at Room Temperature	142
5.4.2 Contribution of the Triplet CT Character to the RTP Organic Inclusion Crystals.....	148
5.4.3 Triplet CT Character in the Organic Inclusion Crystals Including Iodine Atom in the Guests.....	155
5.5 Conclusion	157
Figures.....	158
Tables.....	180
References.....	190

Chapter 6

Concluding Remarks..... 201

Acknowledgements..... 204

Chapter 1

General Introduction

1.1 Photo-Functional π -Conjugated Organic Materials

Functional organic dyes have attracted great attention in terms of organic solar cell (OSC), organic light emitting diode (OLED), chemical sensors, bioimaging materials, security protection, and organic mechanoluminochromic materials because of a flexible and low-cost material. Especially, phosphorescent materials have been regarded as useful luminescent materials and they are promising for room-temperature emissive materials with long lifetime and with higher quantum yield.^{1–10}

Expanded porphyrins are known to show considerably red-shifted absorption bands relative to those of porphyrins due to their larger π -conjugation networks.^{11–15} They have attracted great attention as functional dyes, nonlinear optical materials, multi-metal ligands, stable organic radicals, and aromatic and/or antiaromatic molecules.^{12,13} Importantly, some expanded porphyrins have been shown to take on twisted conformations showing the Möbius aromaticity or antiaromaticity.^{12,13,16–19} In Möbius aromatic molecules, the π -orbitals are lying along twisted topologies with phase inversion of the macrocycle like Möbius strip.^{18,20}

In the functional materials including the OLEDs, triplet state is important from a perspective of exciton formation. Namely, when the charge carriers recombine, triplet exciton is produced up to 75% while singlet exciton formation efficiency is restricted to 25%.^{21–24} And also, in these systems, the charge transfer (CT) interaction between the donor and the acceptor molecules, and the distance between the guest and the host in the exciplex affects the efficiency of the electron transfer or the energy transfer.^{25–31} In order

to control of the photoluminescent and electroluminescent properties, the clarification of the electronic structure of phosphorescent compounds in the excited triplet state at room-temperature is needed.

1.2 Transition Processes between Ground and Excited States

When a molecule absorbs light, the molecule becomes an excited state. Then the molecule returns to its ground state going through some processes, such as radiative decays and nonradiative decays. The electronic energy levels of the molecule and its transitions are shown in [Figure 1.1](#). If a molecule in the ground state absorbs light energy, the molecule is transitioned to an excited singlet state. This transition occurs by absorbing light of a specific wavelength and this transition is peculiar to a substance. While a molecule in the excited state loses the energy going through radiative decay and/or nonradiative decay. One of the radiative decay process is fluorescence. This proceeds when the electron in the excited state emits light returning to its ground state. The other radiative decay process is phosphorescence. This occurs when the electron in the excited singlet state is transitioned to an excited triplet state that energy level is lower by intersystem crossing (ISC), in which two electron spins are parallel.

Phosphorescence emission is a spin-forbidden radiative decay process from the lowest excited triplet state (T_1) to the ground state (S_0), while the fluorescence emission is the spin-allowed radiative relaxation process from the lowest excited singlet state (S_1). In the metal-free organic phosphors, the nonradiative process dominates the relaxation processes due to the rate of radiative phosphorescence is slow, because of molecular motion and molecular collision in the solution and/or at room-temperature, and the

excited triplet state is quenched by oxygen (O_2) molecule.^{32,33}

In general, the triplet lifetimes for phosphorescent organic compounds are in the orders of $10^{-6} - 10^1$ s whereas the fluorescence lifetimes are in the orders of $10^{-9} - 10^{-6}$ s for fluorescent organic molecules.¹ However, the quantum yield of the phosphorescent emission from the organic compound is very limited relative to the inorganic and organometallic materials because of a weak spin-orbit coupling. So, precious metals have been used for facilitating the rate of phosphorescence (SOC).^{10,34-37}

1.3 Room Temperature Phosphorescent Organic Crystals

Precious-metal-free phosphors that exhibit highly efficient room temperature phosphorescence (RTP) have attracted great attention as new photofunctional materials because of a low-cost and flexibility. The pure organic RTP materials have been widely promising for organic light-emitting diodes (OLED), time-resolved bioimaging materials and molecular sensing materials due to highly efficient luminescence.^{7,21,38-42}

To achieve the highly efficient phosphorescent emission at room temperature, the intersystem crossing (ISC) from the S_1 state to the T_1 state needs to be faster than fluorescence that is a spin-allowed radiative transition from the S_1 state to the S_0 state and the nonradiative internal conversion (IC).^{10,32,37} However, it has been quite difficult for the organic compounds to emit RTP efficiently because of the slow ISC rate. So, generally, most RTP materials are composed of inorganic or organometallic molecules containing precious-metals such as iridium or platinum because of strong spin-orbit coupling (SOC) rather than organic compound.^{35,36}

In recent years, organic crystals and co-crystals with long lived emission lifetime over the millisecond-order and with high quantum yield at room-temperature have been

reported.^{33,43–51} Then, controls of the emission color and the lifetime have been successful for tuning the emission properties.⁴⁷ These luminescent properties have been achieved because of a restriction of molecular vibrations, molecular collisions, and oxygen quenching thanks to the aggregation and the crystallizations. The long-lived emissions of these organic crystals were assigned to the phosphorescence. Thus, crystallization, solid state, and aggregation,^{48–50,52,53} and in addition the hybrid excited-state configurations ((n, π^*) and (π , π^*) configurations) are the key factors for archiving the persistent efficient pure organic RTP, with a help of the theoretical calculations.^{54–56} Moreover, heavy halogen atoms such as iodine and bromine play an important role in the metal-free pure organic RTP materials to accelerate ISC to effectively generate T_1 state due to heavy atom effect on the SOC and to suppress the molecular motion due to intermolecular halogen-bonding interaction in the RTP crystals. The function and the mechanism of the room-temperature phosphorescence have been studied,^{57–63} however, detailed electronic structure has not been understood yet. In fact, phosphorescent triplet state has not been directly observed at room-temperature very much. There is another radiative relaxation process causing the long lifetime, that is, the thermally activated delayed fluorescence (TADF).⁶⁴

1.4 Electron Spin Resonance (ESR) / Electron Paramagnetic Resonance (EPR)

Electron Spin Resonance (ESR) is a spectroscopic method for studies of paramagnetic species. ESR is often called Electron Paramagnetic Resonance (EPR) with almost the same meaning. This method uses magnetic properties of electrons. The method of EPR is related to that of Nuclear Magnetic Resonance (NMR) which uses magnetic properties of nuclei. EPR method is used in systematic studies of transition

metal salts to research on complex biochemical systems. And tracking and identifying free radicals and their reactions followed both in the liquid and the solid state. Here free radicals are the molecules with unpaired electron. In the most commonly used EPR device, the microwave technique in the frequency range of 9-10 GHz is ordinarily used. EPR spectrum is acquired when continuous wave (CW) EPR sweeps the magnet field. The paramagnetic species are clarified by measurements of the g -factor at the center of the spectrum and line splitting result from hyperfine structure due to nuclear spin.⁶⁵

When the free electron and the unpaired electron have an angular momentum by orbital motion and spin, the magnetic moment appears with them. The magnetic moment is affected from a magnetic field. When a molecular with an unpaired electron or a radical is applied an external magnetic field, the spin of the unpaired electron can align in two different energy levels generating two spin state by Zeeman effect. The magnetic moment of radical can be either parallel to the direction of applied magnetic field corresponds to the lower energy state or antiparallel to the direction of applied magnetic field corresponds to the higher energy state. The two energy levels have different energies, as shown in [Figure 1.2](#). This difference in energy (ΔE) is given by Bohr frequency condition:

$$\Delta E = h\nu = g\beta B_0 \quad (1.1)$$

where, h , ν , and β are the Planck's constant, the microwave frequency, and the Bohr magneton, respectively, and these parameters are invariable during the experiment. g -factor is inversely proportional to B_0 . The g -factor for a free electron is 2.0023.

The magnetic field modulation method is used in the EPR measurement for the purpose of reducing noise and observing the EPR spectrum with high sensitivity. Therefore EPR spectrum is observed as a differential waveform against the spectrum

from the spectroscopic device is observed as an absorption wave pattern.⁶⁵

In a time-resolved EPR (TREPR) method, EPR signal is tracked along the time axis. A continuous type microwave, a pulse light source, and a wide band amplifier are prepared in this method. TREPR method is used to detect intermediate products generated by a pulsed light in nanosecond region to microsecond region. Then short-lived paramagnetic species generated by photochemical reaction can be observed and identified without magnetic field modulation.⁶⁶ In TREPR measurements, the short-lived paramagnetic species or radicals are not in the thermal equilibrium or in the thermal polarization instantly after generation. And there is a great difference between each population. Therefore EPR line is given in emission rather than absorption.

1.5 Goal and Outline of This Study

The goal of this study is to understand the photoinduced functionality of the excited triplet states in π -conjugated systems. Efficient conversion and storage of light energy and electrical energy have been the greatest challenges in the field of solar energy technologies. This is inspired by biological photosynthetic systems that convert photon energy into other stable forms of the energy storage. The principles of energy migration, energy transfer, and electron transfer of the excited singlet and excited triplet states in the intramolecular and intermolecular systems encouraged ones to develop photofunctional systems. Then, organic compounds and their self-assemblies such as π -conjugated and supramolecular materials are one of the candidates for the photofunctional solid-state materials that can absorb and emit wide range of photon energy similar to solar energy. As mentioned above, especially, excited triplet state plays an important role to efficient energy migration, energy transfer, and electron transfer in

terms of controls for quantum yield and lifetime. Thus, it is important to understand the mechanism and the electronic structure that contribute photoinduced functionality of the excited triplet states in the π -conjugated systems. In order to reveal the main purpose, time-resolved EPR (TREPR) method was utilized in combination of UV-vis absorption spectroscopy, and theoretical calculations.

In Chapter 4, the electronic character of the lowest excited triplet (T_1) state of a Möbius aromatic [28]hexaphyrin was elucidated by employing a TREPR method with applied magnetophotoselection measurements at 77 K. Möbius aromatic molecules have attracted great attention as new functional materials because of their π -orbital cyclic conjugations lying along the twisted Möbius topology. Electronic structure in the Möbius strip ring of the T_1 state revealed by analyses of the EPR parameters is discussed. And deactivation process of the T_1 state is also discussed with respect to the electronic configuration and aromaticity/antiaromaticity.

In Chapter 5, the excited triplet state of the organic inclusion crystals consisting of host and guest molecules with halogen (Br and I) atoms were observed using a TREPR method at room temperature. Organic inclusion crystals having Br atom in a guest molecule showed longer-lived emission-lifetime over the milliseconds-order and with higher quantum yield at room-temperature than those without Br and I atoms. The electronic structure, the emission mechanism, and the ISC mechanism clarified by the EPR parameters are discussed. The degree of the intermolecular interaction between the host and the guest estimated by the EPR analyses in combination with the results of the electrochemical measurements of the host and guest molecules is also discussed.

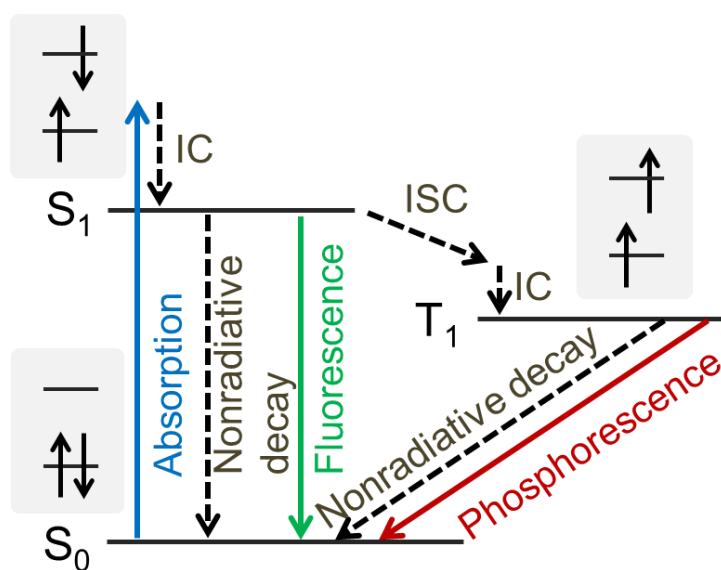


Figure 1.1. Schematic representation of energy diagram.

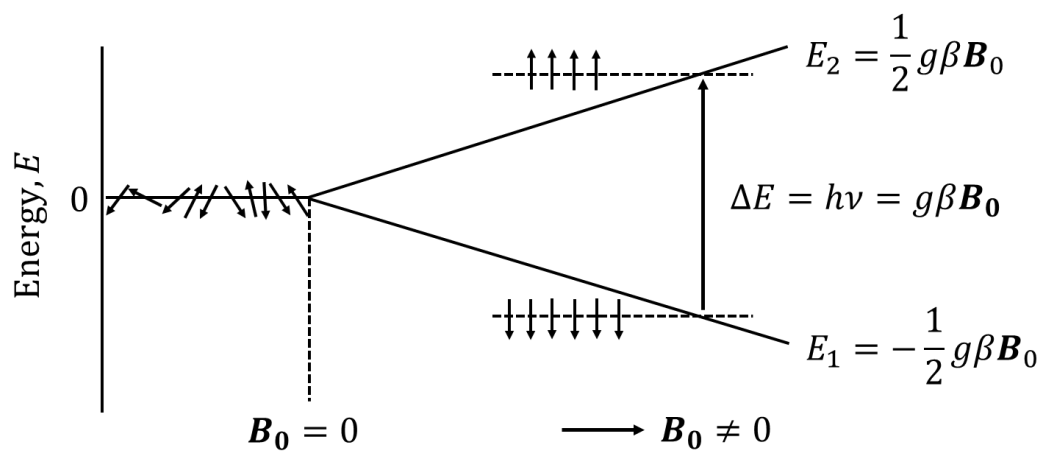


Figure 1.2. Schematic illustration of the EPR transition.

References

- (1) Shao, Y.; Yang, Y. Efficient Organic Heterojunction Photovoltaic Cells Based on Triplet Materials. *Adv. Mater.* **2005**, *17* (23), 2841–2844.
- (2) Gong, Y.; Chen, G.; Peng, Q.; Yuan, W. Z.; Xie, Y.; Li, S.; Zhang, Y.; Tang, B. Z. Achieving Persistent Room Temperature Phosphorescence and Remarkable Mechanochromism from Pure Organic Luminogens. *Adv. Mater.* **2015**, *27* (40), 6195–6201.
- (3) Li, C.; Tang, X.; Zhang, L.; Li, C.; Liu, Z.; Bo, Z.; Dong, Y. Q.; Tian, Y. H.; Dong, Y.; Tang, B. Z. Reversible Luminescence Switching of an Organic Solid: Controllable On-Off Persistent Room Temperature Phosphorescence and Stimulated Multiple Fluorescence Conversion. *Adv. Opt. Mater.* **2015**, *3* (9), 1184–1190.
- (4) Mao, Z.; Yang, Z.; Mu, Y.; Zhang, Y.; Wang, Y. F.; Chi, Z.; Lo, C. C.; Liu, S.; Lien, A.; Xu, J. Linearly Tunable Emission Colors Obtained from a Fluorescent-Phosphorescent Dual-Emission Compound by Mechanical Stimuli. *Angew. Chem. Int. Ed.* **2015**, *54* (21), 6270–6273.
- (5) Xue, P.; Sun, J.; Chen, P.; Wang, P.; Yao, B.; Gong, P.; Zhang, Z.; Lu, R. Luminescence Switching of a Persistent Room-Temperature Phosphorescent Pure Organic Molecule in Response to External Stimuli. *Chem. Commun.* **2015**, *51* (52), 10381–10384.
- (6) Chen, H.; Yao, X.; Ma, X.; Tian, H. Amorphous, Efficient, Room-Temperature Phosphorescent Metal-Free Polymers and Their Applications as Encryption Ink. *Adv. Opt. Mater.* **2016**, *4* (9), 1397–1401.

- (7) Kabe, R.; Notsuka, N.; Yoshida, K.; Adachi, C. Afterglow Organic Light-Emitting Diode. *Adv. Mater.* **2016**, *28* (4), 655–660.
- (8) Kanosue, K.; Ando, S. Polyimides with Heavy Halogens Exhibiting Room-Temperature Phosphorescence with Very Large Stokes Shifts. *ACS Macro Lett.* **2016**, *5*, 1301–1305.
- (9) Wang, C. R.; Gong, Y. Y.; Yuan, W. Z.; Zhang, Y. M. Crystallization-Induced Phosphorescence of Pure Organic Luminogens. *Chinese Chem. Lett.* **2016**, *27* (8), 1184–1192.
- (10) Baroncini, M.; Bergamini, G.; Ceroni, P. Rigidification or Interaction-Induced Phosphorescence of Organic Molecules. *Chem. Commun.* **2017**, *53*, 2081–2093.
- (11) Shin, J.; Furuta, H.; Yoza, K.; Igaraashi, S.; Osuka, A. Meso-Aryl-Substituted Expanded Porphyrins. *J. Am. Chem. Soc.* **2001**, *123*, 7190–7191.
- (12) Saito, S.; Osuka, A. Expanded Porphyrins: Intriguing Structures, Electronic Properties, and Reactivities. *Angew. Chem. Int. Ed.* **2011**, *50* (19), 4342–4373.
- (13) Lim, J. M.; Yoon, Z. S.; Shin, J. Y.; Kim, K. S.; Yoon, M. C.; Kim, D. The Photophysical Properties of Expanded Porphyrins: Relationships between Aromaticity, Molecular Geometry and Non-Linear Optical Properties. *Chem. Commun.* **2009**, 7345 (3), 261–273.
- (14) Misra, R.; Chandrashekar, T. K. Structural Diversity in Expanded Porphyrins. *Acc. Chem. Res.* **2008**, *41* (2), 265–279.
- (15) Shimizu, S.; Osuka, A. Metalation Chemistry of Meso-Aryl-Substituted Expanded Porphyrins. *Eur. J. Inorg. Chem.* **2006**, 1319–1335.
- (16) Tanaka, Y.; Saito, S.; Mori, S.; Aratani, N.; Shinokubo, H.; Shibata, N.; Higuchi, Y.; Yoon, Z. S.; Kim, K. S.; Noh, S. B.; et al. Metalation of Expanded

- Porphyrins: A Chemical Trigger Used to Produce Molecular Twisting and Möbius Aromaticity. *Angew. Chem. Int. Ed.* **2008**, 47 (4), 681–684.
- (17) Jux, N. The Porphyrin Twist: Hückel and Möbius Aromaticity. *Angew. Chem. Int. Ed.* **2008**, 47 (14), 2543–2546.
- (18) Yoon, Z. S.; Osuka, A.; Kim, D. Möbius Aromaticity and Antiaromaticity in Expanded Porphyrins. *Nat. Chem.* **2009**, 1 (2), 113–122.
- (19) Osuka, A.; Saito, S. Expanded Porphyrins and Aromaticity. *Chem. Commun.* **2011**, 47 (15), 4330–4339.
- (20) Sankar, J.; Mori, S.; Saito, S.; Rath, H.; Suzuki, M.; Inokuma, Y.; Shinokubo, H.; Suk Kim, K.; Yoon, Z. S.; Shin, J.-Y.; et al. Unambiguous Identification of Möbius Aromaticity for Meso-Aryl-Substituted [28]Hexaphyrins(1.1.1.1.1.1). *J. Am. Chem. Soc.* **2008**, 130 (41), 13568–13579.
- (21) Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. Highly Efficient Phosphorescent Emission from Organic Electroluminescent Devices. *Nature* **1998**, 395 (September), 151–154.
- (22) Baldo, M. A.; Thompson, M. E.; Forrest, S. R. High-Efficiency Fluorescent Organic Light-Emitting Devices Using a Phosphorescent Sensitizer. *Nature* **2000**, 403 (6771), 750–753.
- (23) Furukawa, T.; Nakanotani, H.; Inoue, M.; Adachi, C. Dual Enhancement of Electroluminescence Efficiency and Operational Stability by Rapid Upconversion of Triplet Excitons in OLEDs. *Sci. Rep.* **2015**, 5, 8429.
- (24) Väh, S.; Tvingstedt, K.; Auth, M.; Sperlich, A.; Dabulienė, A.; Grazulevicius, J. V.; Stakhira, P.; Cherpak, V.; Dyakonov, V. Direct Observation of Spin States Involved in Organic Electroluminescence Based on Thermally Activated Delayed

- Fluorescence. *Adv. Opt. Mater.* **2017**, *5*, 1600926.
- (25) Zhang, Q.; Li, B.; Huang, S.; Nomura, H.; Tanaka, H.; Adachi, C. Efficient Blue Organic Light-Emitting Diodes Employing Thermally Activated Delayed Fluorescence. *Nat. Photonics* **2014**, *8* (March), 326–332.
- (26) Zhou, D.; Siboni, H. Z.; Wang, Q.; Liao, L.; Aziz, H. Host to Guest Energy Transfer Mechanism in Phosphorescent and Fluorescent Organic Light-Emitting Devices Utilizing Exciplex-Forming Hosts. *J. Phys. Chem. C* **2014**, *118*, 24006–24012.
- (27) Hontz, E.; Chang, W.; Congreve, D. N.; Bulović, V.; Baldo, M. A.; Van Voorhis, T. The Role of Electron-Hole Separation in Thermally Activated Delayed Fluorescence in Donor-Acceptor Blends. *J. Phys. Chem. C* **2015**, *119* (45), 25591–25597.
- (28) Zhu, W.; Zheng, R.; Zhen, Y.; Yu, Z.; Dong, H.; Fu, H.; Shi, Q.; Hu, W. Rational Design of Charge-Transfer Interactions in Halogen-Bonded Co-Crystals toward Versatile Solid-State Optoelectronics. *J. Am. Chem. Soc.* **2015**, *137* (34), 11038–11046.
- (29) Nishikitani, Y.; Inokuchi, N.; Nishide, H.; Uchida, S.; Shibamura, T.; Nishimura, S. Effect of π -Conjugated Polyelectrolyte on Performance of White Polymer Light-Emitting Diodes Based on Excitons and Exciplexes Having Long Intermolecular Distances. *J. Phys. Chem. C* **2016**, *120* (26), 13976–13986.
- (30) Subeesh, M. S.; Shanmugasundaram, K.; Sunesh, C. D.; Chitumalla, R. K.; Jang, J.; Choe, Y. Host-Dopant System to Generate Bright Electroluminescence from Small Organic Molecule Functionalized Light-Emitting Electrochemical Cells. *J. Phys. Chem. C* **2016**, *120* (22), 12207–12217.

- (31) Nakanotani, H.; Furukawa, T.; Morimoto, K.; Adachi, C. Long-Range Coupling of Electron-Hole Pairs in Spatially Separated Organic Donor-Acceptor Layers. *Sci. Adv.* **2016**, 2 (2), e1501470.
- (32) Kwon, M. S.; Yu, Y.; Coburn, C.; Phillips, A. W.; Chung, K.; Shanker, A.; Jung, J.; Kim, G.; Pipe, K.; Forrest, S. R.; et al. Suppressing Molecular Motions for Enhanced Room-Temperature Phosphorescence of Metal-Free Organic Materials. *Nat. Commun.* **2015**, 6, 8947.
- (33) Shimizu, M.; Shigitani, R.; Nakatani, M.; Kuwabara, K.; Miyake, Y.; Tajima, K.; Sakai, H.; Hasobe, T. Siloxy Group-Induced Highly Efficient Room Temperature Phosphorescence with Long Lifetime. *J. Phys. Chem. C* **2016**, 120 (21), 11631–11639.
- (34) Yan, D.; Evans, D. G. Molecular Crystalline Materials with Tunable Luminescent Properties: From Polymorphs to Multi-Component Solids. *Mater. Horizons* **2014**, 1 (1), 46–57.
- (35) Yang, X.; Yan, D. Strongly Enhanced Long-Lived Persistent Room Temperature Phosphorescence Based on the Formation of Metal–Organic Hybrids. *Adv. Opt. Mater.* **2016**, 4 (6), 897–905.
- (36) You, Y.; Cho, S.; Nam, W. Cyclometalated Iridium(III) Complexes for Phosphorescence Sensing of Biological Metal Ions. *Inorg. Chem.* **2014**, 53 (4), 1804–1815.
- (37) Zhao, J.; Wu, W.; Sun, J.; Guo, S. Triplet Photosensitizers: From Molecular Design to Applications. *Chem. Soc. Rev.* **2013**, 42 (12), 5323–5351.
- (38) Lee, J.; Chen, H. F.; Batagoda, T.; Coburn, C.; Djurovich, P. I.; Thompson, M. E.; Forrest, S. R. Deep Blue Phosphorescent Organic Light-Emitting Diodes with

- Very High Brightness and Efficiency. *Nat. Mater.* **2016**, *15* (1), 92–98.
- (39) Zhen, X.; Tao, Y.; An, Z.; Chen, P.; Xu, C.; Chen, R.; Huang, W.; Pu, K. Ultralong Phosphorescence of Water-Soluble Organic Nanoparticles for In Vivo Afterglow Imaging. *Adv. Mater.* **2017**, *29* (33), 1–7.
- (40) Hayduk, M.; Riebe, S.; Voskuhl, J. Phosphorescence Through Hindered Motion of Pure Organic Emitters. *Chem. - A Eur. J.* **2018**, *24* (47), 12221–12230.
- (41) Gan, N.; Shi, H.; An, Z.; Huang, W. Recent Advances in Polymer-Based Metal-Free Room-Temperature Phosphorescent Materials. *Adv. Funct. Mater.* **2018**, *1802657*, 1–24.
- (42) Xiao, L.; Wu, Y.; Yu, Z.; Xu, Z.; Li, J.; Liu, Y.; Yao, J.; Fu, H. Room-Temperature Phosphorescence in Pure Organic Materials: Halogen Bonding Switching Effects. *Chem. - A Eur. J.* **2018**, *24* (8), 1801–1805.
- (43) Yuan, W. Z.; Shen, X. Y.; Zhao, H.; Lam, J. W. Y.; Tang, L.; Lu, P.; Wang, C.; Liu, Y.; Wang, Z.; Zheng, Q.; et al. Crystallization-Induced Phosphorescence of Pure Organic Luminogens at Room Temperature. *J. Phys. Chem. C* **2010**, *114*, 6090–6099.
- (44) Bolton, O.; Lee, K.; Kim, H.-J.; Lin, K. Y.; Kim, J. Activating Efficient Phosphorescence from Purely Organic Materials by Crystal Design. *Nat. Chem.* **2011**, *3* (3), 205–210.
- (45) Hirata, S.; Totani, K.; Zhang, J.; Yamashita, T.; Hironori, K.; Marder, S. R.; Watanabe, T.; Adachi, C. Efficient Persistent Room Temperature Phosphorescence in Organic Amorphous Materials under Ambient Conditions. *Adv. Funct. Mater.* **2013**, *23* (27), 3386–3397.
- (46) Hirata, S.; Totani, K.; Kaji, H.; Vacha, M.; Watanabe, T.; Adachi, C. Reversible

- Thermal Recording Media Using Time-Dependent Persistent Room Temperature Phosphorescence. *Adv. Opt. Mater.* **2013**, *1* (6), 438–442.
- (47) An, Z.; Zheng, C.; Tao, Y.; Chen, R.; Shi, H.; Chen, T.; Wang, Z.; Li, H.; Deng, R.; Liu, X.; et al. Stabilizing Triplet Excited States for Ultralong Organic Phosphorescence. *Nat. Mater.* **2015**, *14* (7), 685–690.
- (48) Ventura, B.; Bertocco, A.; Braga, D.; Catalano, L.; D’Agostino, S.; Grepioni, F.; Taddei, P. Luminescence Properties of 1,8-Naphthalimide Derivatives in Solution, in Their Crystals, and in Co-Crystals: Toward Room-Temperature Phosphorescence from Organic Materials. *J. Phys. Chem. C* **2014**, *118* (32), 18646–18658.
- (49) Mei, J.; Hong, Y.; Lam, J. W. Y.; Qin, A.; Tang, Y.; Tang, B. Z. Aggregation-Induced Emission: The Whole Is More Brilliant than the Parts. *Adv. Mater.* **2014**, *26* (31), 5429–5479.
- (50) Li, Q.; Li, Z. The Strong Light-Emission Materials in the Aggregated State: What Happens from a Single Molecule to the Collective Group. *Adv. Sci.* **2017**, 1600484.
- (51) Shimizu, M.; Kinoshita, T.; Shigitani, R.; Miyake, Y.; Tajima, K. Use of Silylmethoxy Groups as Inducers of Efficient Room Temperature Phosphorescence from Precious-Metal-Free Organic Luminophores. *Mater. Chem. Front.* **2018**, *2* (2), 347–354.
- (52) Maity, S.; Mazumdar, P.; Shyamal, M.; Sahoo, G. P.; Misra, A. Crystal Induced Phosphorescence from Benz(a)Anthracene Microcrystals at Room Temperature. *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2016**, *157*, 61–68.
- (53) Shimizu, M.; Kimura, A.; Sakaguchi, H. Room-Temperature Phosphorescence of

- Crystalline 1,4-Bis(Aroyl)-2,5-Dibromobenzenes. *European J. Org. Chem.* **2016**, 2016 (3), 467–473.
- (54) Ma, H.; Shi, W.; Ren, J.; Li, W.; Peng, Q.; Shuai, Z. Electrostatic Interaction-Induced Room-Temperature Phosphorescence in Pure Organic Molecules from QM/MM Calculations. *J. Phys. Chem. Lett.* **2016**, 7 (15), 2893–2898.
- (55) Yang, Z.; Mao, Z.; Zhang, X.; Ou, D.; Mu, Y.; Zhang, Y.; Zhao, C.; Liu, S.; Chi, Z.; Xu, J.; et al. Intermolecular Electronic Coupling of Organic Units for Efficient Persistent Room-Temperature Phosphorescence. *Angew. Chem. Int. Ed.* **2016**, 55 (6), 2181–2185.
- (56) Zhao, W.; He, Z.; Lam, J. W. Y.; Peng, Q.; Ma, H.; Shuai, Z.; Bai, G.; Hao, J.; Tang, B. Z. Rational Molecular Design for Achieving Persistent and Efficient Pure Organic Room-Temperature Phosphorescence. *Chem* **2016**, 1 (4), 592–602.
- (57) Mani, T.; Tanabe, M.; Yamauchi, S.; Tkachenko, N. V.; Vinogradov, S. A. Modulation of Visible Room Temperature Phosphorescence by Weak Magnetic Fields. *J. Phys. Chem. Lett.* **2012**, 3 (21), 3115–3119.
- (58) Reineke, S.; Baldo, M. A. Room Temperature Triplet State Spectroscopy of Organic Semiconductors. *Sci. Rep.* **2014**, 4, 3797.
- (59) Katsurada, Y.; Hirata, S.; Totani, K.; Watanabe, T.; Vacha, M. Photoreversible On-Off Recording of Persistent Room-Temperature Phosphorescence. *Adv. Opt. Mater.* **2015**, 3 (12), 1726–1737.
- (60) Kuno, S.; Akeno, H.; Ohtani, H.; Yuasa, H. Visible Room-Temperature Phosphorescence of Pure Organic Crystals via a Radical-Ion-Pair Mechanism. *Phys. Chem. Chem. Phys.* **2015**, 17 (24), 15989–15995.

- (61) Chen, X.; Xu, C.; Wang, T.; Zhou, C.; Du, J.; Wang, Z.; Xu, H.; Xie, T.; Bi, G.; Jiang, J.; et al. Versatile Room-Temperature-Phosphorescent Materials Prepared from N-Substituted Naphthalimides: Emission Enhancement and Chemical Conjugation. *Angew. Chem. Int. Ed.* **2016**, 55 (34), 9872–9876.
- (62) Hirata, S.; Vacha, M. Circularly Polarized Persistent Room-Temperature Phosphorescence from Metal-Free Chiral Aromatics in Air. *J. Phys. Chem. Lett.* **2016**, 7 (8), 1539–1545.
- (63) Wu, H.; Zhao, P.; Li, X.; Chen, W.; Ågren, H.; Zhang, Q.; Zhu, L. Tuning for Visible Fluorescence and Near-Infrared Phosphorescence on a Unimolecular Mechanically Sensitive Platform via Adjustable CH– π Interaction. *ACS Appl. Mater. Interfaces* **2017**, 9 (4), 3865–3872.
- (64) Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi, C. Highly Efficient Organic Light-Emitting Diodes from Delayed Fluorescence. *Nature* **2012**, 492 (7428), 234–238.
- (65) Lund, A.; Shiotani, M.; Shimada, S. *Principles and Applications of ESR Spectroscopy*; Springer Science+Business Media B.V: Dordrecht Heidelberg London New York, 2011.
- (66) Murai, H.; Imamura, T.; Obi, K. Time-Resolved ESR Detection of Benzophenone $N\pi^*$ Triplet State in Glassy Matrices at 77 K. *Chem. Phys. Lett.* **1982**, 87 (3), 295–298.

Chapter 2

Theory

2.1 Electron Spin Resonance (ESR)¹

A paramagnetic species includes atoms, molecules, or ions with permanent magnetic dipoles. In the case of the hydrogen atom that contains a single electron, a magnetic dipole μ arises by the motion of the electron about the nucleus. Figure 2.1 shows an illustration relationship between angular momentum of the electron moving around the nucleus and magnetic moment. For a current loop (I), it has $\mu = I \cdot A$ (A is enclosed area of the current loop). The current is decided by the electronic charge ($-e$) and speed (v). For a circular orbit, the enclosed area is $A = \pi r^2$, the current $I = -e \cdot v / (2\pi r)$. The magnetic moment becomes $\mu = -e \cdot v \cdot r / 2\pi r = -e \cdot L \cdot r / (2m_e)$, where L is the orbital angular momentum of the electron, which can be written in vector as:

$$\boldsymbol{\mu} = -\frac{e}{2m_e} \mathbf{L} \quad (2.1)$$

The angular momentum of atoms is quantised and can only take the discrete values

$$L = \frac{h}{2\pi} \sqrt{l(l+1)} \quad (2.2)$$

where h is the Planck constant and l is the orbital quantum number that can take the values 0, 1, 2, Also the components of the vector $\mathbf{L}$ are quantised. For the z component, it has:

$$L = \frac{h}{2\pi} m_l, \quad m_l = \pm l, \pm(l-1), \pm(l-2), \dots, \pm 1, 0 \quad (2.3)$$

The energy E_m of a magnetic dipole in a magnetic field (B) directed along z is given by the product as a Bohr magneton:

$$E_m = -\boldsymbol{\mu} \cdot \mathbf{B} = \mu_B \cdot B \cdot m_l, \quad \mu_B = \frac{eh}{4\pi m_e} \quad (2.4)$$

Thus, the energy becomes split in $(2l+1)$ levels.

Atoms having an odd number of electrons are paramagnetic. On the contrary, chemical species are diamagnetic in most instances. An s -orbital ($l = 0$) can include two electrons with different spins, $m_s = \pm 1/2$. Three p -orbitals ($l = 1$) have different $m_l = \pm 1, 0$. Each can include two electrons with different spins. The ions obviously have completely filled electron shells. Closed shells cannot possess spin angular momentum, because the electrons with different spins are paired. There is not angular momentum as well.

Free radicals are molecules that have been modified to include an unpaired electron, and they are paramagnetic. Most free radicals are unstable, and they appear as intermediate products in various chemical reactions. Under suitable conditions, free radicals can have sufficient lifetime to be observed in the liquid. In the solid state, free radicals can become stabilized almost indefinitely in many materials.

Triplet state molecules include two unpaired electrons with parallel spins. For example, triplet state molecules can be generated by irradiation with UV and visible light, so the energy of these becomes excited. The total spin quantum number is $S = 1$ ($1/2+1/2$).

The hydrogen atom in the ground state has $l = 0$, yet it is paramagnetic, because the spin angular momentum (S) of the electron cause a magnetic moment similar to that from the orbit. The spin angular momentum is quantised as well and has the magnitude:

$$S = \frac{h}{2\pi} \sqrt{s(s+1)} \quad (2.5)$$

where $s = 1/2$ for an electron. The energy in a magnetic field becomes:

$$E_m = g\mu_B B m_s, \quad m_s = \pm 1/2 \quad (2.6)$$

where g is g -factor. Thus, the energy becomes split in $(2s+1) = 2$ (Zeeman levels) as shown in [Figure 2.2](#). A transition between the two Zeeman levels can be induced if the

system takes up energy in the form of electromagnetic radiation of a suitable frequency (ν). Then the resonance condition applies:

$$h\nu = E_m(m_s = 1/2) - E_m(m_s = -1/2) = g\mu_B B \quad (2.7)$$

The frequency is usually maintained constant, and the magnetic field strength is varied so that resonance occurs. Then the system will absorb energy from the electromagnetic field, which includes both an electric and a magnetic component. The magnetic dipole transitions are induced by magnetic field vector (B_1). [Figure 2.3](#) represents classical model how this field is oriented perpendicular to the static field (B), in contrast, the B_1 field vector rotates about the direction of static field (B). The magnetic moment precesses about the static field (B) with an angular frequency ($\omega_L = e/(2m_e) \cdot B$), the Larmor precession of the electron spin magnetic moment ($\omega_L = g e/(2m_e) \cdot B = \gamma B$), where the gyromagnetic ratio γ has been introduced. When the rotating magnetic field follows the magnetic moment, resonance occurs, giving a torque that makes the moment flip its orientation, namely when $\nu = \nu_L$ (or $\omega = \omega_L$; $\omega = 2\pi\nu$).

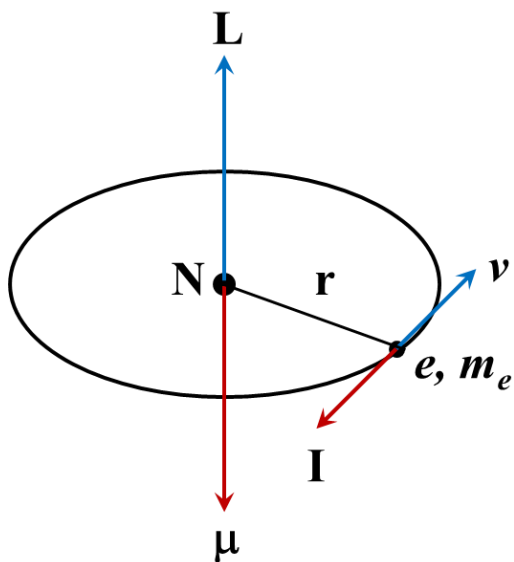


Figure 2.1. Classical model representing relationship between angular momentum ($L = me \cdot v \cdot r$) of electron (e) moving around a nucleus (N) and magnetic moment (μ).

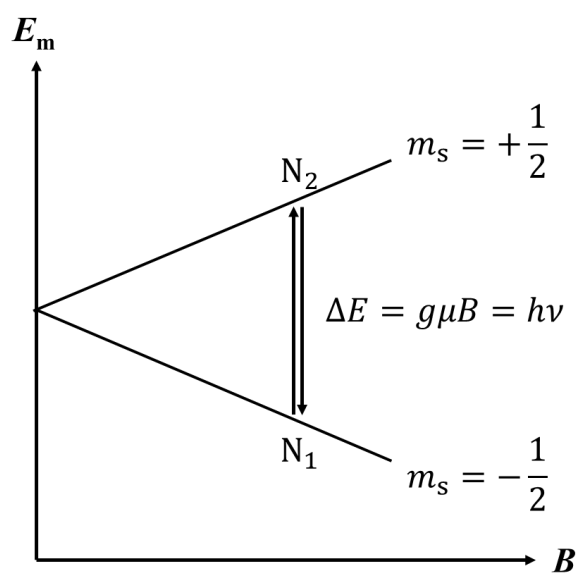


Figure 2.2. Zeeman splitting of energy levels of an electron placed in a magnetic field (B).

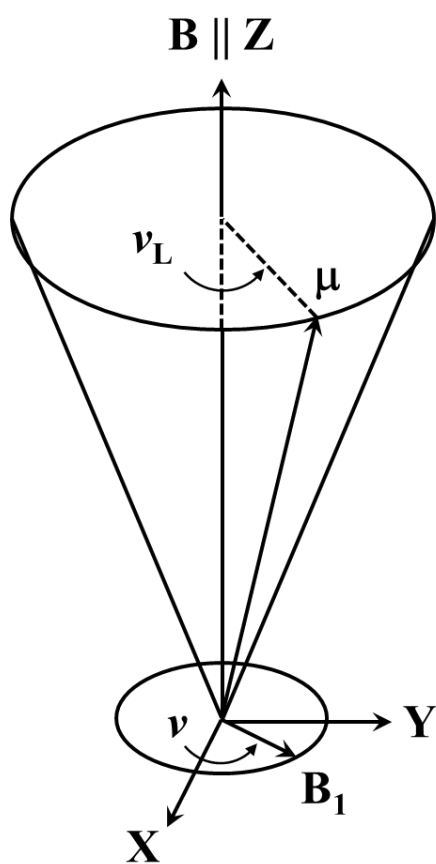


Figure 2.3. Larmor precession of magnetic moment (μ) about stationary field (B).

2.2 Spin Polarization^{1,2}

Resonance absorption can be detected only if there is a population difference between the two spin levels. When the number of species containing N spins are placed in a steady magnetic, and there are N_1 spins in the lower state and N_2 spins in the upper state ($N_1 + N_2 = N$) as shown in [Figure 2.2](#), there is a slight excess of spins in the “1” state in thermal equilibrium. At equilibrium, the ratio is

$$\frac{N_2}{N_1} = e^{-\Delta E/kT} = e^{-g\mu_B B/kT} \quad (2.8)$$

predicted by the Boltzmann distribution. The spin state changes from the lower to the higher state by the absorption of energy from microwave at resonance. If the energy of the higher state could not be released, the number of species in the two states would rapidly become equal ($N_1 = N_2$). At ordinary temperature, $g\mu_B B \ll kT$, and the Boltzmann factor $g\mu_B B/kT$ is approximately $1 + (g\mu_B B/kT)$. The populations of the spin states are almost equal, then

$$N_1 = \frac{1}{2}N \left[1 + \frac{g\mu_B B}{2kT} \right], \quad N_2 = \frac{1}{2}N \left[1 - \frac{g\mu_B B}{2kT} \right], \quad N_2 - N_1 = \frac{g\mu_B B}{2kT}N \quad (2.9)$$

are given. To obtain the strong EPR signal, ΔE must be large, and the sensitivity increases with increasing energy difference ΔE , namely, the microwave frequency.

2.3 Excited Triplet State^{2,3}

Triplet states are important intermediates of organic chemistry, and the various triplet molecules are available via photochemical excitation techniques. A molecule exists in a triplet when its total spin angular momentum quantum number $S = 1$. A triplet state is a paramagnetic even-electron species that possesses three distinct but energetically similar electronic states in consequence of the magnetic interaction of two unpaired electron spins. Thus, a triplet should display paramagnetism in a magnetic field. This paramagnetism serves as the basis for experimental magnetic susceptibility and electron spin resonance studies of the triplet state.

A triplet may result whenever a molecule possesses two electrons that both orbitals are unpaired and spins are unpaired. Orbital unpairing of electrons results when a molecule absorbs a photon of UV or visible light. Direct formation of a triplet as results of this photon absorption is a very improbable process because both orbit and spin of the electron would have to change simultaneously. Thus, a singlet state is generally formed by absorption of light. However, quite often the lifetime of this single state is sufficiently long to allow the spin of one of the two electrons to invert, thereby generating a triplet as shown in [Figure 2.4](#). Some of the important physical properties of a molecule in the triplet state are paramagnetism, absorption between triplet sublevels, electronic absorption from the lowest triplet to upper triplets, and electronic emission from the lowest triplet to a lower singlet ground state if the triplet level is not the ground state.

The paramagnetism of the triplet caused by the interaction of unpaired spins and the fact that an unpaired spins represents a paramagnetic effect in a magnetic field. Absorption between triplet sublevels would be observed directly by using an electron

spin resonance spectrometer. For most organic molecules, the lowest triplet state is an excited electronic state and may emit light and pass to the ground singlet state. Because light absorption to generate a triplet from a singlet is improbable, the symmetrically related emission of light from a triplet retuning to a ground state is likewise improbable. This phenomenon is known as phosphorescence and it is to be contrasted with fluorescence, the emission of light from an excited singlet state retuning to a singlet ground state. Phosphorescence that shows long-lived emission was the first method employed to study triplets. Even paramagnetism is not an infallible for a triplet state because free radicals which are also paramagnetic are often generated by the absorption of light. Electron spin resonance (ESR)/electron paramagnetic resonance (EPR) is the most powerful method for establishing that a molecule is in its triplet state.

Two electrons have well known symmetry property under exchange required by the Pauli principle. The total spin angular momentum for vector for two electrons is $S = s_1 + s_2$ ($=1/2 + 1/2$) = 1 (triplet state) or 0 (singlet state), and the possible wavefunctions are

$$\begin{aligned} |T_+ \rangle &= |\alpha(1)\alpha(2) \rangle \\ |T_0 \rangle &= \frac{1}{\sqrt{2}}(|\alpha(1)\beta(2) \rangle + |\beta(1)\alpha(2) \rangle) \\ |T_- \rangle &= |\beta(1)\beta(2) \rangle \end{aligned} \tag{2.10}$$

for the triplet spin state ($S = 1$)

$$|S \rangle = \frac{1}{\sqrt{2}}(|\alpha(1)\beta(2) \rangle - |\beta(1)\alpha(2) \rangle)$$

for the singlet spin state ($S = 0$). [Figure 2.5](#) illustrates spin states of the singlet and triplets. In the ground state of an organic molecule, each bonding orbital holds two electrons and the all the spins are paired. To uncouple a pair of electrons, it is important to take one electron from a doubly occupied orbital and promote it to a vacant orbital of

higher energy. The promotion energy is least if one excites an electron from the highest filled orbital into the lowest empty orbital. The electrostatic exchange energy of the two electrons is large and negative when the spins are parallel. Thus, triplet usually lies lower than the singlet. The energy gap between the ground singlet state and the excited triplet state is determined by the difference between the orbital promotion energy and the exchange integral.

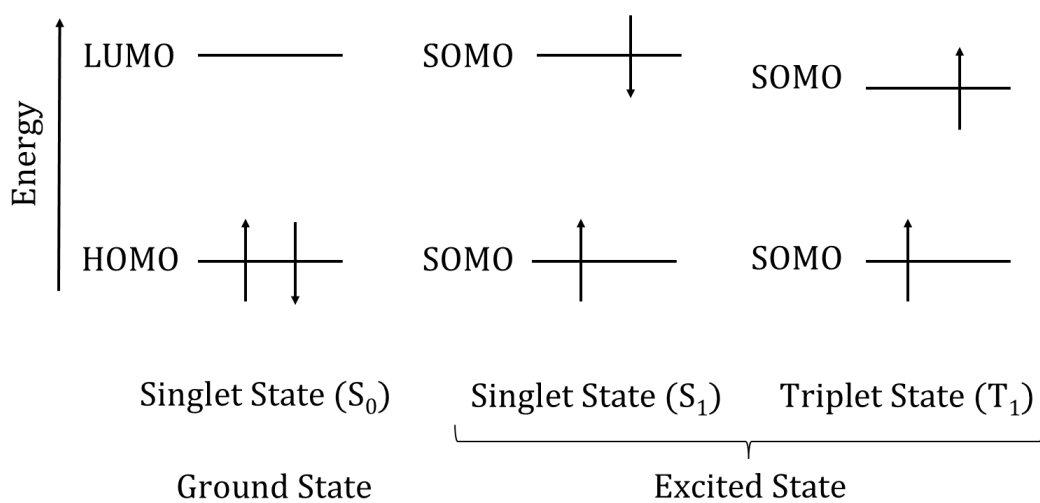


Figure 2.4. Simplified molecular orbital (MO) description of singlets and triplets.

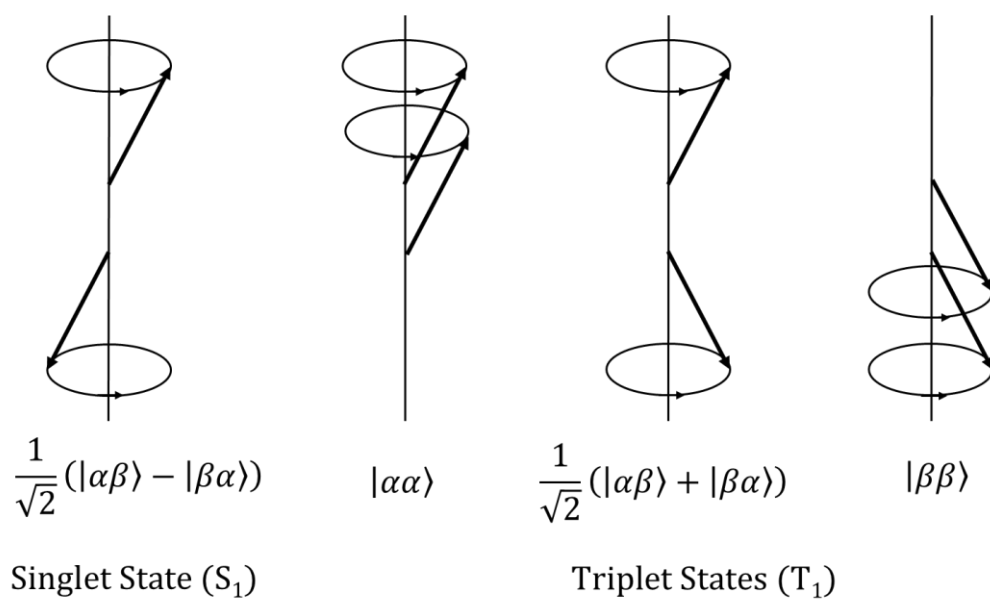


Figure 2.5. Simplified molecular orbital (MO) description of singlets and triplets.

2.4 Spin-Orbit Coupling (SOC) and Intersystem Crossing (ISC)⁴⁻⁶

An electron is a charged particle, so its orbital angular momentum generates a magnetic field. An electric current in a loop generates a magnetic field in an electromagnet. Namely, an electron with orbital angular momentum acts like a tiny bar magnet. An electron also has a spin angular momentum, and it also acts like a tiny bar magnet. The magnet caused by the spin interacts with the magnet caused by the orbital motion and results in the interaction called spin-orbit coupling (SOC), as shown in [Figure 2.6](#). The strength of the SOC increases sharply with atomic number.

SOC mediates the transition between the excited singlet and excited triplet states. The degree of SOC is represented by the following Hamiltonian

$$\hat{H}_{SO} = \sum_i \xi_i(r_i) \hat{\mathbf{l}}_i \cdot \hat{\mathbf{s}}_i \quad (2.11)$$

$$\xi(r) = \frac{Ze^2}{8\pi\epsilon_0 m_e^2 c^2 r^3} \quad (2.12)$$

where $\hat{\mathbf{s}}_i$ is the spin angular moment of electron i and $\hat{\mathbf{l}}_i$ is the orbital angular moment of electron i , r_i is a distance between the atomic nuclei and the electrons, ξ is a SOC constant, Z is the atomic number, e is the charge at electron, m_e is a mass of the electron, and c is the light speed. This means that SOC becomes larger with the increasing atomic number, as known to be heavy atom effect. When the orbital configurations in the singlet and the triplet states are different, the SOC becomes large.

If the only spin functions are different between the singlet and the triplet states, SOC between them is 0. So, different orbital configuration is needed between the singlet and the triplet states, then angular momentum change with respect to the molecular axis is also needed when an electron moves from an orbital to the other orbital. Namely, the orbital on the atom rotates with respect to a certain orbital because the molecular orbital is combined of the each atomic orbital. For example, p_x orbital rotates around the z axis

to be in π orbital. In the matrix elements of the spin-orbit operator between the zero-order (spin-free) (n, π^*) states of nitrogen heterocyclics, to the first order, there is no SOC between singlet and triplet states of the same configuration. The coupling between states of different configurations due to differences in the occupancy of the π^* orbitals, however, including the same nonbonding orbital, have matrix elements similar to those caused by the coupling between (π, π^*) states. As mentioned by El-Sayed, the enhancement of the efficiency of the intersystem crossing in nitrogen heterocyclics with the lowest singlet state of the (n, π^*) type might be because of a $S(n, \pi^*) \rightarrow T(\pi, \pi^*)$ rather than a $S(n, \pi^*) \rightarrow T(n, \pi^*)$ radiationless process by the vibrational overlap consideration. Figure 2.7 shows schematic representation of the ISC process between (n, π^*) and (π, π^*) as an example of a carbonyl compound.

When the spin angular momentum and the orbital angular momentum interact with each other, the directions of the electron spin and the orbit influence each other. Since the molecular orbital reflects the shape of the molecule, the spins align in a specific direction in the molecule. For example, the spins are aligned in perpendicular to the molecular plane in planar molecules. In the presence of SOC, the direction of the spin changes to another direction in the molecule.

Here, the SOC operator as expressed by equation (2.11) is written as follows to apply to the excited triplet state

$$\begin{aligned}\hat{H}_{SO} &= \xi_1 \hat{\mathbf{l}}_1 \cdot \hat{\mathbf{s}}_1 + \xi_2 \hat{\mathbf{l}}_2 \cdot \hat{\mathbf{s}}_2 \\ &= \hat{H}_{SO}^x + \hat{H}_{SO}^y + \hat{H}_{SO}^z\end{aligned}\tag{2.13}$$

where 1 and 2 represent the two unpaired electrons. The SOC between the two states is expressed by the integral of the orbital part and the spin part. When the eigenfunctions of the spin sublevels (T_x , T_y , and T_z) in the zero field are used as the basis,

$\hat{H}_{SO}^x, \hat{H}_{SO}^y, \hat{H}_{SO}^z$ are divided into two parts, as follows.

$$\begin{aligned}\hat{H}_{SO}^x &= \frac{1}{2}(\xi_1 l_{1x} + \xi_2 l_{2x})(s_{1x} + s_{2x}) + \frac{1}{2}(\xi_1 l_{1x} - \xi_2 l_{2x})(s_{1x} - s_{2x}) \\ \hat{H}_{SO}^y &= \frac{1}{2}(\xi_1 l_{1y} + \xi_2 l_{2y})(s_{1y} + s_{2y}) + \frac{1}{2}(\xi_1 l_{1y} - \xi_2 l_{2y})(s_{1y} - s_{2y}) \\ \hat{H}_{SO}^z &= \frac{1}{2}(\xi_1 l_{1z} + \xi_2 l_{2z})(s_{1z} + s_{2z}) + \frac{1}{2}(\xi_1 l_{1z} - \xi_2 l_{2z})(s_{1z} - s_{2z})\end{aligned}\quad (2.14)$$

When the eigenfunctions of the spin sublevels (T_{+1} , T_0 , and T_{-1}) as a function of the magnetic field are used as the basis, elevator operators ($l_{\pm 1} = l_x \pm il_y$, $s_{\pm 1} = s_x \pm is_y$) are used and are written as

$$\hat{H}_{SO} = \xi_1 \left[l_{1z}s_{1z} + \frac{1}{2}(l_{1-}s_{1+} + l_{1+}s_{1-}) \right] + \xi_2 \left[l_{2z}s_{2z} + \frac{1}{2}(l_{2-}s_{2+} + l_{2+}s_{2-}) \right] \quad (2.15)$$

Next, the matrix elements of the SOC between the excited singlet and the excited triplet states are considered. The zero-order wave function of the excited singlet and the excited triplet states are represented as

$$\Psi_S = \Psi_S \cdot |S(1, 2)\rangle = \frac{1}{\sqrt{2}}\xi_1\{\Psi_l(1)\Psi_m(2) + \Psi_m(1)\Psi_l(2)\}|S(1, 2)\rangle \quad (2.16)$$

$$\Psi_{T_i} = \Psi_{T_i} \cdot |T_i(1, 2)\rangle = \frac{1}{\sqrt{2}}\xi_1\{\Psi_l(1)\Psi_m(2) - \Psi_m(1)\Psi_l(2)\}|T_i(1, 2)\rangle \quad (2.17)$$

where, Ψ_S and Ψ_{T_i} are the wave function of the orbit part, $|S(1, 2)\rangle$ and $|T_i(1, 2)\rangle$ are the wave function of the spin part, and i is the triplet sublevels for x, y, and z. The spin function in the singlet state and the spin functions in the triplet states as eigenfunction of the zero-field are exhibited as follows.

$$\begin{aligned}|S\rangle &= \frac{1}{\sqrt{2}}|\alpha_1\beta_2 - \beta_1\alpha_2\rangle \\ |T_x\rangle &= \frac{1}{\sqrt{2}}|\beta_1\beta_2 - \alpha_1\alpha_2\rangle \\ |T_y\rangle &= \frac{i}{\sqrt{2}}|\beta_1\beta_2 + \alpha_1\alpha_2\rangle \\ |T_z\rangle &= \frac{1}{\sqrt{2}}|\alpha_1\beta_2 + \beta_1\alpha_2\rangle\end{aligned}\quad (2.18)$$

Then, matrix elements are described as following

$$\langle \Psi_S | \hat{H}_{SO}^i | \Psi_{T_i} \rangle = \frac{1}{2} \langle \Psi_S | (\xi_1 l_{1i} - \xi_2 l_{2i}) | \Psi_T \rangle \quad (i = x, y, z) \quad (2.19)$$

$$\langle \Psi'_{T_i} | \hat{H}_{SO}^j | \Psi_{T_k} \rangle = \frac{i}{2} \langle \Psi'_T | (\xi_1 l_{1j} + \xi_2 l_{2j}) | \Psi_T \rangle \quad (i \neq j \neq k) \quad (2.20)$$

$$\langle \Psi'_{T_i} | \hat{H}_{SO}^k | \Psi_{T_j} \rangle = -\frac{i}{2} \langle \Psi'_T | (\xi_1 l_{1j} + \xi_2 l_{2j}) | \Psi_T \rangle \quad (i \neq j \neq k) \quad (2.21)$$

Thus, the matrix elements of the SOC have non-zero values not only between the excited singlet and the excited triplet states but also between the two excited triplet states. The [equation \(2.19\)](#) means, the x, y, z components of the SOC connect with T_x , T_y , and T_z to S, respectively. The [equations \(2.20\)](#) and [\(2.21\)](#) mean that SOC does not occur between spin sublevels of the same triplet state. The scheme of the SOC is exhibited in [Figure 2.8](#). Furthermore, if the excited singlet state and the excited triplet state have the same electronic configuration, the matrix element of the SOC becomes zero. In other words, the SOC between states where the orbital parts are the same becomes zero although in the singlet state or the triplet state.

$$\begin{aligned} \langle \Psi_{T_i} | \hat{H}_{SO} | \Psi_{T_i} \rangle &= 0 \\ \langle \Psi_{T_i} | \hat{H}_{SO} | \Psi_{T_j} \rangle &= 0 \\ \langle \Psi_S | \hat{H}_{SO} | \Psi_{T_i} \rangle &= 0 \end{aligned} \quad (2.22)$$

The parameters obtained by time-resolved EPR (TREPR) are the energies of the triplet sublevels T_i ($i = x, y, z$), E_i , the g value (g_i), and population ratio (P_i), as follows. Note that P_i and g are also strongly affected by anisotropic SOC. Thus, the assignment of the triplet sublevels is important. The triplet sublevels (T_i ; $i = x, y$, and z) are split into three by anisotropic spin-spin dipolar coupling and SOC, even in the zero field. Thus, the T_i states have the different energies.

$$E_i = \langle \Psi_{T_1}(\pi\pi^*) | H_{SS} | \Psi_{T_1}(\pi\pi^*) \rangle$$

$$\begin{aligned}
& + \frac{|\langle \Psi_{T_1}(\pi\pi^*)T_i | H_{SO}^i | \Psi_{S_1}(n\pi^*)S \rangle|^2}{E(1n\pi^*) - E(3n\pi^*)} \\
& - \sum_{j,k} \frac{|\langle \Psi_{T_1}(\pi\pi^*)T_{j,k} | H_{SO}^i | \Psi_{T_n}(n\pi^*)T_{k,j} \rangle|^2}{E(3n\pi^*) - E(3\pi\pi^*)} \\
& (j, k = x, y, z) \tag{2.23}
\end{aligned}$$

The anisotropy in the g values ($i = x, y$, and z) in eq. (2.7) is represented as follows:

$$\begin{aligned}
& g_i = g_e - \\
& \sum_{j,k} \frac{|\langle T_1(\pi\pi^*) | L_i | T_n(n\pi^*) \rangle| |\langle T_n(n\pi^*) | H_{SO}^i | T_1(\pi\pi^*)T_{j,k} \rangle|}{E(3n\pi^*) - E(3\pi\pi^*)} \\
& \tag{2.24}
\end{aligned}$$

The anisotropy in the sublevel populations in the triplet state are obtained as,

$$\begin{aligned}
P_i \propto & \frac{|\langle \Psi_{S_1}(\pi\pi^*) | H_{TN} | \Psi_{S_n}(n\pi^*) \rangle|^2 |\langle \Psi_{S_n}(n\pi^*)S | H_{SO}^i | \Psi_{T_1}(\pi\pi^*)T_i \rangle|^2}{(E(1\pi\pi^*) - E(1n\pi^*))^2} \\
& \tag{2.25}
\end{aligned}$$

H_{TN} shows the kinetic energy operator. The analogous equations hold also from higher excited $n\pi$ states. The shifts are illustrated in [Figure 2.8](#). The sublevel energy (E_i) is decided by two contribution in [equation \(2.23\)](#): the spin-spin interactions (first term) and the SOC (second and third terms). The first term is obtained from the zero-field splitting (ZFS) of the molecule. SOC terms are evaluated especially for the metal complexes. The g_i value is a proportionality coefficient of the Zeeman splitting and contains the SOC and molecular angular momentum (L) terms in [equation \(2.24\)](#). The population ratio is proportional to the S_1 - T_1 ($l = x, y$, and z) intersystem crossing (ISC) rate of the sublevel and SOC decides its selectivity. These parameters are assumed as

described by second-order perturbation theory, as represented by [equation \(2.23\)](#), [\(2.24\)](#) and [\(2.25\)](#).

The shift in the sublevel energy in [equation \(2.23\)](#) is caused by a singlet-triplet (E_i^{ST}) SOC and a triplet (E_i^{TT}) SOC, which are represented by [equations \(2.26\)](#) and [\(2.27\)](#), respectively:

$$E_i^{ST} = \frac{|\langle \Psi_{T_1}(\pi\pi^*)T_i | H_{SO}^i | \Psi_{S_n}(n\pi^*)S \rangle|^2}{E(1n\pi^*) - E(3\pi\pi^*)} + \frac{|\langle \Psi_{T_1}(\pi\pi^*)T_i | H_{SO}^i | \Psi_{S_n}(n\pi)S \rangle|^2}{E(1n\pi) - E(3\pi\pi^*)} \quad (2.26)$$

$$E_i^{TT} = \sum_{j,k} \frac{|\langle \Psi_{T_1}(\pi\pi^*)T_{j,k} | H_{SO}^i | \Psi_{T_n}(n\pi^*)T_{k,j} \rangle|^2}{E(3n\pi^*) - E(3\pi\pi^*)} + \sum_{j,k} \frac{|\langle \Psi_{T_1}(\pi\pi^*)T_{j,k} | H_{SO}^i | \Psi_{T_n}(n\pi)T_{k,j} \rangle|^2}{E(3n\pi) - E(3\pi\pi^*)} \quad (2.27)$$

The SOC matrix elements in [equations \(2.26\)](#) and [\(2.27\)](#) can be decomposed into the atomic integrals by linear combination of atomic orbitals (LCAO) approximation and a variable separation method for orbital and spin. For example, [equations \(2.26\)](#) and [\(2.27\)](#) can be rewritten as [equations \(2.28\)](#) and [\(2.29\)](#), respectively, for the SOC between T_1 and higher $n\pi$ state:

$$\langle \pi\pi^*T_j | H_{SO}^i | n\pi S \rangle \propto \langle \pi\pi^* | l_i | n\pi \rangle \langle T_j | s_i | S \rangle = \langle \pi | l_i | n \rangle \langle T_j | s_i | S \rangle \quad (2.28)$$

$$\langle \pi\pi^*T_j | H_{SO}^i | n\pi T_k \rangle \propto \langle \pi\pi^* | l_i | n\pi \rangle \langle T_j | s_i | T_k \rangle = \langle \pi^* | l_i | n \rangle \langle T_j | s_i | T_k \rangle \quad (2.29)$$

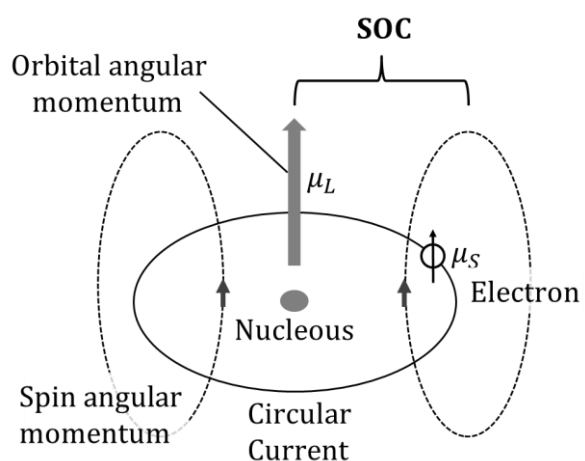


Figure 2.6. Schematic illustration of spin-orbit coupling.

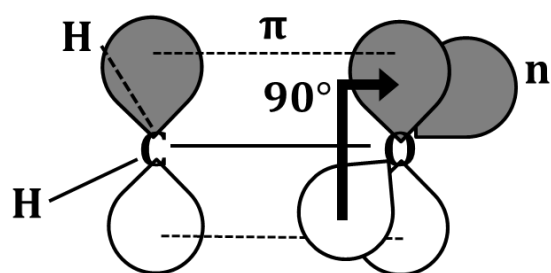


Figure 2.7. Schematic representation of the ISC process between (n, π^*) and (π , π^*) as an example of a carbonyl compound.

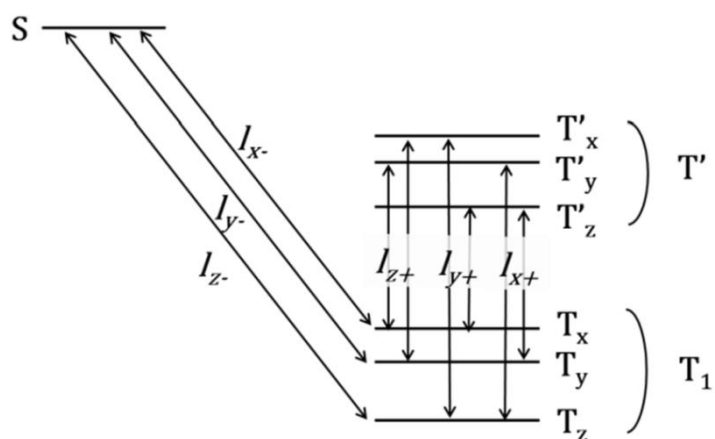


Figure 2.8. Schematic illustration of spin-orbit interaction between T_1 and S_1 .

2.5 Zero-Field Splitting (ZFS) Parameter²

In a suitable spin Hamiltonian, there are at least considered four magnetic interactions as follows: (1) the electronic Zeeman interactions, (2) the interaction of the electron spin with each other, (3) nuclear hyperfine interactions, and (4) nuclear Zeeman interactions.

For the most part, electronic Zeeman interactions (1) and the interaction of the electron spin with each other (2) are concerned and the spin Hamiltonian of two electrons in a triplet state are written as

$$H = g\mu_B \mathbf{B} \cdot (\mathbf{S}_1 + \mathbf{S}_2) + g^2 \mu_B^2 \left\{ \frac{\mathbf{S}_1 \cdot \mathbf{S}_2}{r^3} - \frac{3(\mathbf{S}_1 \cdot \mathbf{r})(\mathbf{S}_2 \cdot \mathbf{r})}{r^5} \right\} \quad (2.30)$$

where $\mathbf{r}$ is the vector joining the two electrons. This representation closely resembles the Hamiltonian expressing the dipolar interaction of two spins in a magnetic field. The two spins $\mathbf{S}_1$ and $\mathbf{S}_2$ are parallel and form a resultant $\mathbf{S}$ spins; the isotropic g value should be replaced by an anisotropic g tensor; the dipolar coupling should be averaged over all possible positions and spin states of the two coupled electrons and represented in terms of the direction of the total $\mathbf{S}$. For most organic triplets, the g tensor anisotropy is rather small and it is first neglected entirely, concentrating on the spin-spin interaction.

Assuming that both electrons are fixed in space and they have some as yet unspecified triplet spin wave function. The expanded dipolar terms are proceeded as follows:

$$H_D = g^2 \mu_B^2 \left\{ S_{1x}S_{2x} \left(\frac{r^2 - 3x^2}{r^5} \right) + S_{1y}S_{2y} \left(\frac{r^2 - 3y^2}{r^5} \right) + S_{1z}S_{2z} \left(\frac{r^2 - 3z^2}{r^5} \right) - (S_{1x}S_{2y} + S_{1y}S_{2x}) \frac{3xy}{r^5} - (S_{1y}S_{2z} + S_{1z}S_{2y}) \frac{3yz}{r^5} - (S_{1z}S_{2x} + S_{1x}S_{2z}) \frac{3zx}{r^5} \right\} \quad (2.31)$$

Because the two spins are corrected, it will be converted to represent everything in terms of the total spin $\mathbf{S}$. At last, an effective spin Hamiltonian can be written by averaging over all positions $\mathbf{r}_1$ and $\mathbf{r}_2$ of the two electrons as

$$H_D = \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} \quad (2.32)$$

$\mathbf{D}$ is a symmetric tensor called the zero-field splitting (ZFS) tensor and its components are given by averages over the electronic wave function:

$$D_{xx} = \frac{1}{2} g^2 \mu_B^2 \langle \frac{r_{12}^2 - 3x_{12}^2}{r_{12}^5} \rangle, \quad D_{xy} = \frac{1}{2} g^2 \mu_B^2 \langle \frac{-3x_{12}y_{12}}{r_{12}^5} \rangle \quad (2.33)$$

and so on. In terms of the principal axes which diagonalize the zero-field tensor, the Hamiltonian becomes

$$H_D = -XS_x^2 - YS_y^2 - ZS_z^2 \quad (2.34)$$

where $-X$, $-Y$, and $-Z$ are the principal values. However, the tensor is traceless ($X + Y + Z = 0$), thus the ZFS can be written in terms of just two independent constants, which are commonly called D and E :

$$D = -\frac{3}{2}D_{zz}, \quad E = \frac{1}{2}(D_{yy} - D_{xx}) \quad (2.35)$$

$$D_{zz} = -\frac{2}{3}D, \quad D_{xx} = \frac{1}{3}D - E, \quad D_{yy} = \frac{1}{3}D + E \quad (2.36)$$

$$H_D = D \left(S_z^2 - \frac{1}{3}S^2 \right) + E(S_x^2 - S_y^2) \quad (2.37)$$

The spin Hamiltonian H_D removes the degeneracy of the three triplet wave functions even if there is no external magnetic field. [Figure 2.9](#) represents ZFS of a triplet states in the case of $D > 0$ and $D < 0$. In transition metal complexes with triplet ground states there is also a ZFS, formally described by a spin Hamiltonian (2.37). However, the splitting is mainly because of spin-orbit coupling (SOC) instead of spin-spin magnetic dipole forces.

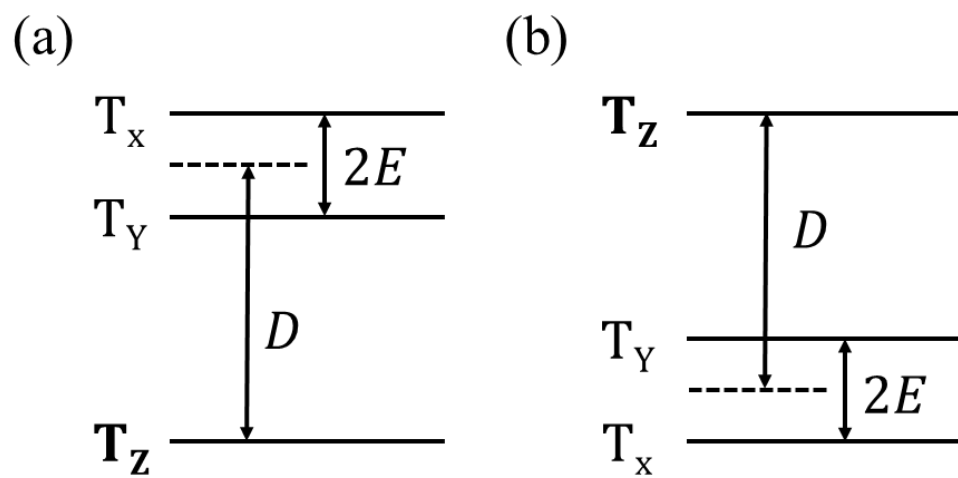


Figure 2.9. Zero-field splitting (ZFS) of a triplet states in the case of (a) $D > 0$ and (b) $D < 0$.

2.6 Energy Splitting As a Function of Magnetic Field²

The spin Hamiltonian of two electrons in a triplet state are written by electronic Zeeman interactions and the interaction of the electron spin with each other (in the last section) as

$$H = g\mu_B \mathbf{B} \cdot \mathbf{S} - XS_x^2 - YS_y^2 - ZS_z^2 \quad (2.38)$$

The energy levels can be calculated by taking the usual triplet spin functions

$$\begin{aligned} |T_+ \rangle &= |\alpha(1)\alpha(2) \rangle \\ |T_0 \rangle &= \frac{1}{\sqrt{2}}(|\alpha(1)\beta(2) \rangle + |\beta(1)\alpha(2) \rangle) \\ |T_- \rangle &= |\beta(1)\beta(2) \rangle \end{aligned} \quad (2.10)$$

in which the spin component S_z has the values +1, 0, -1. However, Three different spin functions are found

$$\begin{aligned} |T_x \rangle &= \frac{1}{\sqrt{2}}|\beta(1)\beta(2) - \alpha(1)\alpha(2) \rangle = \frac{1}{\sqrt{2}}|T_- - T_+ \rangle \\ |T_y \rangle &= \frac{i}{\sqrt{2}}|\beta(1)\beta(2) + \alpha(1)\alpha(2) \rangle = \frac{i}{\sqrt{2}}|T_- + T_+ \rangle \\ |T_z \rangle &= \frac{1}{\sqrt{2}}|\alpha(1)\beta(2) + \beta(1)\alpha(2) \rangle = |T_0 \rangle \end{aligned} \quad (2.39)$$

These new functions have their spin quantized along the x, y, and z axes, respectively, and they thus diagonalize the zero-field Hamiltonian.

The matrix elements of H within the set of basis functions (2.39) are calculated, then the following formulae for the various spin operators are verified on the new functions:

$$\begin{aligned} S_z|T_x \rangle &= i|T_y \rangle, \quad S_z^2|T_x \rangle = |T_x \rangle \\ S_z|T_y \rangle &= -i|T_x \rangle, \quad S_z^2|T_y \rangle = |T_y \rangle \\ S_z|T_z \rangle &= 0, \quad S_z^2|T_z \rangle = 0 \end{aligned} \quad (2.40)$$

and so on. These results are obtained directly from the definitions in (2.39).

The Hamiltonian matrix is thus as following:

$$\begin{aligned}
& \begin{matrix} & |T_x\rangle & |T_y\rangle & |T_z\rangle \\ \langle T_x| & X & -ig_z\mu_B B_z & ig_y\mu_B B_y \\ \langle T_y| & ig_z\mu_B B_z & Y & -ig_x\mu_B B_x \\ \langle T_z| & -ig_y\mu_B B_y & ig_x\mu_B B_x & Z \end{matrix} \\
H_{xyz} = & \begin{matrix} & |T_x\rangle & |T_y\rangle & |T_z\rangle \\ \langle T_x| & \frac{1}{3}D - E & -ig_z\mu_B B_z & ig_y\mu_B B_y \\ \langle T_y| & ig_z\mu_B B_z & \frac{1}{3}D + E & -ig_x\mu_B B_x \\ \langle T_z| & -ig_y\mu_B B_y & ig_x\mu_B B_x & -\frac{2}{3}D \end{matrix} \quad (2.41)
\end{aligned}$$

To be considered, especially, in the case of naphthalene triplet state with the molecular axes that long axis is x axis, short axis is y axis, and the z axis is perpendicular to the plane of the molecule. then the eigenvalues of (2.41) for the field in the z direction, putting $B_x = B_y = 0$. Then T_z is an eigenstate with energy $W = Z$ but T_x and T_y are mix together. The energy matrix for these two states yield the secular determinant

$$\begin{vmatrix} \frac{1}{3}D - E - W & -ig_z\mu_B B_z & 0 \\ ig_z\mu_B B_z & \frac{1}{3}D + E - W & 0 \\ 0 & 0 & -\frac{2}{3}D - W \end{vmatrix} = 0$$

$$\begin{vmatrix} \frac{1}{3}D - E - W & -ig_z\mu_B B_z \\ ig_z\mu_B B_z & \frac{1}{3}D + E - W \end{vmatrix} = 0 \quad (2.42)$$

with eigenvalues

$$W = \frac{1}{2}(X + Y) \pm \sqrt{\frac{1}{4}(X - Y)^2 + (g\mu_B B)^2} \quad (2.43)$$

The energy levels and wave functions for a triplet state with the magnetic field along the z axis would thus be summarized as follows:

$$\begin{aligned}
|\Psi_x\rangle &= \cos\theta |\alpha\alpha\rangle - \sin\theta |\beta\beta\rangle \quad W = \frac{1}{2}(X + Y) + \frac{1}{2}(X - Y)\tan\theta + g\mu_B B \\
|\Psi_y\rangle &= \sin\theta |\alpha\alpha\rangle + \cos\theta |\beta\beta\rangle \quad W = \frac{1}{2}(X + Y) - \frac{1}{2}(X - Y)\tan\theta - g\mu_B B \quad (2.44)
\end{aligned}$$

$$\left| \Psi_z \right\rangle = \frac{1}{\sqrt{2}} \left| \alpha\beta + \beta\alpha \right\rangle \quad W = Z$$

where $2\theta = (X-Y)/2g\mu_B B$. $(X-Y)$ is positive for naphthalene, and B is very small $\theta = \pi/4$, thus the stationary states go smoothly into $|T_x\rangle$, $|T_y\rangle$, and $|T_z\rangle$. In contrast, a strong field breaks up the spin-spin coupling; as θ approaches zero, $|\Psi_x\rangle$ and $|\Psi_y\rangle$ approaches $|\alpha\alpha\rangle$ and $|\beta\beta\rangle$, respectively, then the spin being totally quantized by the magnetic field.

When the magnetic field is in the x direction, $|T_x\rangle$ is an eigenstate but $|T_y\rangle$ and $|T_z\rangle$ are mixed together. The new energies are readily obtained and their variation with, magnetic field strength is summarized in [Figure 2.10](#).

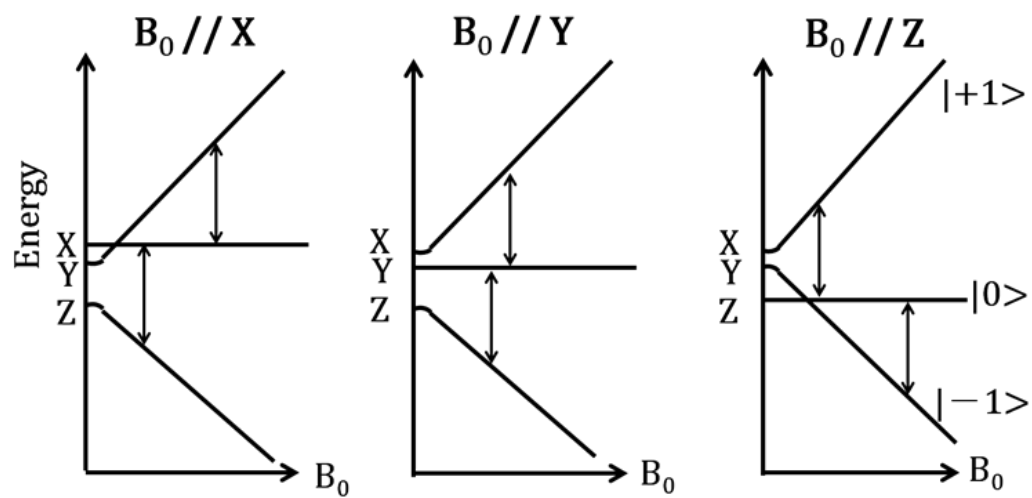


Figure 2.10. Triplet energy levels when the magnetic fields are in the x, y, and z directions.

2.7 Zero-Field Splitting (ZFS) and Electronic Structure⁷

Figure 2.11 illustrates the essence of the molecular symmetry of the zero-field splitting (ZFS) pattern of a molecular triplet state. In a molecule without axial symmetry (not having axes C_n with $n = 3, 4, 5, \dots$) the triplet spin is quantized in three mutually orthogonal planes, $x = 0, y = 0, z = 0$, where x, y, z are the principal axes of the spin-spin dipolar tensor. For a molecule with a symmetry resembling that of a rectangular box these axes are perpendicular to the sides of the box. Whenever there is axial symmetry, two of the spin levels (T_x, T_y) span a two-dimensional irreducible expression and the degeneracy is only partly lifted.

The formal equivalence of the three zero-field spin states is borne out by writing the spin Hamiltonian in zero-field as in section 2.5

$$H_D = -XS_x^2 - YS_y^2 - ZS_z^2 \quad (2.34)$$

For the ZFS parameters D and E that appear in the spin Hamiltonian commonly used for the interpretation of the EPR experiments from equation (2.23):

$$D = \frac{1}{2}(X + Y) - Z = -\frac{3}{2}Z, \quad E = \frac{1}{2}(Y - X) \quad (2.45)$$

The spin functions T_x, T_y , and T_z transform likewise the corresponding infinitesimal rotations and the irreducible expressions to which they belong are indicated in Figure 2.11. In a molecule without axial symmetry, there are three magnetic-dipole allowed transitions in zero-field, one for each pair of spin levels with the transition $T_x \leftrightarrow T_y$ being caused by an oscillating magnetic field.

The D value for porphyrin-like molecules is typically positive, and the z axis of the ZFS tensor corresponding to the out-of-plane orientation, as shown in Figure 2.12.

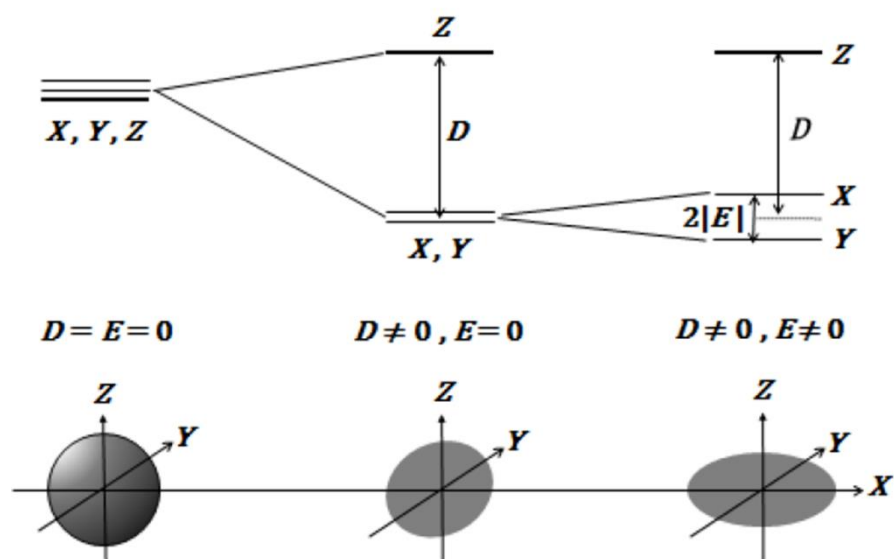


Figure 2.11. The relationship between molecular symmetry and triplet zero-field splitting (ZFS).

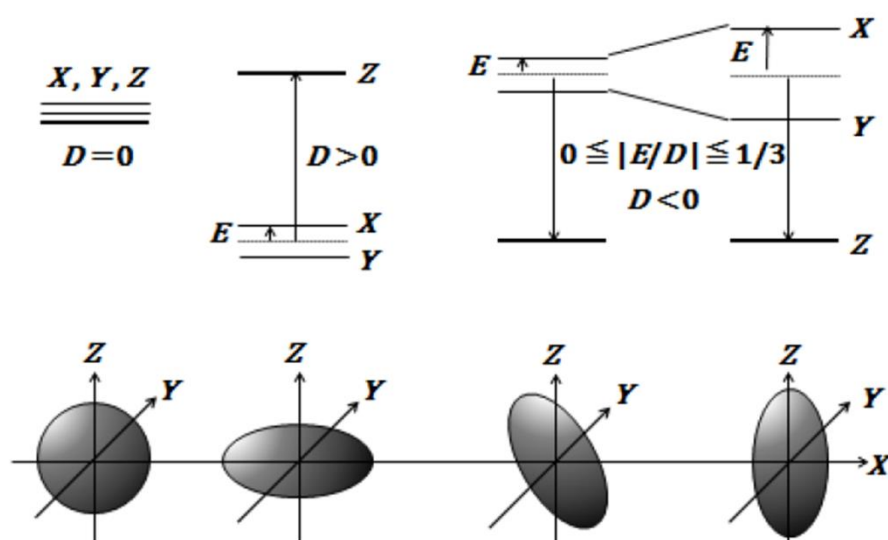


Figure 2.12. The relationship between spin-density distribution and triplet zero-field splitting (ZFS) energy.

2.8 EPR Spectrum of Excited Triplet State^{2,8-10}

At high magnetic fields when the spin is totally quantized by the magnetic field, the levels are classified according to their m_s value and the usual selection rule $\Delta m_s = \pm 1$ holds. Thus, the transitions $\Psi_x \leftrightarrow \Psi_z$ and $\Psi_y \leftrightarrow \Psi_z$ are allowed, the oscillating field being perpendicular to B_z . At lower magnetic field, however, the operator S_z has a nonvanishing matrix element between Ψ_x and Ψ_y thus a new transition (forbidden in the sense that $\Delta m_s = \pm 2$) is allowed when the oscillating field is parallel to B_z . The intensity of the new transition is decided by the square of the matrix element

$$\begin{aligned} \langle \Psi_x | S_z | \Psi_y \rangle &= \langle \alpha\alpha \cos \theta - \beta\beta \sin \theta | S_z | \alpha\alpha \sin \theta + \beta\beta \cos \theta \rangle \\ &= \langle \alpha\alpha \cos \theta - \beta\beta \sin \theta | \alpha\alpha \sin \theta - \beta\beta \cos \theta \rangle \quad (2.46) \\ &= + \sin 2\theta \end{aligned}$$

and in zero-field, the only nonvanishing matrix elements of $\mathbf{S}$ are

$$\langle T_y | S_x | T_z \rangle = \langle T_z | S_y | T_x \rangle = \langle T_x | S_z | T_y \rangle = -i \quad (2.47)$$

from equation (2.40). Therefore the zero-field transitions are polarized along the x, y, and z directions, respectively. The terms $\Delta m_s = \pm 1$ or $\Delta m_s = \pm 2$ are conventional in spectroscopy. The magnetic fields required to satisfy the resonance condition for $\Delta m_s = \pm 1$ transitions vary over a wide range. The $\Delta m_s = \pm 2$ transition expresses a rather different situation in that it is relatively isotropic. The precise position and shape of the $\Delta m_s = \pm 2$ line in a glass depends on the values of D and E , thus they can both be decided if the line is visible. The $\Delta m_s = \pm 2$ transition has an intense peak at the low magnetic field edge $B_{\min}$ of the spectrum, at the position

$$g\mu_B B_{\min} = \sqrt{\frac{1}{4}(h\nu)^2 - \frac{1}{3}(D^2 + 3E^2)} \quad (2.48)$$

As described by equations (2.37) and (2.38), the spin Hamiltonian of a triplet state in a magnetic field

$$H = g\mu_B \mathbf{B} \cdot \mathbf{S} + D \left(S_z^2 - \frac{1}{3} S^2 \right) + E (S_x^2 - S_y^2) \quad (2.49)$$

in terms of the high magnetic field spin eigen-functions $|T_+\rangle$, $|T_0\rangle$, $|T_-\rangle$ is

$$\begin{pmatrix} \frac{1}{3}D + g\mu_B Bn & (g\mu_B B/\sqrt{2})(l - im) & E \\ (g\mu_B B/\sqrt{2})(l + im) & -\frac{2}{3}D & (g\mu_B B/\sqrt{2})(l - im) \\ E & (g\mu_B B/\sqrt{2})(l + im) & \frac{1}{3}D - g\mu_B Bn \end{pmatrix} \quad (2.50)$$

where l , m , n are the direction cosines between the external magnetic field and the principal axes X , Y , Z fixed in the molecular system, as shown in [Figure 2.13](#). In the case of the dipolar interaction in the molecules is generally about 1 order of magnitude smaller than the Zeeman term, it might be regarded as a small perturbation on the latter interaction. The eigenvalues of the Hamiltonian (2.49) become $\pm g\mu_B B$, 0 and the corresponding eigenfunctions are given as follows by introducing D and E as the perturbation, the energy levels to first order are the elements of the diagonalized Hamiltonian matrix:

$$\begin{pmatrix} g\mu_B B - C(D, E, \theta, \varphi) & 0 & 0 \\ 0 & 2C(D, E, \theta, \varphi) & 0 \\ 0 & 0 & -g\mu_B B - C(D, E, \theta, \varphi) \end{pmatrix} \quad (2.51)$$

where

$$C(D, E, \theta, \varphi) = \frac{1}{6}D(1 - 3n^2) - \frac{1}{2}E(l^2 - m^2) \quad (2.52)$$

The effective g value is obtained as follows: In [equation \(2.38\)](#), g is 3×3 matrix demonstrating the anisotropic Zeeman interaction. Generally, a coordinate system can be found the g -matrix principal axes where g is diagonal. When g is diagonal in the same coordinate system, their principal axes are regarded to be coincident. In the system with two or more unpaired electrons, the fine structure term have to be added to the spin Hamiltonian to express electron spin-spin coupling. When a radical species is oriented in a space where the direction of the magnetic field is located by the polar and azimuthal

angles (θ and φ) relative to the g -matrix principal axes, the resonant magnetic field is represented as

$$B = B_0 - \sum_i \frac{A_i m_i}{g \mu_B} \quad (2.53)$$

where

$$B_0 = \frac{h\nu}{g \mu_B} \quad (2.54)$$

$$g^2 = (g_x^2 \cos^2 \varphi + g_y^2 \sin^2 \varphi) \sin^2 \theta + g_z^2 \cos^2 \theta \quad (2.55)$$

During the radical species are dilute, they can be investigated in the solid state as solutions in single crystals, powders, glasses, or frozen solutions. EPR spectra in these frozen solutions have to be taken in solvents that form good glasses. The EPR spectra of radical species such as in a dilute single crystal are obtained for various orientations, usually the magnetic field is perpendicular to one of the crystal axes. Individual spectrum is usually regarded as if they were isotropic to get an effective g -value for the orientation. Because the g -matrix principal axes are not important the same as the crystal axes, the matrices, written in the crystal axis system, usually would possess off-diagonal elements. Therefore, if spectra were obtained for various orientations in the crystal xy -plane, the effective g -value is represented as follows

$$g_{eff}^2 = (g_{xx} \cos \varphi + g_{yx} \sin \varphi)^2 + (g_{xy} \cos \varphi + g_{yy} \sin \varphi)^2 + (g_{xz} \cos \varphi + g_{yz} \sin \varphi)^2 \quad (2.56)$$

or

$$g_{eff}^2 = K_1 + K_2 \cos 2\varphi + K_3 \sin 2\varphi \quad (2.57)$$

where

$$K_1 = \frac{1}{2}(g_{xx}^2 + g_{yy}^2 + g_{xz}^2 + g_{yz}^2 + 2) \quad (2.58)$$

$$K_2 = \frac{1}{2}(g_{xx}^2 - g_{yy}^2 + g_{xz}^2 - g_{yz}^2) \quad (2.59)$$

$$K_3 = g_{xy}g_{xx} + g_{xy}g_{yy} + g_{xz}g_{yz} \quad (2.60)$$

In the case of another crystal plane, another set of K_1 , K_2 , and K_3 are given depend on other combinations of the g_{ij} . Then the g -matrix is diagonalized to obtain the principal values and transformation matrix, their elements are the direction cosines of the g -matrix principal axes relative to the crystal axes.

An EPR spectrum is a measure of the transverse component of the total magnetization of the sample, that is, the expectation value of $\hat{S}_+ = \hat{S}_x + i\hat{S}_y$. To calculate this, the density matrix formalism using the Zeeman eigenfunctions as basis is given as

$$\langle \hat{S}_+ \rangle = \text{tr}(\rho \hat{S}_+) = \text{tr} \left[\begin{pmatrix} \rho_{11} & \rho_{12} & \rho_{13} \\ \rho_{21} & \rho_{22} & \rho_{23} \\ \rho_{31} & \rho_{32} & \rho_{33} \end{pmatrix} \cdot \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix} \right] = \rho_{21} + \rho_{32} \quad (2.61)$$

The density matrix itself can be acquired from its equation of motion

$$\dot{\rho}_{ij} = i[\rho, H]_{ij} - \frac{1}{T_2} \rho_{ij} \quad (2.62)$$

The Hamiltonian in [equation \(2.62\)](#) breaks down into three parts:

$$H = H_{Zeeman} + H_{Dipolar} + \gamma B_1 (\hat{S}_x \cos \omega t + \hat{S}_y \sin \omega t) \quad (2.63)$$

The first two terms are accounted above, the third is the microwave driving term. The second term in [equation \(2.62\)](#) describes phenomenological relaxation of ρ_{ij} toward thermal equilibrium value. This exponential decay generates a Lorentzian line shape with line width $1/T_2$ that is mainly decided by hyperfine interactions. In the rotating frame and making the steady-state slow passage assumption, $\dot{\rho} = 0$, the two transitions are obtained as

$$\begin{aligned}
\rho_{21} &= \omega_1(\rho_{11} - \rho_{22}) \frac{-\Delta + 2C(D, E, \theta, \varphi) + i/T_2}{(1/T_2)^2 + [\Delta - 2C(D, E, \theta, \varphi)]^2} \\
\rho_{32} &= \omega_1(\rho_{22} - \rho_{33}) \frac{-\Delta - 2C(D, E, \theta, \varphi) + i/T_2}{(1/T_2)^2 + [\Delta + 2C(D, E, \theta, \varphi)]^2}
\end{aligned} \tag{2.64}$$

where $\Delta = \mathbf{B} \cdot \boldsymbol{\omega}/\gamma$, $\omega_1 = \gamma \mathbf{B}_1$. Therefore, for arbitrary orientation of $\mathbf{B}$ in the molecular frame, defined by θ, φ the absorption line shape is $I(\mathbf{B}, \theta, \varphi)$ given by the imaginary part of $\{\rho_{21} + \rho_{32}\}$. The population differences $(\rho_{ii} - \rho_{jj})$ is needed to obtain the line shape. Because the molecules assume a certain distribution and all of them contribute to the absorption, all possible transitions have to be summed over a possible orientation-dependent contributions with the proper weighing function $M(\theta, \varphi)$, in a spherical distribution $M(\theta, \varphi) = \sin \theta d\theta d\varphi$. The angular dependence of the line shape is

$$I(\mathbf{B}) = \sum_{\substack{i=1,2 \\ j=i+1}} \int_0^{\pi/2} \int_0^{\pi/2} \text{Im} [\rho_{ij}(\theta, \varphi)] M(\theta, \varphi) \tag{2.65}$$

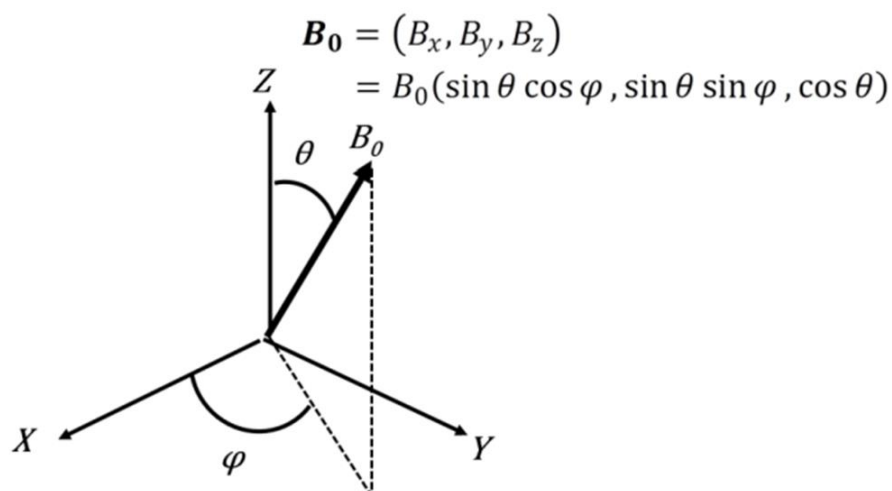


Figure 2.13. The relationship between the principal axes X , Y , Z and the external magnetic field with respect to the molecular axes (x , y , z).

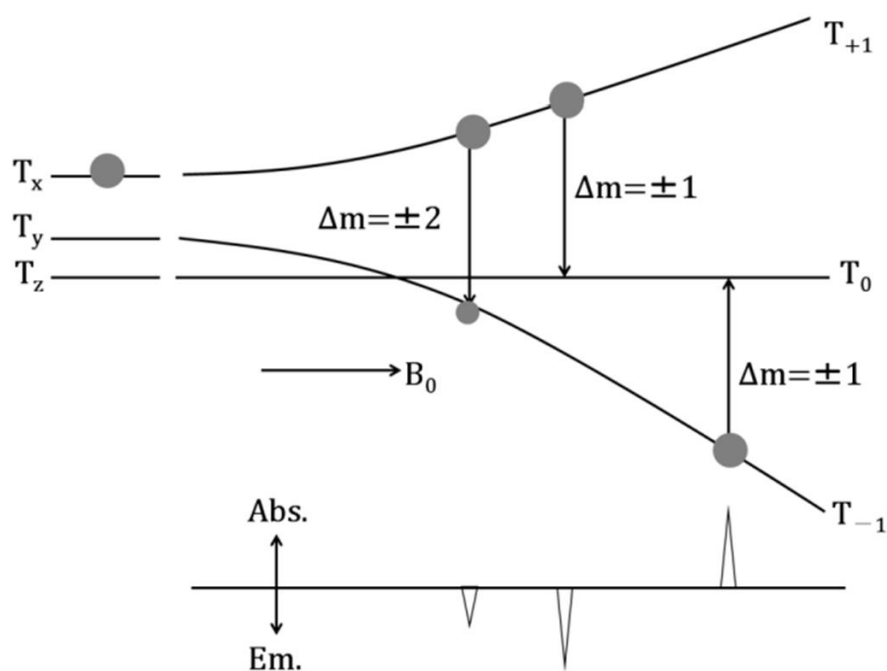


Figure 2.14. Triplet energy levels and $\Delta m_s = \pm 1$ and $\Delta m_s = \pm 2$ EPR transitions when the magnetic field is in the z direction.

2.9 Magnetophotoselection¹¹⁻¹⁴

Magnetophotoselection (MPS) techniques have been used to study the triplet state observed by electron spin resonance (ESR)/ electron paramagnetic resonance (EPR). The peaks observed in the common compounds of the EPR absorption spectrum of a randomly oriented set of triplet state molecules are because of those molecules that have one of the principal axes of their electron spin-spin coupling tensor essentially oriented along the magnetic field (magnetoselection). By exciting the molecules with plane polarized light with the electric vector of the light either parallel or perpendicular to the magnetic field in a triplet EPR measurement, the light can excite molecules at different orientations relative to the magnetic field, depending on the polarization of the $S_0 \rightarrow S_1$ transition (photoselection), as represented in [Figure 2.15](#). The measurement combines the properties of the two selection techniques. One is the selective excitation by polarized light, the other is the selective observation of triplets by ordinary EPR. So that the method is used to assign the optical transitions when the triplet magnetic molecular axes are known or conversely the magnetic axes can be studied when the polarizations of the optical transitions with respect to a molecular framework are available. For MPS experiments, conventional EPR with field modulation and lock-in detection was ordinary used. Time-resolved EPR in conjugation MPS have been used to study photosynthetic systems and aromatic molecules in frozen solutions because of the important advantage of the detection of the initial spin polarization of the signal prior to spin-lattice relaxation or triplet depopulation develops.

Photoselection effects can be accounted for by introducing intensity coefficients for each orientation of triplet molecule in the magnetic field, equal to the cosine square of the angle between the optical transition dipole (μ) and the electric vector of the light (L).

Isotropic spectrum corresponding to the case of equal excitation probability of any orientation of triplet molecule and the spectrum is independent of the orientation of the optical transition dipole in the axis frame of the triplet molecule as expressed by equation (2.65) in section 2.8.

$$I(\mathbf{B}) = \sum_{\substack{i=1,2 \\ j=i+1}} \int_0^{\pi/2} \int_0^{\pi/2} \text{Im} [\rho_{ij}(\theta, \varphi)] M(\theta, \varphi) \quad (2.65)$$

This is constructed by the summation of $\mathbf{L} \parallel \mathbf{B}_0$ spectrum and two $\mathbf{L} \perp \mathbf{B}_0$ spectra. Here, the $\mathbf{L} \parallel \mathbf{B}_0$ and $\mathbf{L} \perp \mathbf{B}_0$ spectra are the experimental spectra obtained under excitation by plane-polarized with its electric vector parallel and perpendicular, respectively, to the constant magnetic field of the EPR spectrometer.

The relationship between the optical transition dipole ($\boldsymbol{\mu}$) and the external magnetic field ($\mathbf{B}_0$) are written as

$$\boldsymbol{\mu} \cdot \mathbf{B}_0 = |\boldsymbol{\mu}| |\mathbf{B}_0| \cos \alpha \quad (2.66)$$

$$\cos^2 \alpha = \frac{|\boldsymbol{\mu} \cdot \mathbf{B}_0|^2}{|\boldsymbol{\mu}|^2 |\mathbf{B}_0|^2} \quad (2.67)$$

where α is the angle between $\boldsymbol{\mu}$ and $\mathbf{B}_0$. Decomposing $\boldsymbol{\mu}$ and $\mathbf{B}_0$ into its components along the principal magnetic axes acquired

$$\mathbf{B}_0 = B_0 (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta) \quad (2.68)$$

$$\boldsymbol{\mu} = \mu (\sin \gamma \cos \delta, \sin \gamma \sin \delta, \cos \gamma) \quad (2.69)$$

where θ is the angle between $\mathbf{B}_0$ and the z magnetic axis, and ϕ is the angle between the component of $\mathbf{B}_0$ in the xy plane and the x magnetic axis. Similarly, γ and δ are the angle locating $\boldsymbol{\mu}$ in the magnetic axis system, as illustrated in Figure 2.16.

The intensity coefficients for the two orthogonal orientations of $\mathbf{L}$ relative to $\mathbf{B}_0$ averaged over all orientations of the triplet molecule relative to the electric vector $\mathbf{L}$ with its θ and φ coordinates fixed are as follows:

In the case of $\mathbf{L} \parallel \mathbf{B}_0$,

$$M_{\parallel}(\theta, \phi) = \cos^2 \alpha \sin \theta$$

$$= (\sin \gamma \cos \delta \sin \theta \cos \phi + \sin \gamma \sin \delta \sin \theta \sin \phi + \cos \gamma \cos \theta)^2 \sin \theta \quad (2.70)$$

In the case of $\mathbf{L} \perp \mathbf{B}_0$,

$$M_{\perp}(\theta, \phi) = \frac{1}{2} \sin^2 \alpha \sin \theta$$

$$= \frac{1}{2} \left\{ 1 - (\sin \gamma \cos \delta \sin \theta \cos \phi + \sin \gamma \sin \delta \sin \theta \sin \phi + \cos \gamma \cos \theta)^2 \right\} \sin \theta \quad (2.71)$$

Polarization ratio can be observed as

$$P_i = \frac{M_{i\parallel}(\theta, \phi) - M_{i\perp}(\theta, \phi)}{M_{i\parallel}(\theta, \phi) + M_{i\perp}(\theta, \phi)} \quad (2.72)$$

where $i = x, y$, and z , and $M_{\parallel}(\theta, \phi)$ and $M_{\perp}(\theta, \phi)$ are the intensity corresponding to $\Delta m_s = \pm 1$ transition, for light polarized parallel and perpendicular to the magnetic field.

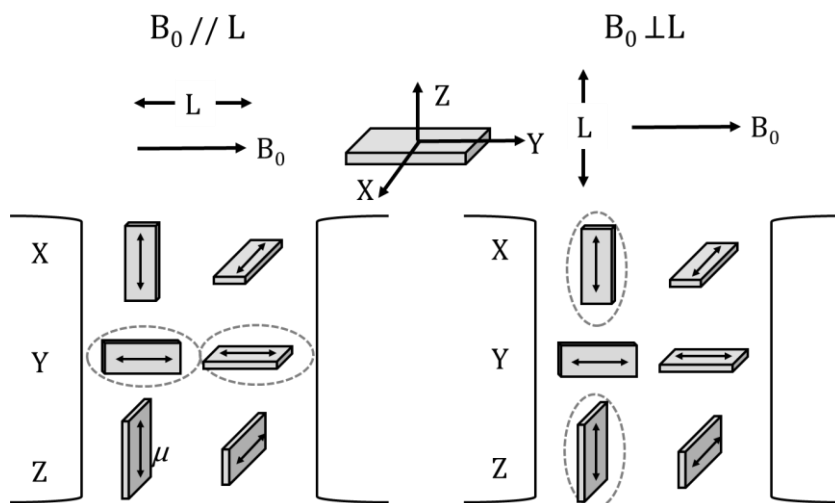


Figure 2.15. Illustration of magnetophotoselection (MPS) for excitation polarized along the y axis when the molecules are excited with plane polarized light with the electric vector of the light ($\mathbf{L}$) either parallel or perpendicular to external magnetic field ($\mathbf{B}_0$).

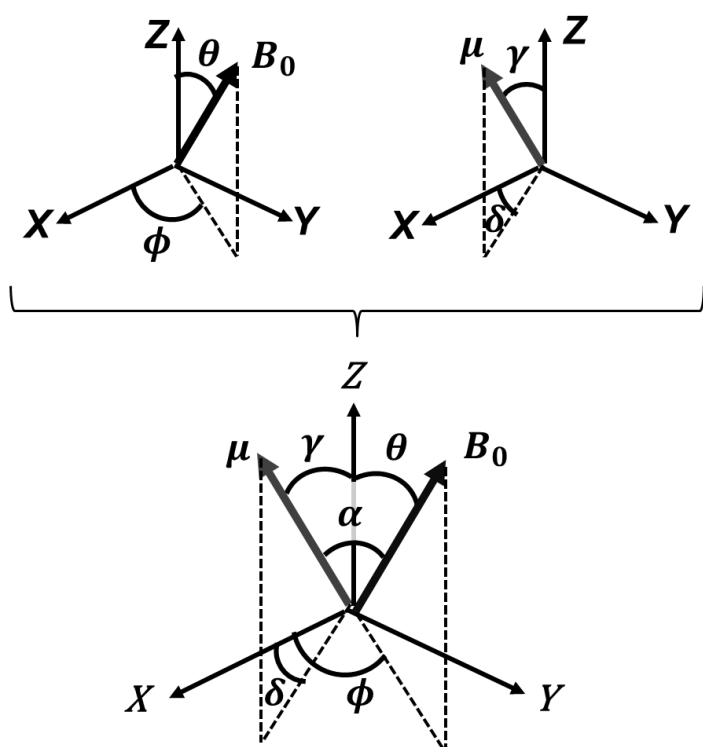


Figure 2.16. The relationship between the optical transition dipole (μ) and the external magnetic field ($\mathbf{B}_0$) with respect to the principal magnetic axes.

2.10 Magnetic Coupling: Dipolar Coupling and Exchange Coupling¹

The interaction between two $S = 1/2$ compounds (total $S = 1$) is confirmed as magnetic dipolar coupling and exchange coupling. The dipolar coupling gives rise to an anisotropic coupling and it can be demonstrated because of the coupling between the magnetic moments of the two electron spins. It induces a splitting in two lines (d) (Figure 2.17), depending on the distance (R) between the electron spins. The point-dipole approximation can be applied under the condition which the magnitude of the exchange energy is much larger than the magnetic dipolar coupling ($|J| \gg D$), namely, the electron spins or the electron and nuclear spins is large in comparison to the extension of the orbitals of the unpaired electrons. The approximation is often applied in the case of the longer electron-electron distance ($> 5-6 \text{ \AA}$) and electron-nuclear distance ($> 2.5 \text{ \AA}$), respectively. Then the coupling is inversely proportional to R^3 , so that distances can be estimated from the measured coupling. The electron-electron dipolar coupling (d) between the magnetic moments of two unpaired electrons is in the point-dipole approximation expressed by

$$d = D(1 - 3 \cos^2 \theta) \quad (2.73)$$

where θ is the angle between the magnetic field ($\mathbf{B}_0$) and the line joining the spins (Figure 2.17).

$$D / \text{mT} = \frac{\mu_0}{4\pi} \frac{3g\mu_B}{2R^3} = \frac{2780}{(R/\text{\AA})^3} \quad \text{with } g = 2.00232 \quad (2.74)$$

The exchange coupling (J) is caused by the electrostatic Hisenberg exchange term in quantum mechanics. The sum of the zero-field and exchange interactions in demonstrated with a Hamiltonian:

$$H_{12} = \mathbf{S}_1 \mathbf{D}_{12} \mathbf{S}_2 + J_{12} \mathbf{S}_1 \mathbf{S}_2 \quad (2.75)$$

A representation for the exchange interaction can be calculated using the relation for the

addition of the spin angular moment vectors in quantum mechanics:

$$\begin{aligned} S(S+1) &= \mathbf{S}^2 = (\mathbf{S}_1 + \mathbf{S}_2)^2 \\ &= S_1(S_1+1) + S_2(S_2+1) + 2 \cdot \mathbf{S}_1 \cdot \mathbf{S}_2 = \frac{3}{4} + \frac{3}{4} + 2 \cdot \mathbf{S}_1 \cdot \mathbf{S}_2 \end{aligned} \quad (2.76)$$

Then,

$$S = 1: \mathbf{S}_1 \cdot \mathbf{S}_2 = \frac{1}{2} \left(2 - \frac{3}{2} \right) = \frac{1}{4}, \quad S = 0: \mathbf{S}_1 \cdot \mathbf{S}_2 = \frac{1}{2} \left(0 - \frac{3}{2} \right) = -\frac{3}{4} \quad (2.77)$$

are given. The exchange energy is $E_J^0 = -(3J/4)$ for the singlet ($S = 0$), $E_J^1 = J/4$ for the triplet ($S = 1$). In the triplet, there are three degenerate states, as shown in [Figure 2.18](#), which degeneracy is caused by the different quantum numbers $m_S = 1, 0, -1$. Thus, the exchange coupling contributes only a constant energy shift to the energy levels of the triplet state, and so that it has no influence on the EPR spectrum.

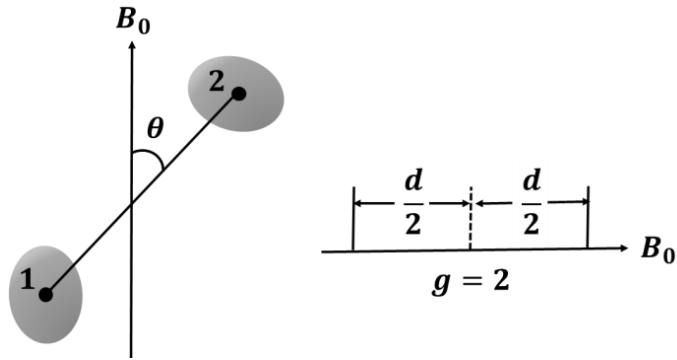


Figure 2.17. Fine structure due to Spin-spin dipolar coupling between the magnetic moments of the two electron spins.

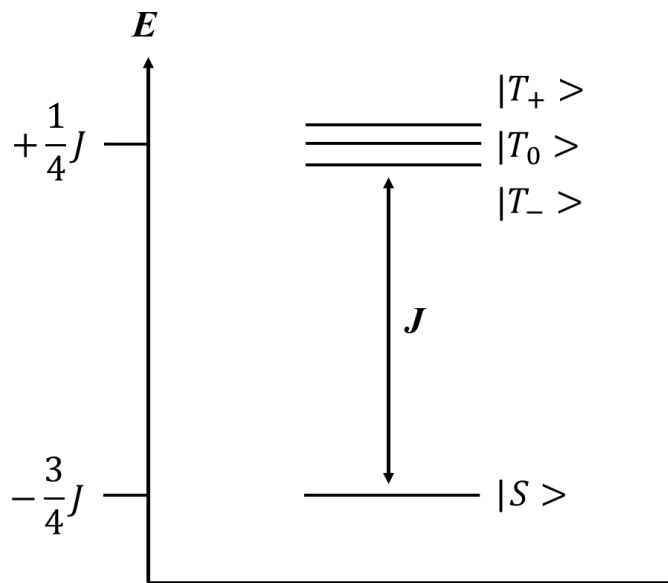


Figure 2.18. The singlet-triplet energy gap for $S = 1$ system in case of $J > 0$.

2.11 Transition Pathway¹⁵

The rate of a fluorescence or phosphorescence that is spontaneous radiative transitions in the gas phase is expressed by the Einstein coefficient

$$A = \frac{(E_1 - E_0)^3}{3\epsilon_0\pi\hbar^4c^3} |\vec{\mu}_{1 \rightarrow 0}|^2 \quad (2.78)$$

where E_1 and E_2 are the energies of the excited and ground states, and $\vec{\mu}_{1 \rightarrow 0}$ is the corresponding transition dipole moment. In the case of the fluorescence decay rate k_{rad}^S , the transition dipole moment $\vec{\mu}_{S_1 \rightarrow S_0}$ and the S_1 vertical transition energy from the relaxed S_1 geometry were inserted.

The radiative transition between the lowest triplet state (T_1) and the ground state (S_0) induce to a T_1 - S_0 phosphorescence signal. The corresponding radiative decay rate k_{rad}^T is one component of the overall triplet decay rate k_{tot}^T :

$$k_{tot}^T = \frac{1}{k_{tot}^T} = k_{rad}^T + k_{nonrad}^T \quad (2.79)$$

As a consequence of the spin-orbit coupling (SOC), each state of predominant singlet character acquires a certain amount of triplet admixture and vice versa. In organic systems, SOC is considered to be a small correction to purely nonrelative electronic states. The spin-orbit Hamiltonian in central-field approximation is given as

$$\hat{H}_{SO} = \alpha_F^2 \sum_{\mu}^N \sum_i^n = \frac{Z_{\mu}}{r_{i\mu}^3} \vec{L}_i \vec{S}_i \quad (2.80)$$

where α_F is the fine-structure constant, Z is the effective nuclear charge at nucleus μ , and S is the spin angular moment of electron i and L is the orbital angular moment of electron i . The expectation value for the SOC is demonstrated in the framework of first-order perturbation theory as

$$\langle \Psi_S^{(0)} | \hat{H}_{SO} | \Psi_T^{(0)} \rangle = \alpha_F^2 \sum_{\mu}^N \sum_i^n \langle \frac{Z_{\mu}}{r_{i\mu}^3} \varphi_S^{(0)} | \hat{H}_{SO} | \varphi_T^{(0)} \rangle \times$$

$$\left\langle \frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha) \left| \vec{S} \right| \begin{bmatrix} \alpha\alpha \\ \frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha) \\ \beta\beta \end{bmatrix} \right\rangle \quad (2.81)$$

where $\Psi_S^{(0)}$ ($\varphi_S^{(0)}$) and $\Psi_T^{(0)}$ ($\varphi_T^{(0)}$) are the total spatial electronic wavefunctions of the singlet and triplet states, respectively, in the undisturbed system. Formulated in the framework of first-order perturbation theory, the radiative transition probability k_{rad}^T between T_1 and S_0 and is proportional to the transition dipole moment $\vec{\mu}_{S_1 \rightarrow S_0}$ squared

$$\begin{aligned} \vec{\mu}_{T_1 \rightarrow S_0} &= \langle \Psi_T^{(0)} | \vec{\mu} | \Psi_S^{(0)} \rangle \\ &= \sum_k \frac{\langle \Psi_{T(1)}^{(0)} | \hat{H}_{SO} | \Psi_{S(k)}^{(0)} \rangle}{E_{T(1)} - E_{S(k)}} \times \vec{\mu}_{S_k \rightarrow S_0} + \sum_m \frac{\langle \Psi_{T(m)}^{(0)} | \hat{H}_{SO} | \Psi_{S(0)}^{(0)} \rangle}{E_{T(m)} - E_{S(0)}} \times \vec{\mu}_{T_m \rightarrow T_1} \end{aligned} \quad (2.82)$$

where the summation of k and m run over all singlet and triplet states, respectively.

The decay rate of the population in state S_n because of intersystem crossing (ISC) to any state T_n is expressed by

$$k_{ISC}^n = \sum_m k_{ISC}^{nm} \quad (2.83)$$

Each ISC channel is treated as a nonradiative transition between S_n and T_m , demonstrated by the Fermi Golden rule, using the Franck-Condon-weighted density of state (FCWD):

$$k_{ISC}^{nm} = \frac{2\pi}{\hbar} \langle \Psi_{S(n)}^{(0)} | \hat{H}_{SO} | \Psi_{T(m)}^{(0)} \rangle^2 \times \text{FCWD} \quad (2.84)$$

If the relaxation via internal conversion into the S_1 state is fast enough, ISC essentially proceeds from S_1 . However, ISC contributions associated with higher-lying singlet states can be added by weighting their formal rates k_{ISC}^n by their Boltzmann distribution population $\sim \exp[(E_n - E_1)/k_B T]$, where T is the temperature and k_B is the Boltzmann

constant.

Two independent contributions enter the decay rate. One is the SOC matrix element squared and the other is the FCWD that ensures energy conversion. FCWD is expressed in the framework of Marcus-Levich-Jortner theory as

$$\text{FCWD} = \frac{1}{\sqrt{4\pi\lambda k_B T}} \sum_{n=0}^{\infty} \exp(-S)^2 \frac{S^n}{n!} \left[-\frac{(\Delta E + n\hbar\omega + \lambda)^2}{4\lambda k_B T} \right] \quad (2.85)$$

where λ is the Marcus reorganization energy because of intramolecular, low-frequency vibrations, (λ_L) and solvent-induced relaxation (λ_S), is ΔE is the difference between the energies of S_1 and the triplet state at their equilibrium energy (Figure 2.19), $\hbar\omega$ is the energy of an effective nonclassical vibrational mode included in the transition, and S is the associated Huang-Rhys factor.

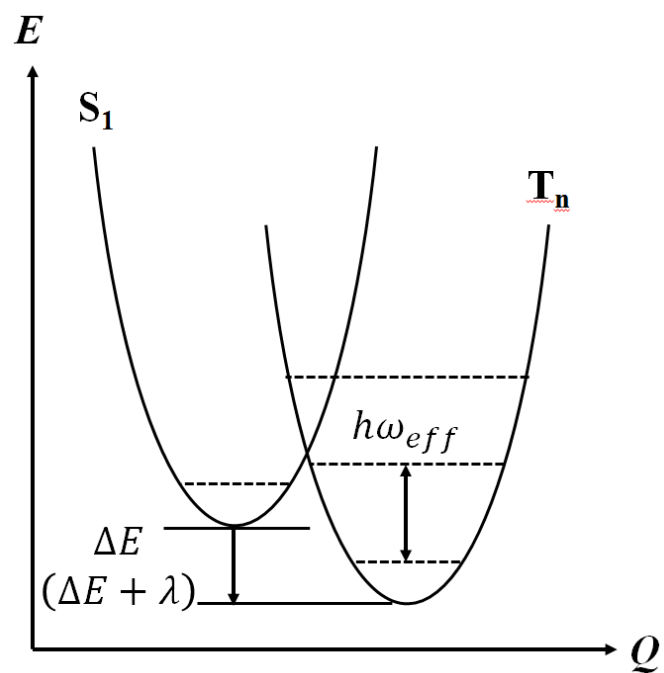


Figure 2.19. Schematic representation of the displaced potential energy surfaces corresponding to the S_1 state and a T_n ($n = 1, 2, 3, \dots$) state.

2.12 Electronic Coupling¹⁶⁻¹⁸

The electronic coupling between the orbitals including in the jump and the energy difference between the tunneling electron and the orbitals can be determined by the two energies, namely the energies of the donor and the acceptor. The one electron parameters for hydrocarbons were taken from experimental and theoretical studies of the optical properties of crystalline solids and small molecules, which lead to self-consistent predictions of the mediation properties of a large family of bridging species. Bridges with more complex and varied bonds and contacts makes the selection of parameters more difficult. For example, the off diagonal matrix elements can be written as

$$H_{ij} = \langle \varphi_i | H | \varphi_j \rangle \cong \frac{(E_i + E_j)}{2} S_{ij} K \quad (2.86)$$

where K is a fitting constant, typically between one and three, and the approximation is only valid for orbitals with nonzero overlap. In the hydrocarbon systems, K is equal to one based on the values of the E 's and fitting to the most closely associated experimental and theoretical data. It is being found that the donor-acceptor interaction is importantly a one-electron property. Then extended-Hückel estimates for the interaction parameters.

The electronic interaction energy or electron exchange matrix element ($V_{DA}(r)$) decides the dependence of the electron transfer rate on the distance between the reactants. $V_{DA}(r)$ has been estimated as the interaction between a pair of potential wells that decays exponentially with distance (R) as following:

$$V_{DA}(r) = V_{DA}(r_0) \exp[-\gamma(r - r_0)] \quad (2.87)$$

$$\gamma = \frac{\sqrt{2m_e B}}{\hbar} \quad (2.88)$$

where $V_{\text{DA}}(r_0)$ is the coupling matrix element for a donor-acceptor pair at van der Waals separation (r_0 ; 4-6 Å) and B (eV) is the binding energy at the electron donor, or barrier height: the difference between the energy level of the electron on the donor and the energy of the lowest condition states of the medium. r is the center to center distance from the donor to the acceptor, and m_e is the mass of the electron.

References

- (1) Lund, A.; Shiotani, M.; Shimada, S. *Principles and Applications of ESR Spectroscopy*; Springer Science+Business Media B.V: Dordrecht Heidelberg London New York, 2011.
- (2) Alan, C.; Andrew, D. M. *INTRODUCTION TO MAGNETIC RESONANCE WITH APPLICATIONS TO CHEMISTRY AND CHEMICAL PHYSICS*, Harper Int.; Harper & Row: New York, Evanston, London, 1967.
- (3) Turro, N. J. The Triplet State. *J. Chem. Educ.* **1969**, 46 (1), 2.
- (4) Tanabe, M.; Matsuoka, H.; Ohba, Y.; Yamauchi, S.; Sugisaki, K.; Toyota, K.; Sato, K.; Takui, T.; Goldberg, I.; Saltsman, I.; et al. Time-Resolved Electron Paramagnetic Resonance and Phosphorescence Studies of the Lowest Excited Triplet States of Rh(III) Corrole Complexes. *J. Phys. Chem. A* **2012**, 116 (39), 9662–9673.
- (5) Peter, A.; Julio, de P. *Elements Of Physical Chemistry*, Fifth edit.; OXFORD UNIVERSITY PRESS: Oxford, New York, 2009.
- (6) El-Sayed, M. A. Spin-Orbit Coupling and the Radiationless Processes in Nitrogen Heterocycles. *J. Chem. Phys.* **1963**, 38, 2834.
- (7) Waals, J. H. EPR of Photo-Excited Triplet States: A Personal Account. *Appl. Magn. Reson.* **2001**, 20 (4), 545–561.
- (8) Gonen, O.; Levanon, H. Line-Shape Analysis of Transient Triplet Electron Paramagnetic Resonance Spectra. Application to Porphyrins and Chlorophylls in Nematic Uniaxial Liquid Crystals. *J. Phys. Chem.* **1984**, 88 (28), 4223–4228.
- (9) Wasserman, E. ESR of the Triplet States of Randomly Oriented Molecules. *J.*

- Chem. Phys.* **1964**, 41 (6), 1763–1772.
- (10) Philip, H. R. *Electron Spin Resonance Analysis and Interpretation*; The Royal Society of Chemistry: Cambridge, 2007.
 - (11) Borovykh, I. V.; Proskuryakov, I. I.; Klenina, I. B.; Gast, P.; Hoff, A. J. Magnetophotoselection Study of the Lowest Excited Triplet State of the Primary Donor in Photosynthetic Bacteria. *J. Phys. Chem. B* **2000**, 104 (17), 4222–4228.
 - (12) Thurnauer, M. C.; Norris, J. R. The Ordering of the Zero Field Triplet Spin Sublevels in the Chlorophylls. A Magnetophotoselection Study. *Chem. Phys. Lett.* **1977**, 47 (1), 100–105.
 - (13) Frank, H. A.; Bolt, J.; Friesner, R.; Sauer, K. Magnetophotoselection of the Triplet State of Reaction Centers from Rhodospseudomonas Sphaeroides R-26. *Biochim. Biophys. Acta* **1979**, 547, 502–511.
 - (14) Thurnauer, M. C.; Norris, J. R. Magnetophotoselection Applied to the Triplet State Observed by EPR in Photosynthetic Bacteria. *Biochem. Biophys. Res. Commun.* **1976**, 73 (2), 501–506.
 - (15) Schmidt, K.; Brovelli, S.; Coropceanu, V.; Beljonne, D.; Cornil, J.; Caronna, T.; Tubino, R.; Meinardi, F.; Shuai, Z.; Brdas, J.; et al. Intersystem Crossing Processes in Nonplanar Aromatic Heterocyclic Molecules Intersystem Crossing Processes in Nonplanar Aromatic Heterocyclic Molecules. *J. Phys. Chem.* **2007**, 111 (42), 10490–10499.
 - (16) Onuchic, J. N.; Beratan, D. N. A Predictive Theoretical Model for Electron Tunneling Pathways in Proteins. *J. Chem. Phys.* **1990**, 92 (1), 722–733.
 - (17) Miller, J. R.; Beitz, J. V. Long Range Transfer of Positive Charge between Dopant Molecules in a Rigid Glassy Matrix. *J. Chem. Phys.* **1981**, 74 (12), 6746–

6756.

- (18) Closs, G. L.; Miller, J. R. Intramolecular Long-Distance Electron Transfer in Organic Molecules The Basic Models and the Foundation of Their LTheoretical Description. *Science* (80-.). **1988**, 240, 440–447.

Chapter 3

Experimental

3.1 Materials

Meso-hexakis(pentafluorophenyl) [26]Hexaphyrins(1.1.1.1.1.1) and *meso*-hexakis(pentafluorophenyl) [28]Hexaphyrins(1.1.1.1.1.1) ([26]Hex and [28]Hex) were provided from Prof. Atsuhiko Osuka's group in Kyoto University. Details about the hexaphyrins are described in [Chapter 4.2](#).

Organic inclusion crystals consisting of *N,N'*-bis(pyrid-3-yl)-1,4,5,8-pyromellitic diimide (PMDI); 3-bromo-1-fluorobenzene (3BrF) or 4-bromo-1-fluorobenzene (4BrF); and tris(pentafluorophenyl)-borane (TPFB) (PMDI-3BrF and PMDI-4BrF) were provided from Prof. Yoshio Hisaeda's group in Kyusyu University. Organic inclusion crystals consisting of *N,N'*-bis(pyrid-3-yl)-1,4,5,8-naphthalenediimide (NDI); 1-fluoro-3-iodobenzene (3IF), or 3-iodo-1-methylbenzene (3IMe); and TPFB (NDI-3IF and NDI-3IMe) were also provided from Prof. Yoshio Hisaeda's group. Details about the organic inclusion crystals are described in [Chapter 5.2](#).

3.2 UV-vis Absorption Measurements

UV-vis absorption spectra at room temperature were measured on a SHIMAZDU UV-1650PC spectrometer with a 0.1 cm optical path length quartz cell. UV-vis absorption spectra at 77 K were measured on a JASCO V-650 equipped with an integrating sphere unit ISVC-747, where the sample tube including sample solution was set into a dewar bottle filled with liquid nitrogen.

3.3 Emission Spectra Measurements

Emission spectra were measured using a fluorescence spectrometer (JASCO, FP-8300) at room-temperature or at 77 K. Especially at 77 K, a dewar bottle which was filled with liquid nitrogen was used and the sample tube including sample solution was set into the dewar bottle.

3.4 Electro Chemical Measurements

Electrochemical measurements were performed using electrochemical analyzer (BAS Inc., ALS, model 608ES) with a standard three-electrode configuration. The cyclic voltammograms of sample solutions were acquired by taking grassy carbon, Pt, and Ag/AgCl as the working electrode, the counter electrode, and the reference electrode, respectively at room-temperature. Sample solutions were deoxygenated by Ar gas bubbling for 5 minutes before measurement.

3.5 Time-resolved EPR Measurements

Time-resolved EPR (TREPR) spectra were measured using a Bruker EMX X-band continuous wave (CW) EPR spectrometer without magnetic field modulation at 77 K or at room temperature. The EPR sample tubes which were deoxygenated were set inside the EPR cavity. A nanosecond-pulsed OPO laser (Spectra-Physics, basiscan/L13P-KE; $\lambda = 568$ nm and 650 nm, 10 Hz) pumped by a pulsed Nd:YAG laser (Spectra-Physics, Quanta-Ray Lab-130; $\lambda = 355$ nm) or a nanosecond pulsed Nd:YAG laser (Continuum, Minilite; $\lambda = 355$ nm) were used as an excitation light. Detected EPR signals were amplified by a wide-band preamplifier and taken in a digital oscilloscope (Tektronix, DPO 3054). The time-resolved measurements were carried out by synchronizing the

pulsed laser to the digital oscilloscope, as shown in [Figure 3.1](#). A quartz depolarizer (Sigmakoki, DEQ-1N) was employed for depolarized laser excitations. Details about the TREPR measurements are described in [Chapter 4.2](#) and [Chapter 5.2](#).

3.6 Theoretical Calculations

Molecular orbital calculations of PMDI was carried out using the time-dependent density functional theory (TD-DFT) method with the Becke's three parameter hybrid exchange functional and Lee-Yang-Parr correlation functional (B3LYP)¹⁻³ with a 6-31G* or 6-31G** basis set^{4,5} by Gaussian 09 program package.⁶ Details about the theoretical Calculations are described in [Chapter 4.2](#) and [Chapter 5.2](#).

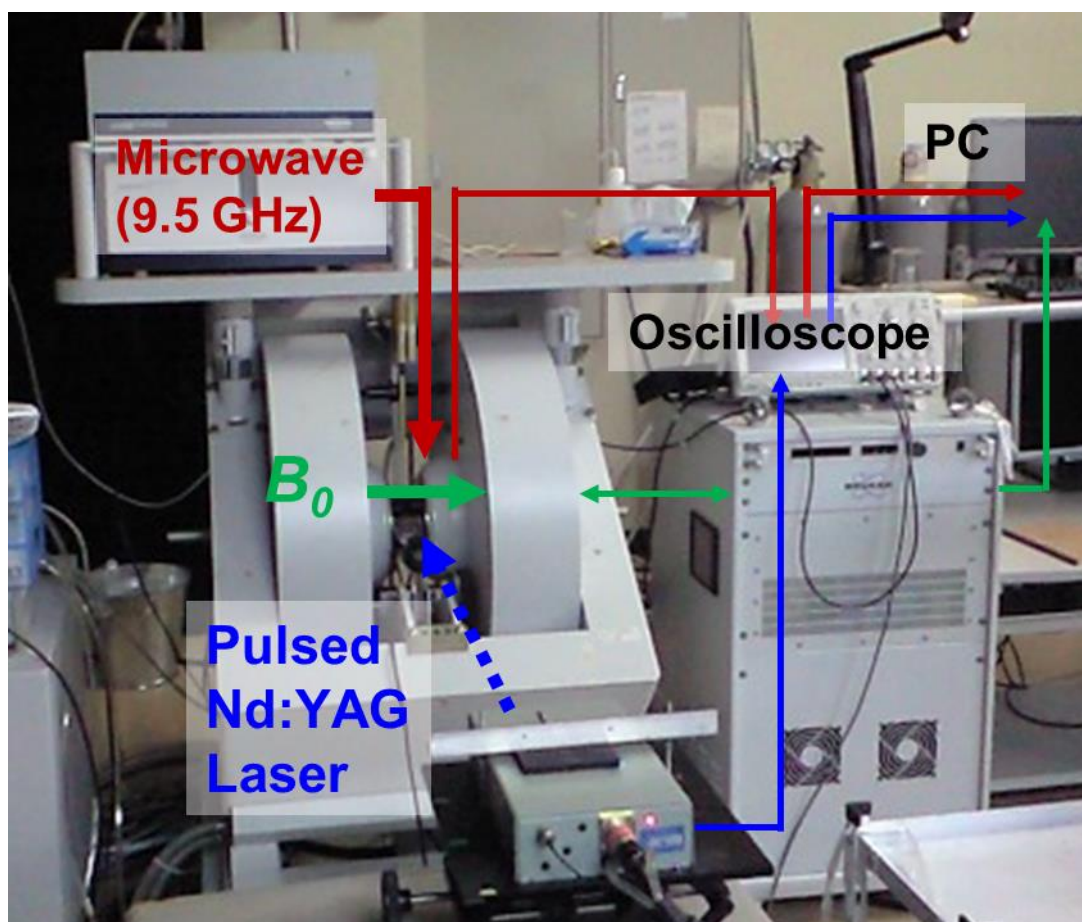


Figure 3.1. TREPR equipment.

References

- (1) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, 98 (7), 5648.
- (2) Weita Yang, R. G. P. C. L. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, 37 (2), 785–789.
- (3) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. Results Obtained with the Correlation Energy Density Functionals of Becke and Lee, Yang and Parr. *Chem. Phys. Lett.* **1989**, 157 (3), 200–206.
- (4) Petersson, G. A.; Al-Laham, M. A. A Complete Basis Set Model Chemistry. II. Open-Shell Systems and the Total Energies of the First-Row Atoms. *J. Chem. Phys.* **1991**, 94 (9), 6081–6090.
- (5) Peterson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. A Complete Basis Set Model Chemistry. I. The Total Energies of Closed-Shell Atoms and Hydrides of the First-Row Elements. *J. Chem. Phys.* **1988**, 89 (4), 2193–2218.
- (6) Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenb, D. J. Gaussian 09, Revision D.01. Gaussian, Inc.: Wallingford CT 2013.

Chapter 4

Electronic Structure of Möbius Antiaromatic Excited Triplet State of Twisted [28]Hexaphyrin

4.1 Chapter Introduction

Aromaticity is widely known to be one of the most important concepts in the field of chemistry.¹⁻⁷ Chemical properties and reactivities of macrocyclic π -conjugated molecules are determined by their aromatic or antiaromatic characters.^{8,9} As a complement of the Hückel rule,¹⁰ Heilbronner predicted that molecules having $[4n]$ and $[4n+2]$ π -electrons with singly twisted topology exhibit aromaticity and antiaromaticity, respectively.¹¹ The aromatic compounds represent diatropic ring currents, negative nucleus-independent chemical shift (NICS) values at the ring center, and large harmonic oscillator model of aromaticity (HOMA) values.¹² In addition, a resonance energy which is estimated based on the π -bond energies in annulenes can be a criteria of aromatic stabilization. A cyclic chain of annulenes are composed of single bonds and double bonds between the carbon atoms. The π -bond energies in the annulenes are evaluated by the total π -energies of the single bonds and double bonds based on Hückel molecular orbital. Then aromatic and antiaromatic compounds have positive and negative resonance energies, respectively.^{7,13} Aromatic and antiaromatic molecules exhibit positive and negative resonance integral (β), respectively. For example, benzene that shows aromaticity in the ground state has been found to have negative resonance energy in the first excited state, which represents that benzene shows antiaromatic character in the first excited state. Thus, aromaticity in the ground state was reversed to antiaromaticity in the excited state.¹ Möbius aromaticity has been intriguing both

experimental and theoretical researchers because its character is complementary to the common Hückel aromaticity that rule predicts aromatic character for the molecule with $[4n+2]$ π -electrons having a normal plane. Recently, Möbius aromatic macrocyclic compounds have been synthesized extensively.^{14–17}

In order to synthesize the chemically stable Möbius aromatic molecules, a twisted Möbius topology and overall cyclic conjugation of $[4n]$ π -electronic macrocycles have been implemented within one molecule. However, it is very difficult to observe the Möbius antiaromaticity experimentally because there are electronic destabilization arising from the antiaromaticity to cause structural constraints concerned with conformational twist within the molecule.¹⁸ That is, $[4n+2]\pi$ Möbius antiaromatic compounds have been attempted to obtain from the corresponding $[4n]\pi$ Möbius aromatic compounds by oxidation with its twisted formations with a hope. The result was, however, that $[4n+2]\pi$ Hückel aromatic compounds with nontwisted formations were obtained through the topological changes from the twisted formations. Then, their aromatic or antiaromatic characters have been confirmed experimentally in the S_0 state,^{19–23} but their properties in the electronic excited state, especially in T_1 state, have been scarcely investigated so far. Expanded porphyrins demonstrate considerably red-shifted absorption bands compared with those of porphyrins owing to their larger π -conjugated macrocycles.^{24–28} They attract great attentions as optical materials, functional dyes, nonlinear multi-metal ligands, stable organic radicals.^{25,26} Importantly, some expanded porphyrins exist as a twisted conformers showing the Möbius aromaticity or antiaromaticity.^{16,17,19,23,25,26}

In the Möbius aromatic compounds, the π -orbitals are lying along the twisted macrocycles with phase inversion of the topology similar to the Möbius strip.^{20,23}

Commonly, organic radicals represent high reactivity thus to be short-lived.^{29,30} In order to make long-lived organic radical species, a method of steric protection have been utilized. Placement of heteroatoms such as nitrogen atom and sulfur atom adjacent to the radical center was also utilized. Delocalization of the spin-density over large π -conjugation pathway is another effective way for stabilizing the organic radical species. Porphyrins including expanded porphyrins can stabilize species because of their ability of the radical delocalization.^{31–34} Cyclic delocalization of π -electrons in these species induce thermodynamic stability, which is concerned with relative low reactivity, bond length equalization, characteristic UV-vis absorption, susceptibility, and diamagnetic ring current of aromatic species.^{35–38}

Meso-aryl-substituted hexaphyrin(1.1.1.1.1.1)s can be a [26] or [28] π -electronic state.^{20,39,40} Planar [26]hexaphyrin and [28]hexaphyrin (Figure 4.1) exhibit aromatic and antiaromatic characters, respectively, in the S_0 state.^{19,20,23} These aromatic and antiaromatic natures are reversed in the T_1 state.^{22,41,42} [28]hexaphyrin exists in a fast equilibrium in solution mainly between antiaromatic planar conformation and Möbius aromatic twisted conformation at room temperature.²⁰ The electronic structure of [28]hexaphyrin has seemed to be mysterious since its discovery because the ^1H NMR represented a simple signal pattern indicating a highly symmetrical structure and the several X-ray crystal structures exhibited as a planar rectangular conformer. However, the values of the ^1H NMR chemical shifts and UV-vis-NIR absorption spectra supported its aromatic character. Then, measurement of ^1H NMR spectrum at low-temperature demonstrated [28]hexaphyrin was frozen as a Möbius conformer. The aromaticity and antiaromaticity of twisted hexaphyrins in the excited states has received great attention in relation to Baird's rule.^{13,43–45} Details about the electronic structures concerned with

the aromaticity and antiaromaticity, however, have not been studied in twisted Möbius aromatic molecules in the T_1 state.

The Goal of this work was to clarify the electronic structure of the T_1 states of *meso*-hexakis(pentafluorophenyl) [26]hexaphyrin(1.1.1.1.1.1) (**[26]Hex**) and *meso*-hexakis(pentafluorophenyl) [28]hexaphyrin (1.1.1.1.1.1) (**[28]Hex**) (Figure 4.1) using an X-band TREPR method in combination with magnetophotoselection (MPS) experiments. Finally, the origin of Möbius antiaromaticity in the T_1 state has been revealed.

4.2 Materials and Methods

4.2.1 Materials and Sample Preparations

The detail process in synthesis of *meso*-hexakis(pentafluorophenyl) [26]Hexaphyrins(1.1.1.1.1.1) and *meso*-hexakis(pentafluorophenyl) [28]Hexaphyrins(1.1.1.1.1.1) (**[26]Hex** and **[28]Hex**; Provided from Prof. Osuka's group in Kyoto University) are described in the previous reports.^{24,46} Toluene (JIS Special Grade) and 2-methyltetrahydrofuran (MTHF, Wako Special Grade) were purchased from Wako Pure Chemical Industries, Ltd., and they were used as received. For UV-vis absorption and TREPR experiments, **[26]Hex** and **[28]Hex** were dissolved in toluene and MTHF, respectively. The concentrations of these solutions were 100-200 μM . For the TREPR measurements, moreover, these solutions were deoxygenated by the freeze-pump-thaw cycles and they were sealed in quartz EPR sample tubes before the X-band TREPR measurements.

4.2.2 UV-vis Absorption Measurements

UV-vis absorption spectra at room temperature were measured on a SHIMADZU UV-1650PC spectrometer with a 0.1 cm optical path length quartz cell. UV-vis absorption spectra at 77 K were measured on a JASCO V-650 equipped with an integrating sphere unit ISVC-747, where the sample tube including sample solution was set into a Dewar bottle filled with liquid nitrogen.

4.2.3 Time-resolved EPR (TREPR) Measurements

TREPR spectra were measured using a Bruker EMX X-band continuous wave (CW) EPR spectrometer without magnetic field modulation at 77 K. The EPR sample tubes were placed in a Dewar bottle filled with liquid nitrogen, which was set inside the EPR cavity. A nanosecond-pulsed OPO laser (Spectra-Physics, basiscan/L13P-KE; $\lambda = 568$ nm and 650 nm, 10 Hz) pumped by a pulsed Nd:YAG laser (Spectra-Physics, Quanta-Ray Lab-130; $\lambda = 355$ nm) was utilized as an excitation light source as reported previously.⁴⁷ Microwave power was 4-5 mW. A quartz depolarizer (Sigmakoki, DEQ-1N) was employed for depolarized laser excitations. A quartz $\lambda/2$ waveplate (Sigmakoki, WPQW-65/78-2M) was used for introducing the polarized light converting the direction of polarization in 90 degrees. In magnetophotoselection (MPS) experiments, the polarization directions of the laser (L) were set parallel ($B_0//L$) and perpendicular ($B_0 \perp L$) to the direction of the external magnetic field (B_0). In the MPS measurements, the excitation wavelengths were chosen as described in [Figure 4.2](#) and [Figure 4.3](#).

4.2.4 Theoretical Calculations

Geometry optimizations of the ground state of **[26]Hex** and **[28]Hex** were carried out by the density functional theory (DFT) method with the Becke's three parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP)^{48–50} with 6-31G* and 6-31G** basis sets^{49,51} in Gaussian 03⁵² and Gaussian 09 program packages.⁵³ The Cartesian coordinates of the optimized geometries are listed in [Table 4.1](#), [4.2](#), and [4.3](#). The pentafluorophenyl groups of **[26]Hex** and **[28]Hex** were replaced with hydrogen atoms. The calculations for the excitation energy and the oscillator strength were performed by the ZINDO/S method^{54,55} in ORCA 3.0.3 program package^{56,57} and the ZINDO method⁵⁴ in Gaussian 09 program package for the B3LYP/6-31G** optimized geometry. The configuration interaction singles (CIS) calculations⁵⁸ were carried out using the restricted Hartree–Fock (RHF) method with a cc-pVDZ basis set⁵⁹ in Gaussian 03 program package for the B3LYP/6-31G* optimized geometry. The calculation of the zero-field splitting (ZFS) tensors was performed with Gaussian 03 program suite by Prof. Takui and Prof. Sato's Group in Osaka City University. The spin–spin contributions to the ZFS parameters (D^{SS} and E^{SS}) were estimated by the McWeeny–Mizuno equation^{60–63} with CIS/cc-pVDZ spin-densities at the B3LYP/6-31G* optimized geometries. The two-electron dipole–dipole integrals were calculated by homemade codes developed in Osaka City University.⁶³ It is noted that the CIS spin density-based approach shows a tendency to overestimate the D value for an extended π -conjugated system. The CIS calculations, nevertheless, deserved important consideration in determining the sign of the D value and the principal axes orientations of the D tensor of the systems under study, as shown in [Figure 4.1](#).^{64,65}

The NICS values were calculated by the gauge including atomic orbital (GIAO)

method^{66,67} at the B3LYP/6-31G** level for the S_0 state or at the UB3LYP/6-31G** level for the T_1 state based on the optimized geometries. The NICS values were computed for the centers of the hexaphyrin macrocycles with zero height as NICS(0) values, as given in the previous reports.^{20,41}

The T_1 - S_0 energy gaps were obtained as following. The geometry optimizations for the S_0 state using RB3LYP/6-31G** were carried out. For the optimized geometries, the single point energy calculations for the triplet states were performed by using UB3LYP/6-31G**. The geometry optimization for the twisted **[28]Hex** model molecule as the triplet state was also carried out. However, the optimized geometry represented a planer conformation which is categorized as the planar **[28]Hex**. Thus, the optimized geometries for the excited states were not adopted, since the structure in the T_1 state is frozen as described below. The SCF energy differences between these states are listed in [Table 4.4](#). The conformational preference of the twisted **[28]Hex** in the S_0 state was obtained by the RB3LYP/6-31G** calculations as shown in [Table 4.4](#). It is known that the basis function does not largely affect the state energies but the level of theory does. This preference is probably an accidental coincidence with the predominance of the twisted conformation at lower temperature, because the theoretical calculations were carried out for the model molecules of the hexaphyrins in which the pentafluorophenyl groups were replaced with the hydrogen atoms. It is known that the B3LYP theory exaggerates the delocalization of π -conjugated pathways, overstabilizing the Möbius structures.⁶⁸ However, the lack of the pentafluorophenyl groups in the B3LYP/6-31G** calculations seems to compensate for this overstabilization, giving rise to the preference of the twisted structure, while the other method of M05-2X is reported to result in the energetic preference of the Hückel structure for the **[28]Hex** model without the

pentafluorophenyl substituents as mentioned previously.⁶⁸ From the above argument, the S_0 state energies in Table 4.4 seem to be appropriate for the aromaticity molecules of [28]Hex and [26]Hex in Figure 4.1.

4.3 Results

4.3.1 UV-vis Absorption Measurements for the [26]Hex and [28]Hex

Figure 4.2 and Figure 4.3 show the absorption spectra of [28]Hex and [26]Hex obtained at 77 K. In the absorption spectrum of [28]Hex at 77 K (Figure 4.2) the strong absorption peak is observed at 619 nm. Also, the shoulder band around 640 nm is obtained. These absorption bands correspond to the transition dipole moments along the long and short molecular axes in the twisted Möbius [28]Hex, on the basis of the calculated absorption spectrum²⁰ and Figure 4.3 calculated by the ZINDO method. Thus, 650 nm excitation wavelength as pointed in Figure 4.2 was used to excite the transition dipole moment along the short molecular axis. This will avoid the excitation of the other transition dipole moments around 620 nm. A different MPS effect was observed when 598 nm excitation light was chosen, because this light corresponds to the long-axis excitation. Similar to the case of [28]Hex, 560 nm excitation wavelength was utilized to excite the transition dipole moment along the long molecular axis, based on the theoretically obtained absorption spectrum²⁰ calculated by the ZINDO method.

4.3.2 Time-resolved EPR experiments for the [26]Hex and [28]Hex

Figure 4.5 and Figure 4.6 show TREPR spectra of [28]Hex and [26]Hex, respectively. These were obtained by irradiating the depolarized light, the light (L) parallel to B_0 ($L // B_0$), and the light perpendicular to B_0 ($L \perp B_0$). The symmetrical EPR lines were

highly dependent upon the L direction. These effects indicate that the TREPR spectra originate from anisotropic spin-spin dipolar interaction i.e. the ZFS interaction. This tensor orientation is defined with respect to the optical transition dipole moment in the molecule.^{64,69} [Figure 4.7](#) shows dependence of the TREPR spectra on the delay time for **[28]Hex**.

4.3.3 Molecular Orbital Calculations for the **[26]Hex** and **[28]Hex**

Molecular orbitals (MOs) were computed for the planar **[26]Hex** and the twisted Möbius **[28]Hex** in the T_1 states. In these calculations, the pentafluorophenyl groups in [Figure 4.1](#) were replaced with hydrogen atoms. [Figure 4.8](#) illustrates the spin density distributions of **[26]Hex** and **[28]Hex** obtained by the CIS method (CIS/cc-pVDZ). [Figure 4.9](#) and [Figure 4.10](#) represent the MOs of **[26]Hex** and **[28]Hex** calculated also by the CIS method (CIS/cc-pVDZ). The data in [Figure 4.8](#), [Figure 4.9](#) and [Figure 4.10](#) were provided from Prof. Takui and Prof. Sato's group in Osaka City University.

As for the T_1 states, such overstabilization effect will not happen in the aromatic molecules due to the positive resonance energy in the antiaromatic π -conjugation macrocycles. Because the localized spin density distribution has been obtained in the T_1 state of the twisted **[28]Hex** model, the delocalization effect should be minor in the T_1 state energy. The T_1 state calculation was performed at UM05-2X/6-31G* level in the twisted **[28]Hex** model molecule for the optimized geometry by M05-2X/6-31G* level in the S_0 state. The spin density distribution has been clarified to be slightly more delocalized than the distribution obtained by the UB3LYP/6-31G*.

4.4 Discussion

4.4.1 Identification of the ZFS Tensor

The ZFS tensor can thus be determined by analyzing the TREPR spectra. And thus we may characterize the electronic structures of the T_1 states. The ZFS parameters of D and E are defined in the spin-spin dipolar coupling, as expressed by [equation \(2.33\)](#) in [Chapter 2](#). Computations of the TREPR spectra were performed based on line shape theory for the triplet state, as reported previously.⁷⁰ Details of the line shape analyses are described as [equation \(2.57\)](#), [\(2.62\)](#) and [\(2.63\)](#) in [Chapter 2](#).

Spin polarization of the microwave absorption (A) and the emission (E) originate from the ISC anisotropy in the initial sublevel populations P_X , P_Y , and P_Z in the wave functions of T_X , T_Y , and T_Z .⁷¹ The TREPR spectra of **[28]Hex** measured in toluene at 0.5 μ s in [Figure 4.5](#) represented an E/A/E/A/E/A polarization pattern. The ZFS parameters of **[28]Hex** were thus obtained to be $|D| = 532 (\pm 3)$ MHz and $|E| = 18.2 (\pm 2)$ MHz. The ZFS parameters of **[26]Hex** ([Figure 4.6](#)) and those of a butadiyne-substituted free base diarylporphyrin (H_2P)⁷¹ are also listed in [Table 4.5](#).

The $|E|$ value in **[28]Hex** is quite smaller than the $|E|$ values of **[26]Hex** and H_2P . This denotes negligibly small spin density distribution difference between the X and Y directions in **[28]Hex**. Since **[26]Hex** molecule is planar⁴⁰ like H_2P , the D value of **[26]Hex** is expected to be positive ($D > 0$) because r_{12}^2 is greater than $3z_{12}^2$.^{72–74} In this case, the principal Z-axis direction is out-of-plane. In contrast, the X- and Y-axes are located at in-planes of **[26]Hex** in [Figure 4.1a](#).^{73,74} Therefore, the large $|E|$ value in **[26]Hex** is explained by the delocalized electronic distribution for the planar rectangular π -skeleton, supporting larger $|E/D|$ value in **[26]Hex** than $|E/D|$ in H_2P in [Table 4.5](#). This is because H_2P is rather square shaped. Under the present cryogenic conditions, the

twisted conformer is predominant in **[28]Hex**. This is confirmed by the absorption spectrum in the ground state in [Figure 4.2](#) and [Figure 4.3](#).³⁹ The quite small $|E|$ value compared with $|D|$ ($|E/D| = 0.0342$) in **[28]Hex** in [Table 4.5](#) thus indicates that the unpaired electrons are not delocalized in the disordered molecular framework in [Figure 4.1b](#). The small $|E/D|$ also excludes conformation changes of the twisted $^3\text{[28]Hex}^*$ to yield planar $^3\text{[28]Hex}^*$ at 77 K.³⁹ One possible interpretation of this small $|E|$ is that the unpaired electrons are separated from each other as a charge-transfer (CT) state, resulting in $\langle (y_{12}^2 - x_{12}^2)/r_{12}^5 \rangle \approx 0$ in E due to the twisted framework. For such separated spins, $D < 0$ is reasonable in **[28]Hex**. The other possible explanation would be that the two unpaired spins are both locally distributed at one side of the twisted ring of **[28]Hex**. If these electrons reside along a long axis (Z), $D < 0$ is also expected. This situation is attributable to the spin density distribution in the excited triplet state of a carotenoid.^{75–}

77

The gross spin density distributions ([Figure 4.8a](#)) denoted a delocalized character in planar **[26]Hex**. This well supports $D > 0$ together with the larger $|E|$ value of the rectangular molecule than $|E|$ of $^3\text{H}_2\text{P}$ in [Table 4.5](#). In contrast, the twisted Möbius **[28]Hex** demonstrated a localized spin density distribution ([Figure 4.8b](#)). This suggests that the two unpaired spins are located at one side of the strip ring. This denotes the local excitation (LE) state. Using the calculated configuration interaction (CI) coefficients, as detailed in [Figure 4.10](#), the contributions of the CT and LE characters were estimated to be ca. CT:LE = 1:5 in the twisted Möbius **[28]Hex**. These LE and CT characters are both good agreement with the anticipated negative D value.

4.4.2 The Orientation of the Principal D-Tensor axes

To determine the orientation of the principal **D**-tensor axes with respect to the transition dipole moment (**M**) direction in **[28]Hex**, the MPS analyses were investigated in Figure 4.5 at 0.5 μ s.^{78–80} 650 nm light was chosen to photoexcite **[28]Hex** based on the UV–vis absorption peaks (Figure 4.2 and Figure 4.3) corresponding to the direction of **M** parallel to the short molecular axis, as reported previously.¹⁹ The calculated **M** in Figure 4.11 agrees with the absorption band at around 650 nm at 77 K (Figure 4.2), as explained in previous study.²⁰ From the line shape analysis to fit the TREPR spectra of Figure 4.5, the principal axis directions of the ZFS interaction of **[28]Hex** for the negative *D* was obtained by using the polar ($\delta = 60^\circ$) and azimuthal ($\gamma = 40^\circ$) angles of **M** in the principal XYZ axes system, as illustrated in Figure 4.11.

Together with the MPS effect, the direction of the Z-axis is determined by using the anisotropy in ISC from the lowest excited singlet (*S*₁) state to the triplet spin sublevels because such anisotropies are affected by the spin-orbit coupling (SOC) scheme between the singlet and triplet characters.^{73,74} In the case of the *D* < 0, *P*_X = 0, *P*_Y = 0.60, and *P*_Z = 0.40 were obtained to fit the E/A/E/A/E/A polarization pattern, as expressed in Figure 4.12. The *S*₁–*T*₁ ISC takes place via the ¹*n* π^* $\rightarrow$ ³ $\pi^*\pi^*$ transition scheme by the SOC with borrowing a high-lying ¹*n* π^* state in the *S*₁ state of ¹ $\pi\pi^*$.⁷² An n-orbital character of orbital number #115 (Figure 4.13) is found from the MO calculation of a **[28]Hex** model molecule at the B3LYP/6-31G* level. In the ZFS principal axes system in Figure 4.11, the n-orbitals on the nitrogen atoms labeled by “N” in Figure 4.13 are directing roughly to the Z- and X-axes. Also, the n-orbitals are orthogonal to the π -orbitals (π^* in Figure 4.14) at the positions of nitrogen atoms. The *S*₁–*T*_n ISCs may thus occur for both the *T*_Y and *T*_Z sublevels (i.e., *P*_Y $\approx$ *P*_Z $\gg$ *P*_X) via SOC during the

$^1n\pi^* \rightarrow ^3\pi'\pi^*$ transitions in Figure 4.14 owing to its twisted molecular topology in Figure 4.13. This is in line with the anisotropy in the ISC scheme obtained for the negative D in Figure 4.12. It is concluded that the sign of D is negative with the principal Z-axis directing along the long axis in the molecule. This also denotes that the spin density distribution is not delocalized in the **[28]Hex** macrocycle in the T_1 state. This is predicted by the MO calculations in Figure 4.8b. It is noted that this localized character in the T_1 state is also totally different from the delocalized character in the S_1 state²⁰ of the twisted **[28]Hex**. This is totally different characteristics from the delocalized spin distributions in $^3[26]\text{Hex}^*$ (Figure 4.8a) and $^3\text{H}_2\text{P}^*$.

4.4.3 Deactivation of the Triplet State of **[28]Hex**

Furthermore, the electronic structure of the T_1 state can be characterized by a change of the EPR line shape, as represented in Figure 4.7 for $t > 5 \mu\text{s}$. From Figure 4.7a,d,g, the line shapes were changed from the E/A/E/A/E/A pattern to A/A/A/E/E/E by the delay time. Previously, time-dependent EPR spectra were explained in terms of sublevel-dependent depopulations by a triplet–triplet energy transfer.⁸¹ In the present case, the A/A/A/E/E/E pattern is explained by a quick T_z depletion, as shown in Figure 4.15. The time dependent transverse magnetizations were quantitatively fitted in Figure 4.16 with taking into account the sublevel populations for the several delay times as determined by depletion rates (k_{-X} , k_{-Y} , and k_{-Z} in Figure 4.15) from the X, Y, and Z sublevels, respectively, as follows.

To compute the kinetic parameters of the non-radiative deactivation rate constants in the excited triplet states, the delay time dependence of the transverse magnetizations was quantitatively analyzed (Figure 4.16) using equation (4.1) by solving the triplet

sublevel populations (ρ_{11} , ρ_{22} and ρ_{33}), as following:

$$\frac{\partial}{\partial t} \begin{pmatrix} \rho_{11} \\ \rho_{22} \\ \rho_{33} \\ \rho_{44} \end{pmatrix} = \begin{pmatrix} -k_{12} - k_{RISC}(1) & k_{21} & 0 & k_{ISC}(1) \\ k_{12} & -k_{21} - k_{23} - k_{RISC}(2) & k_{32} & k_{ISC}(2) \\ 0 & k_{23} & -k_{32} - k_{RISC}(3) & k_{ISC}(3) \\ 0 & 0 & 0 & -k_X - k_Y - k_Z \end{pmatrix} \begin{pmatrix} \rho_{11} \\ \rho_{22} \\ \rho_{33} \\ \rho_{44} \end{pmatrix} \quad (4.4)$$

with

$$k_{ISC}(i) = |C_{ix}|^2 k_X + |C_{iy}|^2 k_Y + |C_{iz}|^2 k_Z \quad (4.5)$$

and

$$k_{RISC}(i) = |C_{ix}|^2 k_{-X} + |C_{iy}|^2 k_{-Y} + |C_{iz}|^2 k_{-Z} \quad (4.6)$$

where (c_{iX} , c_{iY} , c_{iZ}) for $i = 1, 2$ and 3 are the eigenvectors that diagonalize the spin Hamiltonian of the excited triplet state in the presence of the magnetic field. (k_X , k_Y , k_Z) and (k_{-X} , k_{-Y} , k_{-Z}) are the anisotropic S_1 - T_1 and T_1 - S_0 ISC rate constants in the spin sublevels at the zero-field. k_{ij} ($i < j$) are the spin-lattice relaxation rates between the sublevels and are treated as, $k_{ij} = k_{ji} \exp(g\beta B_0/k_B T)$ with $k_{12} = k_{23}$. The spin-lattice relaxation time is thus expressed as, $T_1 = 1/(k_{ij} + k_{ji})$. The time evolution of the density matrix elements, ρ_{11} , ρ_{22} , ρ_{33} and ρ_{S1} can be solved by using the matrices of the eigenvectors (S) and the eigenvalues (η) of the relaxation matrix in [equation\(4.4\)](#) to be $\rho = S \exp(\eta t) S^{-1} \rho(t=0)$, with setting the initial population $\rho(t=0)$ dominated at the excited singlet state (ρ_{S1}). The triplet deactivation rate constant is expressed as,

$$k_T = \frac{1}{3}(k_{-X} + k_{-Y} + k_{-Z}) \quad (4.7)$$

The EPR transition probabilities in T_1 - T_2 and T_2 - T_3 are demonstrated as,⁸²

$$\rho_{21} = \omega_1 \left\{ -Q_{T+} + 3C + \omega_0 - i \left(\frac{1}{T_2} \right) \right\}^{-1} (\rho_{22} - \rho_{11}) \quad (4.8)$$

$$\rho_{32} = \omega_1 \left\{ -Q_{T+} - 3C + \omega_0 - i \left(\frac{1}{T_2} \right) \right\}^{-1} (\rho_{33} - \rho_{22}) \quad (4.9)$$

where

$$Q_{T+} = g_{T,eff}\beta B_0 + \frac{1}{2}\sum_i A_{T,i} M_{T,i} \quad (4.10)$$

$$C = \frac{D}{6}(1 - 3\cos^2\theta) - \frac{E}{2}(\cos^2\phi\sin^2\theta - \sin^2\phi\sin^2\theta) \quad (4.11)$$

In [equation \(4.10\)](#), g_T and A_T denote the effective g values and hyperfine coupling constants in the excited triplet state. In the present system, the g_T and A_T can be regarded to be isotropic because the EPR spectra showed the symmetrical shapes. $A_T = 0$ was assumed. In [equation \(4.10\)](#), D and E are the ZFS constants mentioned above.

On the basis of the kinetic parameters of (k_X, k_Y, k_Z) and (k_{-X}, k_{-Y}, k_{-Z}) determined in [Figure 4.16](#), the sublevel populations for the zero-field levels was also calculated as the function of the delay time, as shown in [Figure 4.15](#). This demonstrates that the A/A/A/E/E/E pattern is explained by the dominant T_Z depletion for the later delay times. The deactivation kinetics of $k_T = (k_{-X} + k_{-Y} + k_{-Z})/3 = 16 \text{ ms}^{-1}$ from [Figure 4.15](#) agrees with the reported lifetime (90 μs) of $^3\text{[28]Hex}^*$ at 170 K determined by the transient absorption spectroscopy.³⁹

Deactivation of the triplet CT character $^3(\text{D}^{+*}-\text{A}^{-*})$ as demonstrated by [Figure 4.17](#) may result in the electron spin polarization in the triplet state. [Figure 4.18](#) shows views of the orbitals of π (number = 122 α) and π^* (123 α) from the Y- and Z-axes, respectively. These pictures are obtained by the DFT method of the T_1 state of the **[28]Hex** model molecule. When these CT unpaired orbitals are adopted to be a configuration contributing to the T_1 state, the two spins are separated from each other as illustrated in [Figure 4.18a](#). Because of the twisted molecular topology in the **[28]Hex** framework, the π^* orbital possesses an atomic orbital contribution that is orthogonal to the atomic orbital participating in the π orbital. These atomic orbital contributions in π^* and π are

represented by the p_x and p_y , respectively, in Figure 4.18. In this case, the change of the angular momentum is possible along the Z-axis through the $\pi^* \rightarrow \pi$ transition by the reverse ISC from $^3\pi\pi^*$ to $^1\pi^2$. This is because the rotation (L_z) of the p_x orbital results in the p_y orbital, as expressed by the dotted arrows in Figure 4.18. The T_z depopulation by the spin-flip is therefore explained by the effective SOC described by the matrix element of $\langle ^1(D-A)|H_{\text{SOC}}|^3(D^{+\bullet}-A^{-\bullet}) \rangle$ in the T_z sublevel. The above SOC-induced deactivation is relevant to an ISC scheme in which SOC is operative during triplet charge recombination between the orthogonal unpaired orbitals of $D^{+\bullet}$ and $A^{-\bullet}$ in the singlet CT state of donor (D)–acceptor (A) linked molecules, as reported by Wasielewski and coworkers.⁸³ The present T_z depopulation character demonstrates that the intramolecular CT character is included in the T_1 state of the twisted **[28]Hex**. This well explains CT:LE = 1:5 obtained from the CI coefficients in the triplet state in Figure 4.10. The D value of $D^{\text{SS}} = -746$ MHz from the spin-spin contribution was calculated based on the unpaired orbital distributions in Figure 4.8b obtained by the CIS method.^{61,63–65} The relation of $D^{\text{SS}} = 1.4D$ is coincident with the correlations between the computed D^{SS} and the D values (Table 4.6) calculated for tetraphenylporphyrins and hexaphyrins. This strongly supports the coexistence of the LE and CT characters in the twisted **[28]Hex**. The theoretically calculated data in Table 4.6 were provided from Prof. Takui and Prof. Sato’s group in Osaka City University.

Because the electronic characters in the T_1 states of the planar **[26]Hex** and the twisted **[28]Hex** are very compatible with the theoretical calculations (Table 4.6), one may evaluate the antiaromatic/aromatic characters of the T_1 states in both **[26]Hex** and **[28]Hex** on the basis of the DFT calculations (Table 4.7 and Table 4.8). The validity of using the (U)B3LYP levels of theory^{68,84} in the model molecules is detailed as below.

The computed D value of $D(\text{M05-2X}) = -763$ MHz obtained by the M05-2X/6-31G* method is almost identical with $D(\text{B3LYP}) = -746$ MHz obtained from the UB3LYP/6-31G* level. This denotes that the electronic structure is unaffected by the level of theory. The NICS(0) of the twisted Möbius **[28]Hex** denotes a large positive NICS(0) of 60 ppm in the T_1 state. This is in contrast to the negative NICS(0) of -15 ppm in the S_0 state in Table 4.7, representing the reversal relationship between the aromaticity and the antiaromaticity in the S_0 and T_1 states, respectively. The state energies (Table 4.4) of the S_0 and T_1 states were also computed by using the DFT calculations for the planar **[26]Hex**, the planar **[28]Hex**, and the twisted **[28]Hex**. In planar **[28]Hex**, which is a conformational isomer of twisted **[28]Hex**, the T_1 - S_0 energy gap of $\Delta E(T_1-S_0)$ was significantly smaller (0.29 eV) than the corresponding gap (1.10 eV) in the twisted **[28]Hex** in Table 4.4. This well explains the aromatic character in the T_1 state of the planar **[28]Hex** since the energy difference (0.1 eV) is quite small between the S_0 states of the planar and twisted **[28]Hex** molecules,³⁹ i.e. T_1 is highly stable in planar **[28]Hex** because of aromaticity in the excited state with reversal to the Hückel $[4n]$ antiaromaticity in S_0 in accordance with Baird's rule. This is confirmed by the negative NICS(0) value of -17 ppm in the T_1 state (Table 4.7). On the ground-state aromatic molecules of **[26]Hex** and twisted **[28]Hex**, $\Delta E(T_1-S_0) = 1.10$ eV was slightly larger in the twisted **[28]Hex** than that (0.95 eV) in **[26]Hex**. The vertical T_1 - S_0 energy gap has been obtained to be 1.21 eV by the UM05-2X/6-31G*. This energy is slightly higher than 1.10 eV in Table 4.4. These results indicate that the localized spin density distribution lowers the T_1 state energy. This is rationalized by the stronger spin-spin exchange coupling in the excited triplet state. Notably, even when the spin density distribution is more localized in the UB3LYP/6-31G* calculation for the twisted

[28]Hex model, the T_1 state energy is still larger than that in the planar [26]Hex model where spin density distribution is highly delocalized. Therefore this higher T_1 level is rationalized by the weakened exchange integral due to the involvement of the intramolecular CT character. The higher T_1 energy in the twisted $^3[28]\text{Hex}^*$ should not be from the LE character, because the delocalized distribution leads to electronic destabilization in the antiaromatic state due to the positive resonance energy¹³ for the extended π -conjugation systems in $^3[26]\text{Hex}^*$ (Figure 4.8a). Therefore, the higher T_1 state energy by the triplet CT character in $^3[28]\text{Hex}^*$ is caused by the electronic destabilization due to a weakened spin-spin exchange interaction between the separated unpaired orbitals in Figure 4.18a.

4.5 Conclusion

We have clarified the electronic structure of the T_1 state of [28]Hex by using the TREPR method in combination with MO calculations for the twisted Möbius aromatic molecules. The involvement of the intramolecular CT character has been clarified although the LE character at one side in the Möbius strip ring of the macrocycle is largely contributing to the electric structure. The weakened spin-spin exchange interaction between the separated unpaired electrons may destabilize the triplet state energy. This will contribute to the antiaromaticity. The quick SOC-induced triplet deactivation faster than $k_T = 10^4 \text{ s}^{-1}$ (Figure 4.15) can be an alternative important barometer to demonstrate the “antiaromaticity” because of the connection between the orthogonal CT character and the triplet instability. It is noted that k_T is usually smaller than 10^4 s^{-1} in $^3\pi\pi^*$ of the planar metal-free Hückel aromatic molecules at cryogenic temperatures for $\Delta E(T_1-S_0) \approx 1 \text{ eV}$.^{85,86} This well represent the remarkably accelerated

deactivation feature by the orthogonal $^3\pi\pi^*$ (Figure 4.17a) in the antiaromatic T_1 state. Thus, the spin-dependent deactivation can be another way to understand the untiaromaticity like the energetics and the ring current effects that are used to evaluate the aromaticity/antiaromaticity. The relationship between the aromaticity/antiaromaticity and the electronic structures is also informative for understanding the fundamental chemical reactivity of Möbius aromatic molecules for future designs of functional organic molecules.

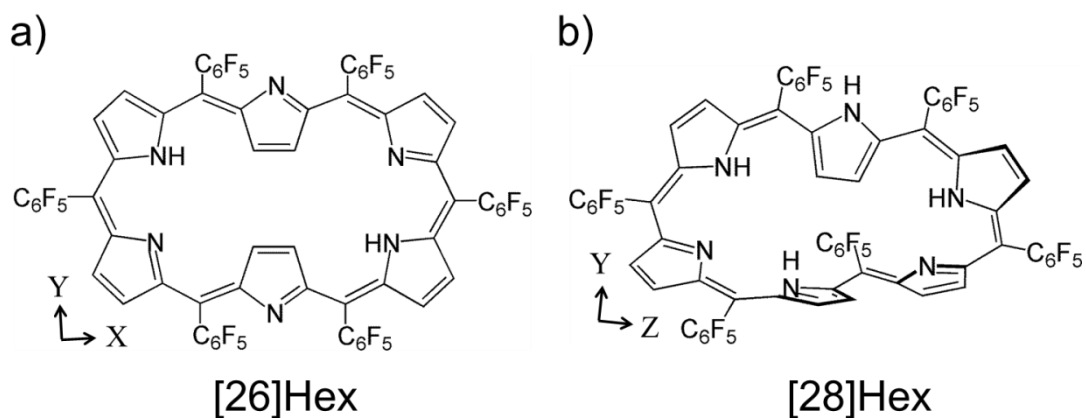


Figure 4.1. Molecular structures of (a) **[26]Hex** and (b) **[28]Hex**.

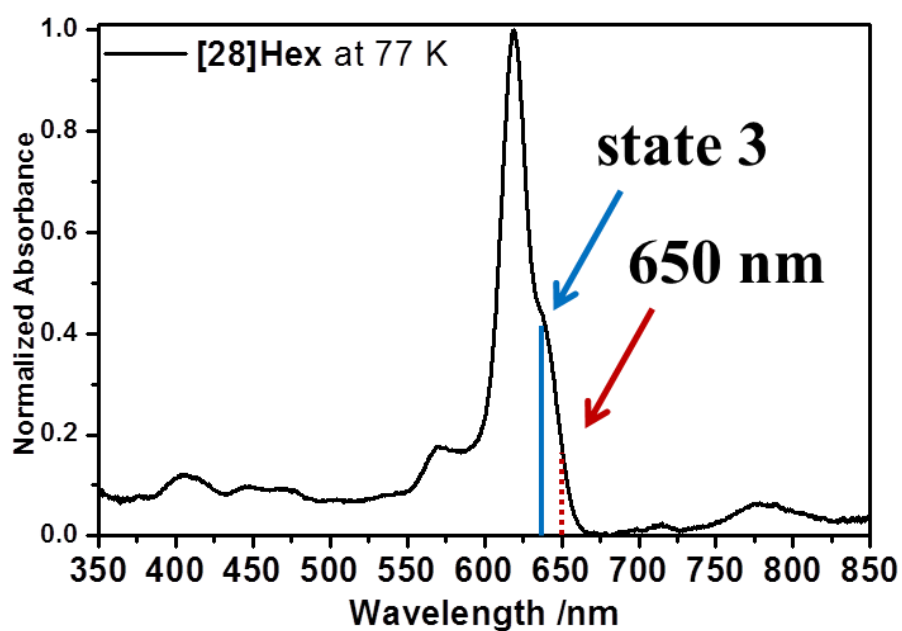


Figure 4.2. UV-vis absorption spectrum of **[28]Hex** in toluene at 77 K. A peak shown by state 3 at 630 nm corresponds to the transition dipole moment along the short molecular axis. This assignment of the direction of the dipole moment was supported by the theoretical calculation by the ZINDO method in [Figure 4.3](#).

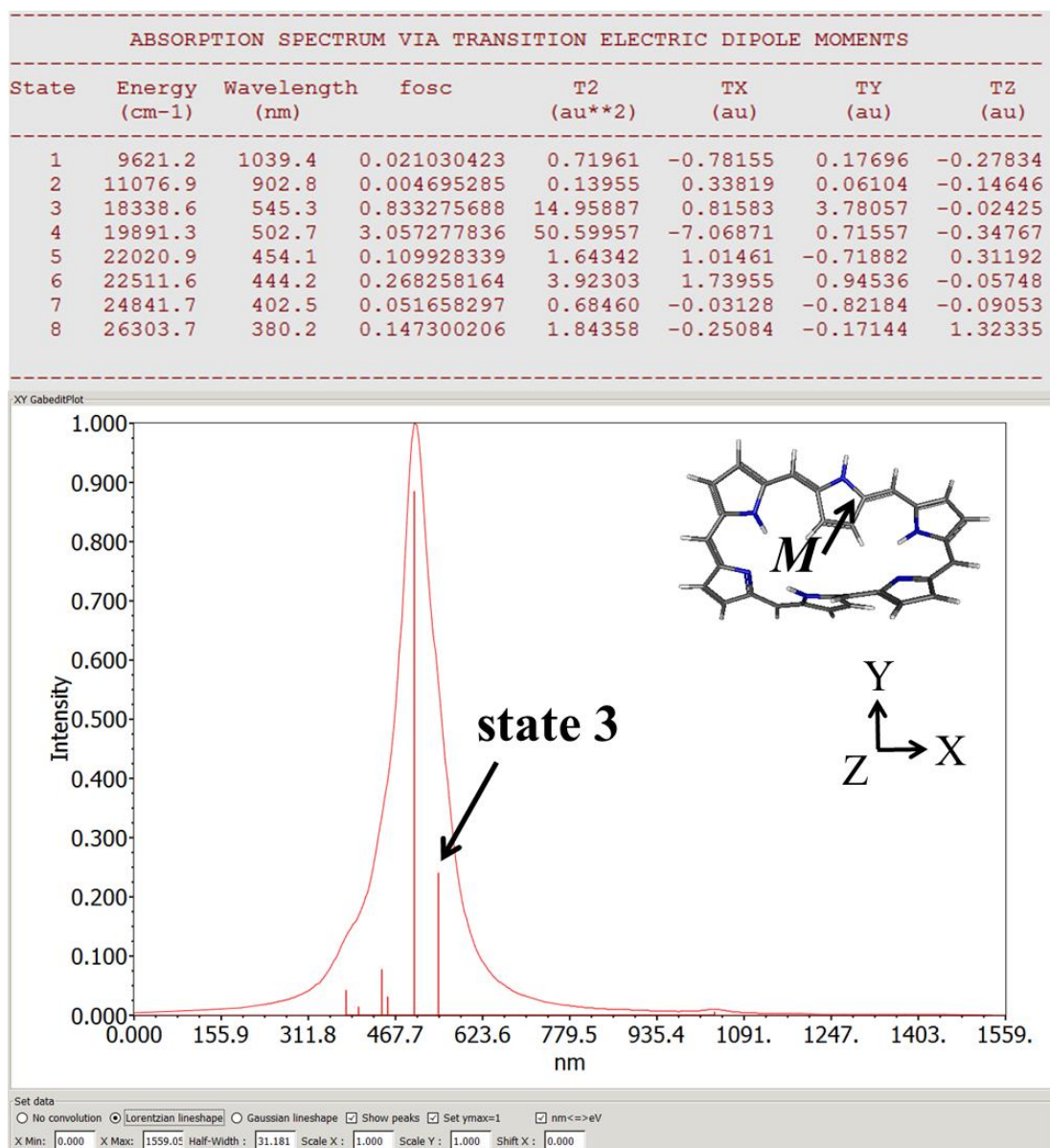


Figure 4.3. Calculated absorption spectrum and oscillator strength of twisted Möbius [28]Hex whose pentafluorophenyl groups are replaced with hydrogen atoms using the ZINDO/S method for the B3LYP/6-31G** optimized geometry. The inset shows the B3LYP/6-31G** optimized geometry and the molecular axes to express the directions of the transition dipole moment. The state 3 (545 nm band as denoted by the arrow) corresponds to the shoulder absorption band at 650 nm indicated by the arrow in Figure 4.3. The large transition intensity at TY in the state 3 is compatible with the direction of *M*.

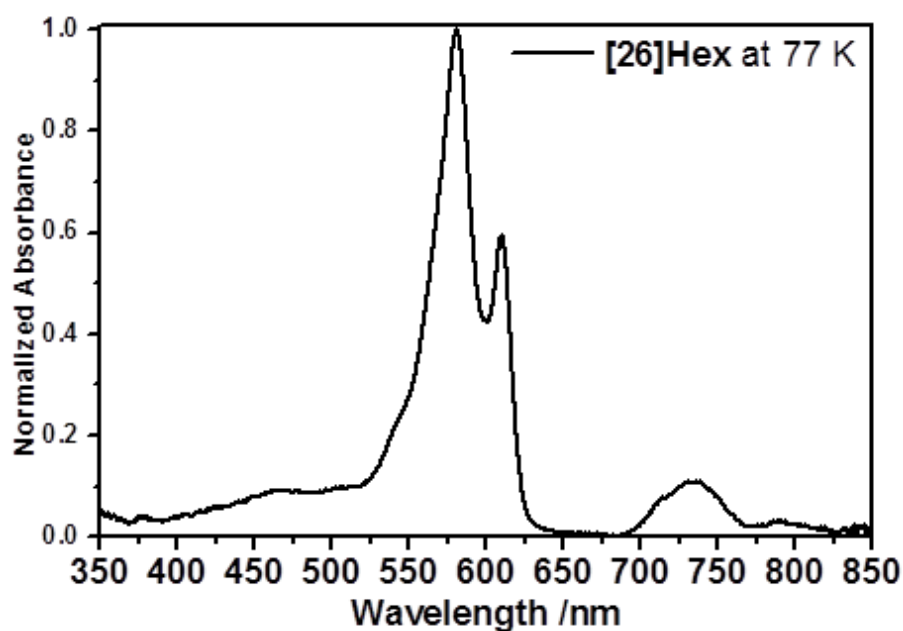


Figure 4.4. UV-vis absorption spectrum of [26]Hex in toluene at 77 K.

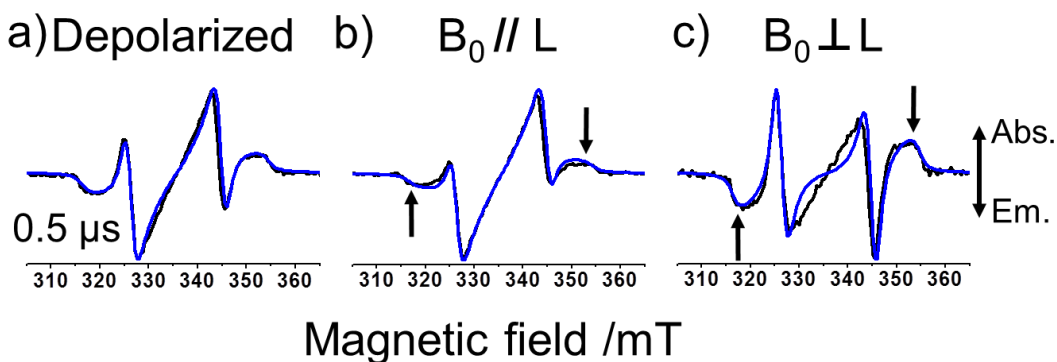


Figure 4.5. Experimental (black) and simulated (blue) TREPR spectra of [28]Hex observed at 0.5 μ s after the 650 nm laser irradiations at 77 K in toluene. Depolarized light was employed in the left. $B_0 \parallel L$ and $B_0 \perp L$ indicate that the polarization directions of the laser light (L) were parallel and perpendicular to the external magnetic field (B_0), respectively.

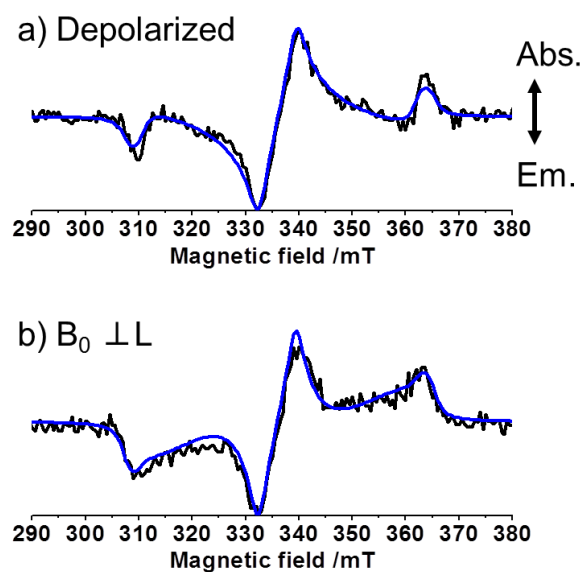


Figure 4.6. Experimental (black) and simulated (blue) TREPR spectra of **[26]Hex** observed at 0.5 μ s after the 568 nm laser irradiations at 77 K in toluene. Depolarized light was employed in the left. $B_0 \perp L$ indicate that the polarization directions of the laser light (L) were perpendicular to the external magnetic field (B_0), respectively.

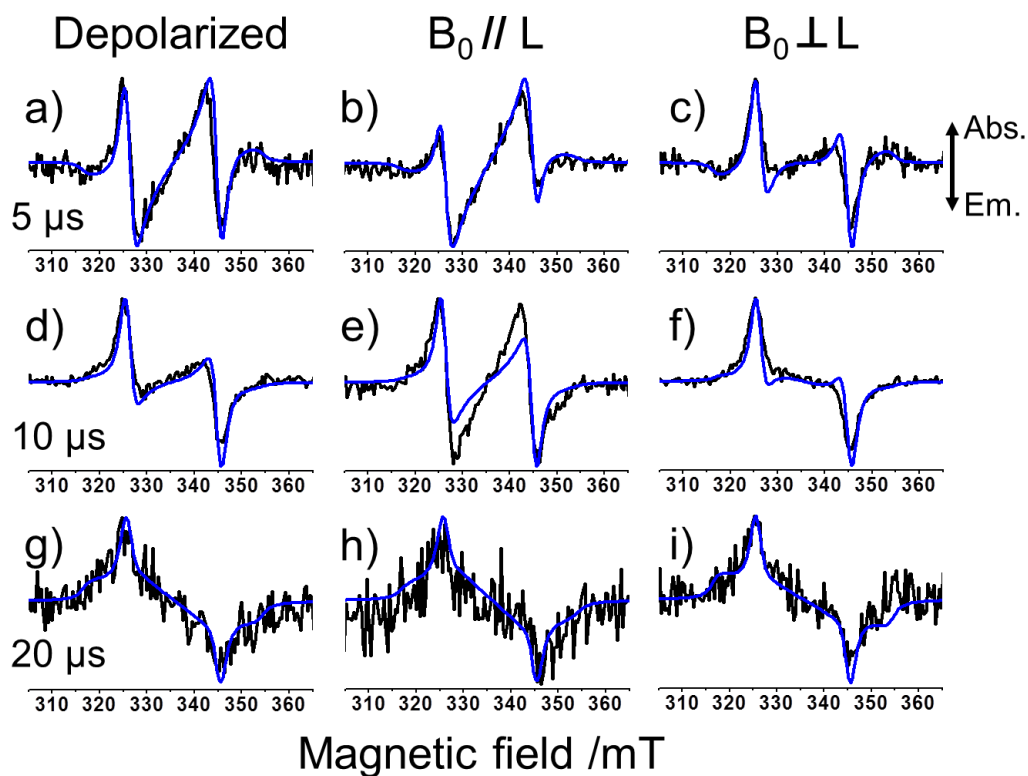


Figure 4.7. Experimental (black) and simulated (blue) TREPR spectra of **[28]Hex** observed at 5 μ s, 10 μ s and 20 μ s after the 650 nm laser irradiations at 77 K in toluene. Depolarized light was employed in the left. $B_0 \parallel L$ and $B_0 \perp L$ indicate that the polarization directions of the laser light (L) were parallel and perpendicular to the external magnetic field (B_0), respectively.

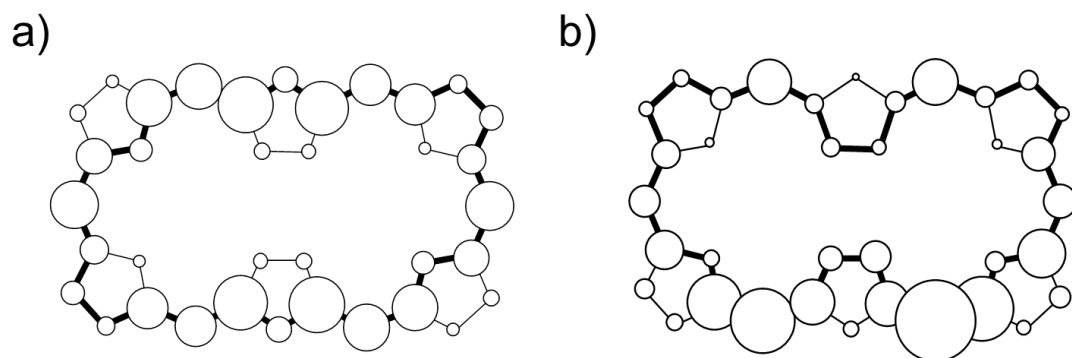


Figure 4.8. Gross spin density distributions of (a) planar **[26]Hex** and (b) twisted Möbius **[28]Hex** whose pentafluorophenyl groups are replaced with hydrogen atoms. The CIS/cc-pVDZ level was employed for the B3LYP/6-31G* optimized geometry in the ground state.

Excited State 1: Triplet-AU
 0.3517 eV 3525.53 nm f=0.0000

118 ->124	0.13710
119 ->125	-0.12997
120 ->122	-0.19312
120 ->123	0.33234
121 ->122	0.49806
121 ->123	0.16107

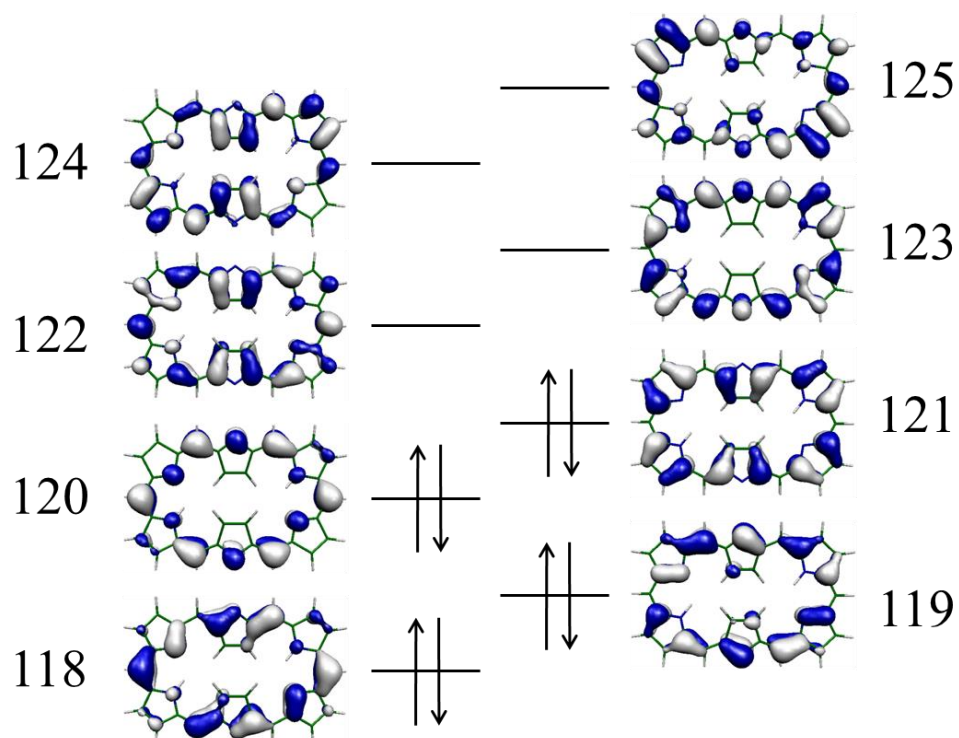


Figure 4.9. Molecular orbitals in the excited triplet state of the model molecule of planar **[26]Hex** obtained by the CIS/cc-pVDZ calculation for the B3LYP/6-31G* optimized geometry.

Excited State 1: Triplet-A
 0.5932 eV 2090.25 nm f=0.0000

119 ->125	0.11875
120 ->126	-0.12515
121 ->123	-0.21174
121 ->124	-0.33737
122 ->123	0.48908
122 ->124	-0.10656

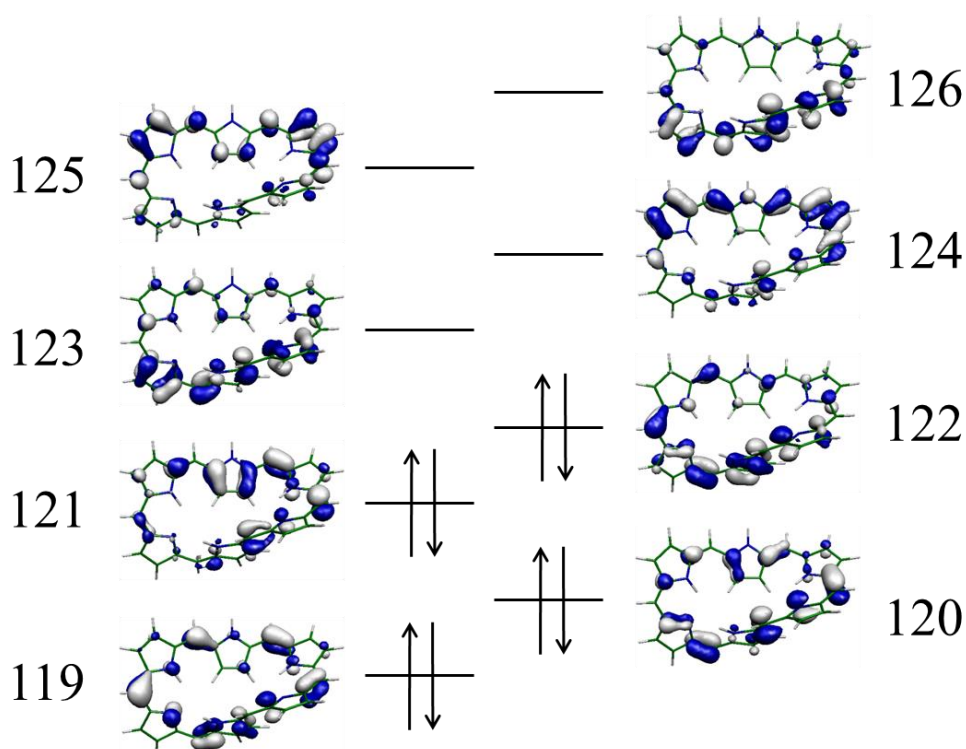


Figure 4.10. Molecular orbitals in the excited triplet state of the model molecule of twisted Möbius **[28]Hex** obtained by the CIS/cc-pVDZ calculation for the B3LYP/6-31G* optimized geometry. The transitions between the orbital numbers of 119 -> 125, 121 -> 123, and 122 -> 124 are regarded as the CT characters. 120 -> 126, 121 -> 124, and 122 -> 123 transitions are attributable to the LE. From the CI coefficients of 0.119, -0.212 and -0.107 for transitions 119 -> 125, 121 -> 123, and 122 -> 124, respectively, the CT character has been obtained to be 0.07 from a summation of the square values of these coefficients. Similarly, from the coefficients of 0.125, -0.337 and -0.489 for 120 -> 126, 121 -> 124, and 122 -> 123, the LE character has been obtained to be 0.369. Thus, CT:LE = 1:5 is obtained.

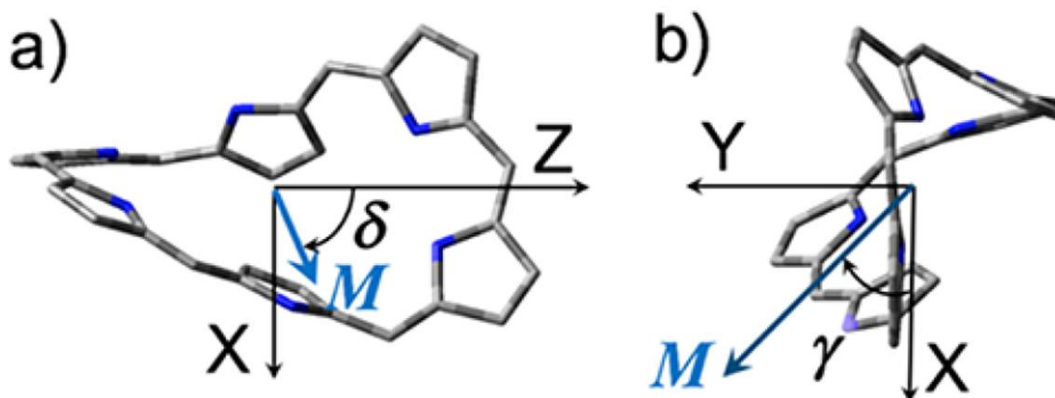


Figure 4.11. Orientations ($\delta = 60^\circ$ and $\gamma = 40^\circ$) of the principal ZFS principal axes with respect to the transition dipole moment (M) of **[28]Hex** determined by MPS. Views of **[28]Hex** from the Y- and the Z-axes are shown in (a) and (b), respectively.

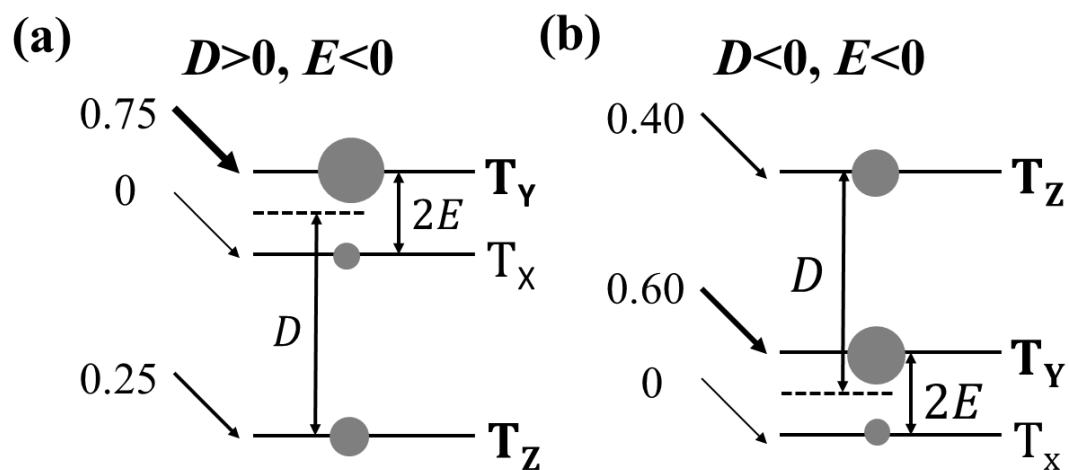


Figure 4.12. Relative populations in the triplet sublevels at $0.5 \mu\text{s}$ in **[28]Hex** in the case of (a) $D > 0$ and (b) $D < 0$, respectively.

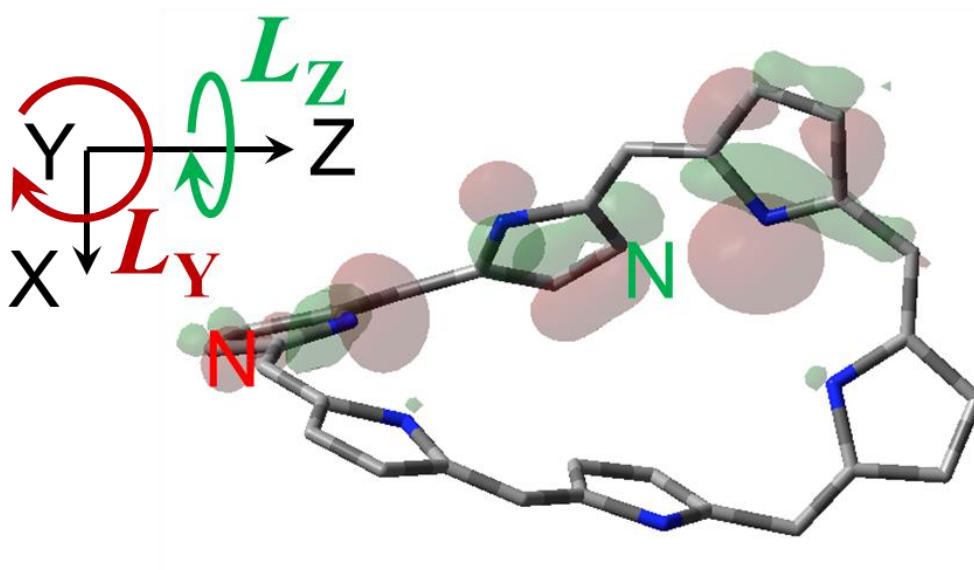


Figure 4.13. n-Orbital character involving the $^1n\pi^* \rightarrow ^3\pi'\pi^*$ ISC, which induces the angular momentum changes along the Y- and Z-axes.

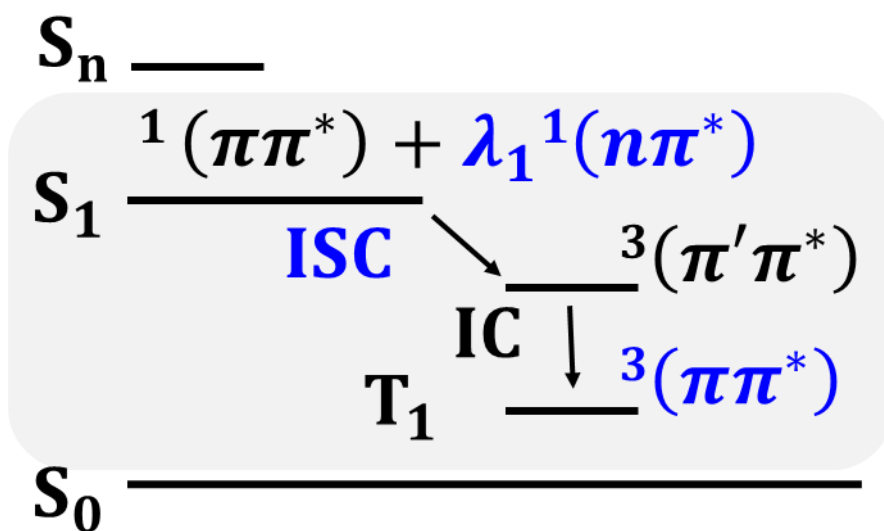


Figure 4.14. Schematic representation of the S_1 – T_1 ISC in [28]Hex.

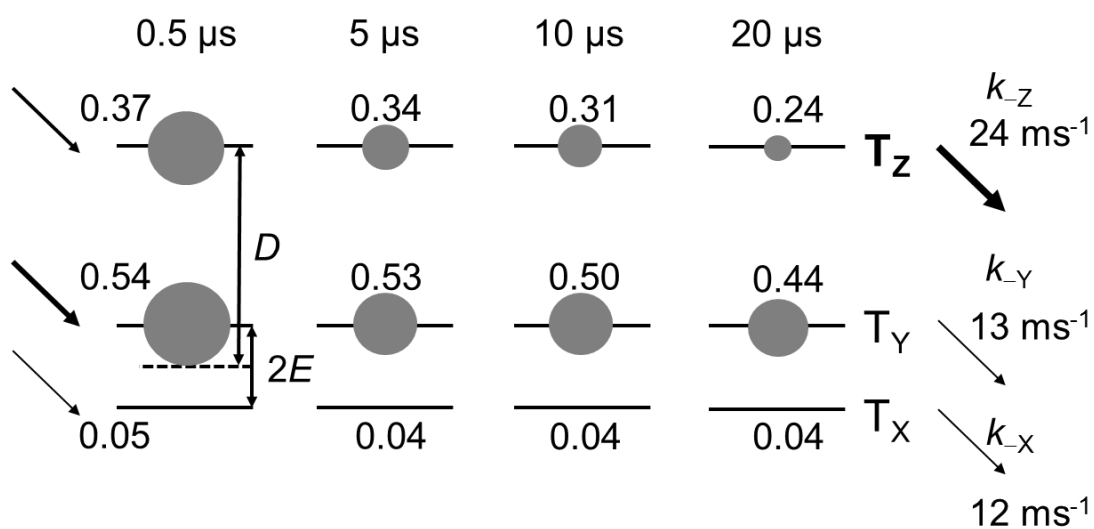


Figure 4.15. Relative populations in the zero-field triplet sublevels obtained for $D < 0$ and $E < 0$ of [28]Hex at several delay times to account for the spin polarization changes.

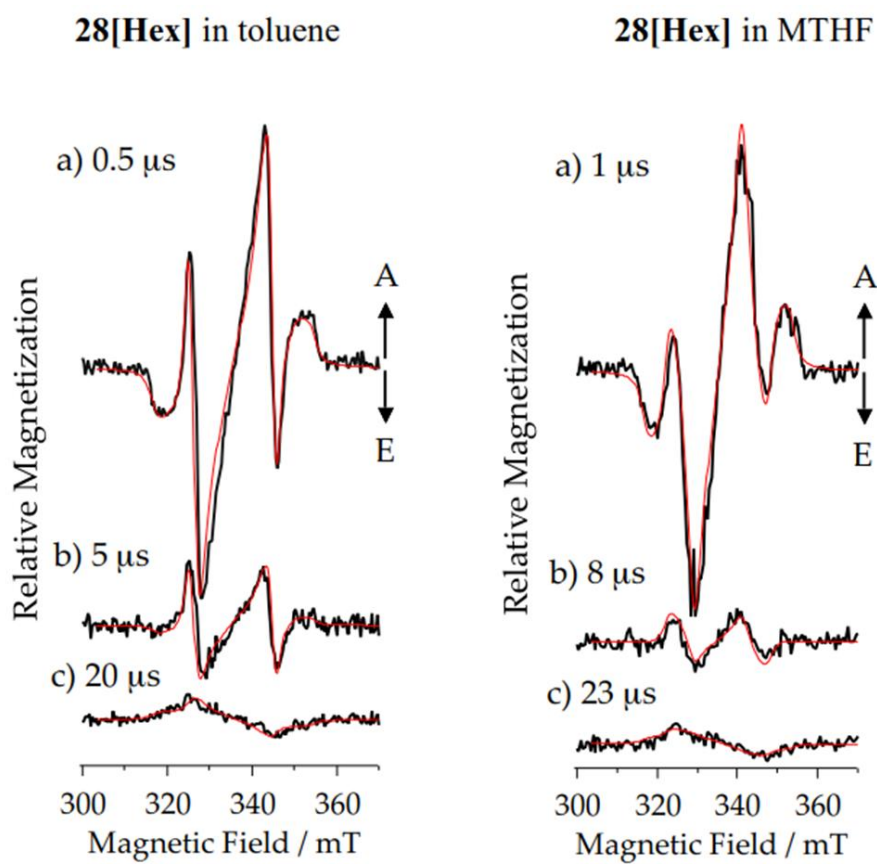


Figure 4.16. TREPR spectra of **28[Hex]** in toluene (left) and in MTHF (right) obtained by the depolarized laser irradiations at 77 K. The computed transverse magnetization curves are shown by the red lines to reproduce the EPR spectra together with their intensities for the given delay times. In toluene, $(k_X, k_Y, k_Z) = (1.0 \times 10^8, 1.2 \times 10^9, 8.0 \times 10^8) \text{ s}^{-1}$ and $(k_{-X}, k_{-Y}, k_{-Z}) = (1.2 \times 10^4, 1.3 \times 10^4, 2.4 \times 10^4) \text{ s}^{-1}$ were set to reproduce the data with $T_1 = 5.5 \text{ } \mu\text{s}$ as the spin-lattice relaxation time. In MTHF, $(k_X, k_Y, k_Z) = (1.1 \times 10^8, 3.1 \times 10^8, 3.0 \times 10^8) \text{ s}^{-1}$ and $(k_{-X}, k_{-Y}, k_{-Z}) = (1.3 \times 10^4, 1.1 \times 10^4, 1.9 \times 10^4) \text{ s}^{-1}$ were set with $T_1 = 7.5 \text{ } \mu\text{s}$. In MTHF, $D = -527 \text{ MHz}$ and $E = -67 \text{ MHz}$ were employed. From [eq.\(4.7\)](#), $k_T = 1.6 \times 10^4 \text{ s}^{-1}$ and $1.4 \times 10^4 \text{ s}^{-1}$ were obtained as the triplet deactivation rate constants in toluene and MTHF, respectively.

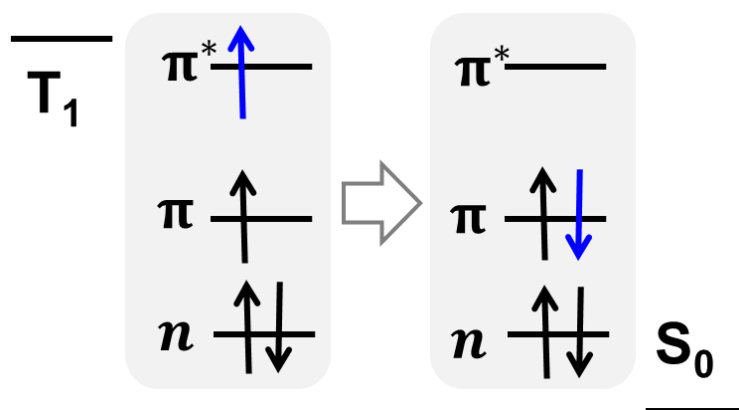


Figure 4.17. Deactivation scheme of the T_1 state leading to S_0 , contributing to anisotropy in the T_1 sublevels to account for spin polarizations for $t > 5 \mu\text{s}$ in [Figure 4.7](#).

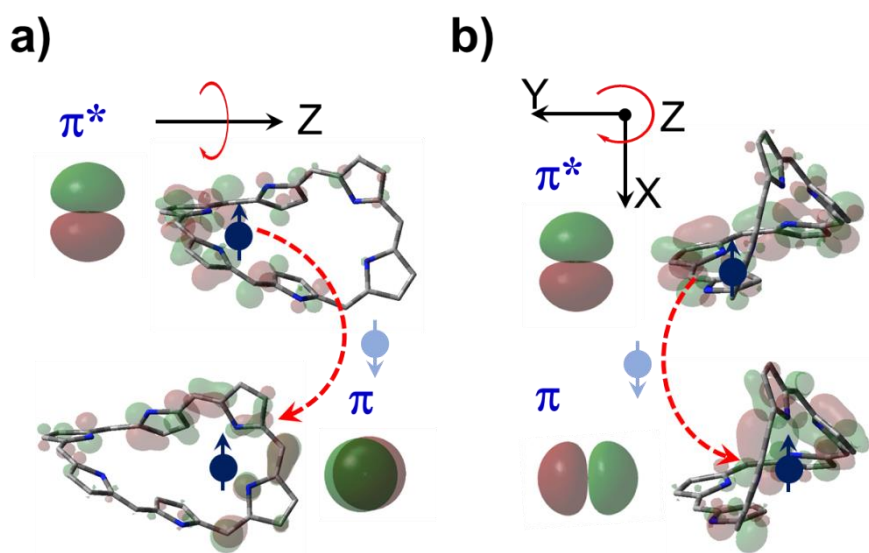


Figure 4.18. The CT character is represented by the orbitals of π (orbital number = 122 α) and π^* (123 α) obtained by the DFT calculation. The twisted molecules are viewed from the Y- and Z-axes in (a) and (b), respectively. Representative topologies of the localized unpaired orbitals are depicted by the p orbitals in (a) and (b), demonstrating that SOC is effective as the angular momentum change (L_Z) along the Z-axis to cause the spin-flip (dotted arrows) for the TZ depopulation during the $\pi\pi^* \rightarrow \pi^2$ transition.

Table 4.1. Cartesian coordinate of B3LYP/6-31G** optimized geometry of the planar [26]Hex whose pentafluorophenyl groups are replaced with hydrogen atoms in the ground state.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.106678	2.917939	0.184994
2	6	0	0.691849	1.589754	0.656693
3	6	0	-0.662921	1.597131	0.645802
4	7	0	-3.808521	1.434611	0.041082
5	6	0	-1.058534	2.924584	0.166768
6	6	0	-2.343431	3.434130	-0.050762
7	7	0	3.808521	-1.434611	-0.041082
8	6	0	-3.581766	2.777149	-0.046001
9	6	0	-5.162999	1.293088	0.001993
10	6	0	-5.837448	0.064878	0.025410
11	6	0	-5.247956	-1.198535	0.028807
12	6	0	-5.886061	-2.478159	0.105943
13	7	0	0.028637	3.706267	-0.061289
14	6	0	-4.904077	-3.434708	0.122428
15	6	0	-3.629070	-2.780904	0.028632
16	6	0	-2.393655	-3.430325	0.017176
17	6	0	-1.106678	-2.917939	-0.184994
18	6	0	-0.691849	-1.589754	-0.656693
19	6	0	0.662921	-1.597131	-0.645802
20	6	0	1.058534	-2.924584	-0.166768
21	7	0	-3.893129	-1.428599	-0.029099
22	6	0	2.343431	-3.434130	0.050762
23	6	0	3.581766	-2.777149	0.046001
24	6	0	5.162999	-1.293088	-0.001993
25	6	0	5.837448	-0.064878	-0.025410
26	6	0	5.247956	1.198535	-0.028807
27	6	0	5.886061	2.478159	-0.105943
28	6	0	4.904077	3.434708	-0.122428
29	6	0	3.629070	2.780904	-0.028632

30	6	0	2.393655	3.430325	-0.017176
31	7	0	-0.028637	-3.706267	0.061289
32	6	0	-4.842947	3.512010	-0.154811
33	6	0	-5.831770	2.587099	-0.102431
34	7	0	3.893129	1.428599	0.029099
35	6	0	4.842947	-3.512010	0.154811
36	6	0	5.831770	-2.587099	0.102431
37	1	0	1.332078	0.790960	1.004451
38	1	0	-1.341892	0.820800	0.961502
39	1	0	-2.370321	4.498061	-0.272274
40	1	0	-4.930332	4.587470	-0.239542
41	1	0	-6.902400	2.740262	-0.144818
42	1	0	-6.922456	0.089267	0.035176
43	1	0	-3.248584	-0.641487	-0.018479
44	1	0	-6.955948	-2.626821	0.150936
45	1	0	-5.026823	-4.507611	0.174998
46	1	0	-2.429951	-4.495924	0.223963
47	1	0	-1.332078	-0.790960	-1.004451
48	1	0	1.341892	-0.820800	-0.961502
49	1	0	2.370321	-4.498061	0.272274
50	1	0	4.930332	-4.587470	0.239542
51	1	0	6.902400	-2.740262	0.144818
52	1	0	6.922456	-0.089267	-0.035176
53	1	0	3.248584	0.641487	0.018479
54	1	0	6.955948	2.626821	-0.150936
55	1	0	5.026823	4.507611	-0.174998
56	1	0	2.429951	4.495924	-0.223963

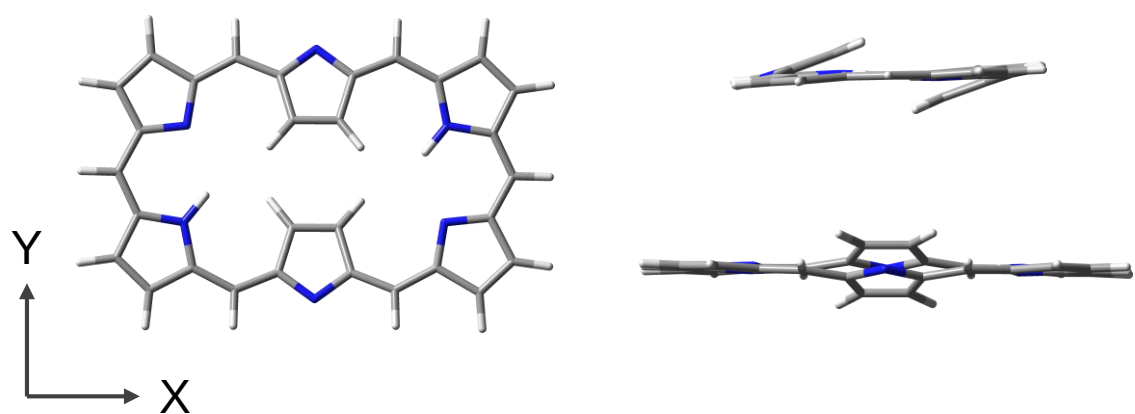


Table 4.2. Cartesian coordinate of B3LYP/6-31G** optimized geometry of the twisted Möbius [28]Hex whose pentafluorophenyl groups are replaced with hydrogen atoms in the ground state.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	5.294390	0.264498	-0.257046
2	6	0	6.207243	1.273641	-0.716129
3	1	0	7.284221	1.212805	-0.638420
4	6	0	5.466157	2.323380	-1.205216
5	1	0	5.837423	3.260244	-1.598314
6	6	0	4.071362	1.995196	-1.070278
7	6	0	2.962736	2.829103	-1.220946
8	6	0	1.631513	2.451404	-0.964787
9	6	0	1.006298	1.173655	-0.978276
10	1	0	1.464406	0.255566	-1.313167
11	6	0	-0.301729	1.316025	-0.558084
12	1	0	-1.020835	0.515311	-0.486417
13	6	0	-0.534414	2.687582	-0.253937
14	6	0	-1.617620	3.355995	0.332713
15	6	0	-2.840030	2.841137	0.765789
16	6	0	-3.875149	3.577974	1.435350
17	1	0	-3.797210	4.623389	1.701920
18	6	0	-4.938698	2.737772	1.656944
19	1	0	-5.880860	2.979391	2.129301
20	6	0	-4.606142	1.454057	1.116208
21	6	0	-5.413337	0.333763	0.924898
22	6	0	-5.030655	-0.803644	0.188585
23	6	0	-5.960187	-1.696964	-0.485859
24	1	0	-7.036131	-1.694197	-0.364703
25	6	0	-5.213603	-2.448264	-1.343720
26	1	0	-5.554554	-3.206981	-2.036750
27	6	0	-3.828393	-2.076315	-1.114384
28	6	0	-2.714373	-2.629715	-1.755716
29	6	0	-1.393403	-2.549402	-1.299635

30	6	0	-0.176348	-2.836832	-1.986904
31	1	0	-0.119052	-3.152205	-3.019818
32	6	0	0.871550	-2.639374	-1.115299
33	1	0	1.926087	-2.781660	-1.294394
34	6	0	0.331238	-2.294074	0.166194
35	6	0	0.982292	-2.289654	1.411010
36	6	0	2.365009	-2.127568	1.573918
37	6	0	3.174829	-2.636531	2.672045
38	1	0	2.803619	-3.180228	3.531735
39	6	0	4.472285	-2.361256	2.351571
40	1	0	5.362322	-2.603333	2.918930
41	6	0	4.432164	-1.590355	1.115664
42	6	0	5.497744	-0.850916	0.558208
43	7	0	4.031818	0.716856	-0.569477
44	1	0	3.233454	0.176592	-0.221274
45	7	0	0.646128	3.345838	-0.579174
46	1	0	0.836267	4.301964	-0.321890
47	7	0	-3.317255	1.555562	0.631148
48	1	0	-2.927718	0.762281	0.125864
49	7	0	-3.745309	-1.083922	-0.171396
50	7	0	-1.036485	-2.218249	-0.007309
51	1	0	-1.724260	-1.904581	0.666324
52	7	0	3.154274	-1.495300	0.657666
53	1	0	-6.449078	0.415255	1.238612
54	1	0	-2.877047	-3.180136	-2.677609
55	1	0	-1.494073	4.422286	0.505656
56	1	0	3.170716	3.876577	-1.421768
57	1	0	6.509682	-1.054371	0.892727
58	1	0	0.384034	-2.495360	2.295971

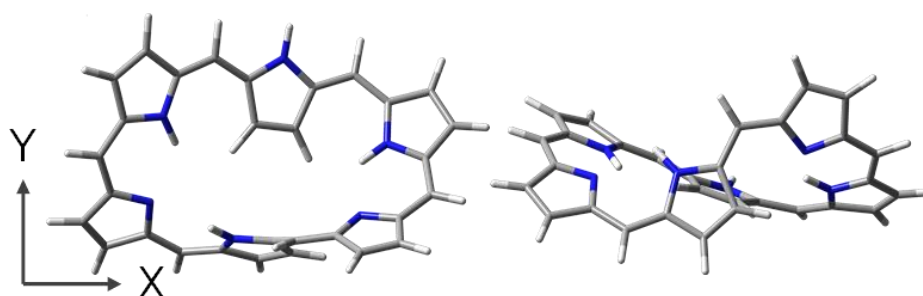


Table 4.3. Cartesian coordinate of B3LYP/6-31G** optimized geometry of the planer [28]Hex whose pentafluorophenyl groups are replaced with hydrogen atoms in the ground state.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.181631	2.948964	0.141404
2	6	0	0.700926	1.656678	0.595236
3	6	0	-0.660903	1.663075	0.585129
4	7	0	-3.848801	1.446056	0.023578
5	6	0	-1.122704	2.956901	0.123279
6	6	0	-2.383519	3.452730	-0.084531
7	7	0	3.848800	-1.446056	-0.023585
8	6	0	-3.643432	2.768191	-0.043826
9	6	0	-5.234174	1.288709	0.012575
10	6	0	-5.893684	0.077307	0.017227
11	6	0	-5.321886	-1.214618	0.017259
12	6	0	-5.958981	-2.469135	0.058062
13	7	0	0.031768	3.707277	-0.068845
14	6	0	-4.966267	-3.446270	0.073493
15	6	0	-3.710498	-2.799102	0.030490
16	6	0	-2.440635	-3.453062	0.057581
17	6	0	-1.181632	-2.948964	-0.141399
18	6	0	-0.700927	-1.656678	-0.595231
19	6	0	0.660901	-1.663076	-0.585128
20	6	0	1.122704	-2.956902	-0.123270
21	7	0	-3.959754	-1.450878	-0.007341
22	6	0	2.383518	-3.452730	0.084531
23	6	0	3.643432	-2.768191	0.043822
24	6	0	5.234173	-1.288710	-0.012579
25	6	0	5.893683	-0.077307	-0.017230
26	6	0	5.321885	1.214618	-0.017259
27	6	0	5.958997	2.469135	-0.058063
28	6	0	4.966267	3.446271	-0.073489
29	6	0	3.710498	2.799103	-0.030486

30	6	0	2.440634	3.453061	-0.057575
31	7	0	-0.031769	-3.707275	0.068853
32	6	0	-4.902417	3.506537	-0.104270
33	6	0	-5.894011	2.579051	-0.055486
34	7	0	3.959753	1.450878	0.007346
35	6	0	4.902416	-3.506536	0.104265
36	6	0	5.894011	-2.579052	0.055475
37	1	0	0.038305	4.592361	-0.550166
38	1	0	1.332287	0.852828	0.945754
39	1	0	-1.329697	0.880046	0.905434
40	1	0	-2.452024	4.511420	-0.326752
41	1	0	-4.993401	4.583796	-0.163705
42	1	0	-6.964829	2.736777	-0.076066
43	1	0	-6.979778	0.106386	0.013588
44	1	0	-3.313981	-0.666575	0.019509
45	1	0	-7.029498	-2.619490	0.077861
46	1	0	-5.100172	-4.518682	0.099760
47	1	0	-2.505770	-4.513231	0.290769
48	1	0	-0.038305	-4.592366	0.550162
49	1	0	-1.332287	-0.852828	-0.945749
50	1	0	1.329695	-0.880048	-0.905436
51	1	0	2.452024	-4.511419	0.326755
52	1	0	4.993401	-4.583795	0.163701
53	1	0	6.964828	-2.736778	0.076051
54	1	0	6.979777	-0.106386	-0.013593
55	1	0	3.313980	0.666574	-0.019503
56	1	0	7.029496	2.619490	-0.077865
57	1	0	5.100171	4.518683	-0.099756
58	1	0	2.505768	4.513231	-0.290761

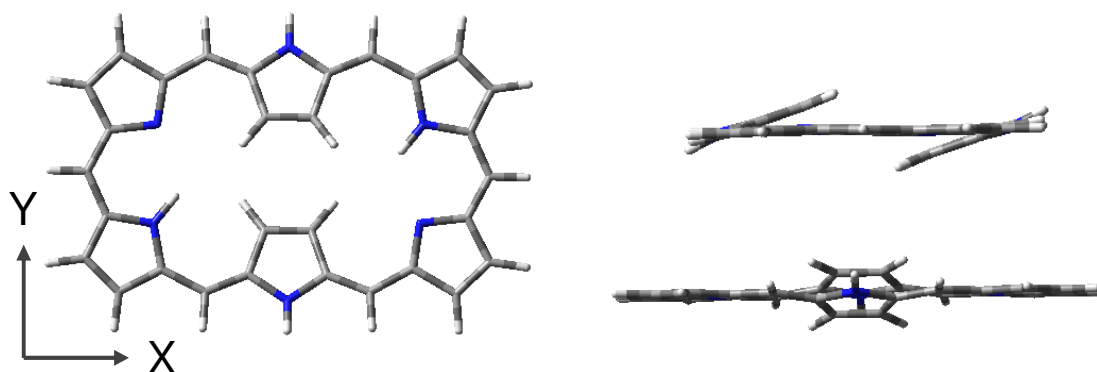


Table 4.4. Calculated state energies and the energy gaps between the T_1 and S_0 states obtained by the (U)B3LYP/6-31G** methods.

	$E(S_0)$ /Hartree	$E(T_1)$ /Hartree ^a	$\Delta E(T_1-S_0)$ / eV
[26]Hex	-1483.688329	-1483.653502	0.95
[28]Hex (planar)	-1484.920999	-1484.910211	0.29
[28]Hex (twisted)	-1484.924953	-1484.884429	1.10 ^b

^a Obtained by the single point calculations for the optimized geometries in the S_0 states.

^b The vertical T_1-S_0 energy gap has been obtained to be 1.21 eV by the (U)M05-2X/6-31G* level for the optimized geometry by M05-2X/6-31G* in the S_0 state. Since the excitation energies are not largely affected by the level of theory, T_1-S_0 energy gap ≈ 1 eV is conclusive for the twisted [28]Hex, highlighting the remarkably accelerated $T_1 \rightarrow S_0$ deactivation character by the orthogonal ${}^3\pi\pi^*$.

Table 4.5. ZFS parameters (D and E) and anisotropies ($P_x : P_y : P_z$) of the populations at the zero-field sublevels in **[26]Hex**, **[28]Hex**, H_2P , and carotenoid.

	D / MHz	E / MHz	$ E/D $	$P_x : P_y : P_z$
[26]Hex ^a	813($\pm$ 3)	-205($\pm$ 3)	0.25	0.05:0.95:0.00
[28]Hex ^b	-532($\pm$ 3)	-18.2($\pm$ 2)	0.034	0.00:0.60:0.40
H_2P ^c	1024($\pm$ 3)	-144($\pm$ 2)	0.14	0.47:0.53:0.00
Carotenoid ^d	-1160($\pm$ 2)	-114($\pm$ 2)	0.098	0.40:0.20:0.40

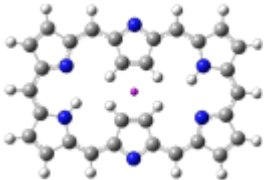
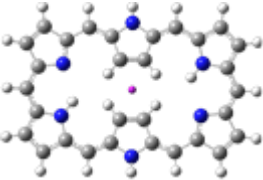
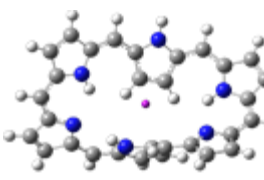
^a In MTHF. ^b In toluene. ^c Taken from reference⁷². ^d Taken from reference⁷⁵. The negative D is conclusive for $P_x : P_y : P_z = 0.4:0.2:0.4$ to account for the E/E/A/E/A/E polarization generated by the triplet-triplet energy transfer.

Table 4.6. Calculated ZFS parameters of D^{SS} and E^{SS} obtained by the CIS calculation together with the experimentally determined ZFS parameters of $D(\text{Exptl.})$ and $E(\text{Exptl.})$ obtained for the phenyl substituted porphyrins (H_2P = Tetraphenylporphyrin, ZnP = Zinc tetraphenylporphyrin, and MgP = Magnesium tetraphenylporphyrin) together with hexaphyrins ([26]Hex and [28]Hex).

	D^{SS}/MHz	E^{SS}/MHz	$ E^{SS}/D^{SS} $	$D(\text{Exptl.})/\text{MHz}$	$E(\text{Exptl.})/\text{MHz}$	$ E/D $
[26]Hex(Planar)	+971 ^a	−24 ^a	0.0258	+813 ^b	−205 ^b	0.252
[28]Hex(Möbius)	−746 ^a	−3 ^a	0.0041	−532 ^c	−18.2 ^c	0.034
H ₂ P	+1508 ^a	−183 ^a	0.121	1148 ^d	−239 ^d	0.209
ZnP	+1334 ^a	−54 ^a	0.040	911 ^e	−270 ^e	0.296
MgP	+1358 ^a	−78 ^a	0.057	914 ^f	−255 ^f	0.279

[a] The CIS calculations were undertaken for corresponding molecules whose phenyl groups (or pentafluorophenyl groups) are replaced with hydrogen atoms at meso positions. The CIS calculations tend to overestimate the D value for the extended π conjugated system due to the computations without the phenyl groups. However, a good correlation obeying $D^{SS} = 1.4 D(\text{Exptl.})$ is obtained between D^{SS} and $D(\text{Exptl.})$. This indicates a validity of the present computed electronic structure shown in Figure 4.11 with CT:LE = 1:5 to explain the ZFS parameters in the twisted [28]Hex. It is also noted that the computed principal axes orientation (Figure 4.1b) of the spin-spin dipolar interaction was consistent with the experimentally determined orientation in Figure 4.13. [b] Obtained in 2-methyltetrahydrofuran, [c] Obtained in toluene. [d] Taken from reference⁸⁷. Absolute sign of D was not determined experimentally. [e] Taken from reference⁸⁷. Absolute sign of D was not determined experimentally. [f] Taken from reference⁸⁷, absolute sign of D was not determined experimentally.

Table 4.7. Calculated NICS values (ppm) at the ring centers in the S_0 and T_1 states of planar [26]Hex, planar [28]Hex and twisted Möbius [28]Hex.

	[26]Hex (Planar)	[28]Hex (Planar)	[28]Hex (Möbius)
NICS(0) position			
S_0	-16.75	45.88	-14.90
T_1	41.72	-17.02	59.51

References

- (1) Rosenberg, M.; Dahlstrand, C.; Kilsa, K.; Ottosson, H. Excited State Aromaticity and Antiaromaticity: Opportunities for Photophysical and Photochemical Rationalizations. *Chem. Rev.* **2014**, *114* (10), 5379–5425.
- (2) Merino, G.; Heine, T.; Seifert, G. The Induced Magnetic Field in Cyclic Molecules. *Chem. - A Eur. J.* **2004**, *10* (17), 4367–4371.
- (3) Gomes, J. A. N. F.; Mallion, R. B. Aromaticity and Ring Currents. *Chem. Rev.* **2001**, *101* (5), 1349–1383.
- (4) Schleyer, P. V. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Van Eikema Hommes, N. J. R. Nucleus-Independent Chemical Shifts: A Simple and Efficient Aromaticity Probe. *J. Am. Chem. Soc.* **1996**, *118* (26), 6317–6318.
- (5) Schleyer, P. V. R.; Jiao, H. What Is Aromaticity? *Pure Appl. Chem.* **1996**, *68* (2), 209–218.
- (6) Kruszewski, J.; Krygowski, T. M. Definition of Aromaticity Basing on the Harmonic Oscillator Model. *Tetrahedron Lett.* **1972**, *13* (36), 3839–3842.
- (7) Aihara, J. Circuit Resonance Energy: A Key Quantity That Links Energetic and Magnetic Criteria of Aromaticity. *J. Am. Chem. Soc.* **2006**, *128* (40), 2873–2879.
- (8) Cyranski, M. K. Energetic Aspects of Cyclic Pi-Electron Delocalization: Evaluation of the Methods of Estimating Aromatic Stabilization Energies. *Chem. Rev.* **2005**, *105* (10), 3773–3811.
- (9) Möbius, K.; Plato, M.; Klihm, G.; Laurich, C.; Savitsky, A.; Lubitz, W.; Szyszko, B.; Stepien', M.; Lechosław, L.-G. Möbius-Hückel Topology Switching in an Expanded Porphyrin Cation Radical as Studied by EPR and ENDOR Spectroscopy. *Phys. Chem. Chem. Phys.* **2015**, *17* (9), 6644–6652.

- (10) Hückel, E. Quantentheoretische Beiträge Zum Benzolproblem - I. Die Elektronenkonfiguration Des Benzols Und Verwandter Verbindungen. *Zeitschrift für Phys.* **1931**, 70 (3–4), 204–286.
- (11) Heilbronner, E. Hückel Molecular Orbitals of Möbius-Type Conformations of Annulenes. *Tetrahedron Lett.* **1964**, No. 29, 1923–1928.
- (12) Krygowski, T. M.; Cyrański, M. Separation of the Energetic and Geometric Contributions to the Aromaticity of π -Electron Carbocyclics. *Tetrahedron* **1996**, 52 (5), 1713–1722.
- (13) Aihara, J. Resonance Energies of Annulenes and Radialenes. *Bull. Chem. Soc. Jpn.* **1975**, 48 (2), 517–520.
- (14) Schaller, G. R.; Topić, F.; Rissanen, K.; Okamoto, Y.; Shen, J.; Herges, R. Design and Synthesis of the First Triply Twisted Möbius Annulene. *Nat. Chem.* **2014**, 6 (7), 608–613.
- (15) Stępień, M.; Latos-Grazyński, L.; Sprutta, N.; Chwalisz, P.; Szterenberga, L. Expanded Porphyrin with a Split Personality: A Hückel-Möbius Aromaticity Switch. *Angew. Chem. Int. Ed.* **2007**, 46 (41), 7869–7873.
- (16) Tanaka, Y.; Saito, S.; Mori, S.; Aratani, N.; Shinokubo, H.; Shibata, N.; Higuchi, Y.; Yoon, Z. S.; Kim, K. S.; Noh, S. B.; et al. Metalation of Expanded Porphyrins: A Chemical Trigger Used to Produce Molecular Twisting and Möbius Aromaticity. *Angew. Chem. Int. Ed.* **2008**, 47 (4), 681–684.
- (17) Jux, N. The Porphyrin Twist: Hückel and Möbius Aromaticity. *Angew. Chem. Int. Ed.* **2008**, 47 (14), 2543–2546.
- (18) Tanaka, T.; Osuka, A. Chemistry of Meso-Aryl-Substituted Expanded Porphyrins: Aromaticity and Molecular Twist. *Chem. Rev.* **2017**, 117 (4), 2584–

2640.

- (19) Osuka, A.; Saito, S. Expanded Porphyrins and Aromaticity. *Chem. Commun.* **2011**, 47 (15), 4330–4339.
- (20) Sankar, J.; Mori, S.; Saito, S.; Rath, H.; Suzuki, M.; Inokuma, Y.; Shinokubo, H.; Suk Kim, K.; Yoon, Z. S.; Shin, J.-Y.; et al. Unambiguous Identification of Möbius Aromaticity for Meso-Aryl-Substituted [28]Hexaphyrins(1.1.1.1.1.1). *J. Am. Chem. Soc.* **2008**, 130 (41), 13568–13579.
- (21) Ottosson, H.; Borbas, K. E. Aromaticity: A Light-Switched Yin and Yang Pair. *Nat Chem* **2015**, 7 (5), 373–375.
- (22) Sung, Y. M.; Yoon, M.-C.; Lim, J. M.; Rath, H.; Naoda, K.; Osuka, A.; Kim, D. Reversal of Hückel (Anti)Aromaticity in the Lowest Triplet States of Hexaphyrins and Spectroscopic Evidence for Baird's Rule. *Nat. Chem.* **2015**, 7 (5), 418–422.
- (23) Yoon, Z. S.; Osuka, A.; Kim, D. Möbius Aromaticity and Antiaromaticity in Expanded Porphyrins. *Nat. Chem.* **2009**, 1 (2), 113–122.
- (24) Shin, J.; Furuta, H.; Yoza, K.; Igaraashi, S.; Osuka, A. Meso-Aryl-Substituted Expanded Porphyrins. *J. Am. Chem. Soc.* **2001**, 123, 7190–7191.
- (25) Saito, S.; Osuka, A. Expanded Porphyrins: Intriguing Structures, Electronic Properties, and Reactivities. *Angew. Chem. Int. Ed.* **2011**, 50 (19), 4342–4373.
- (26) Lim, J. M.; Yoon, Z. S.; Shin, J. Y.; Kim, K. S.; Yoon, M. C.; Kim, D. The Photophysical Properties of Expanded Porphyrins: Relationships between Aromaticity, Molecular Geometry and Non-Linear Optical Properties. *Chem. Commun.* **2009**, 7345 (3), 261–273.
- (27) Misra, R.; Chandrashekar, T. K. Structural Diversity in Expanded Porphyrins.

Acc. Chem. Res. **2008**, *41* (2), 265–279.

- (28) Shimizu, S.; Osuka, A. Metalation Chemistry of Meso-Aryl-Substituted Expanded Porphyrins. *Eur. J. Inorg. Chem.* **2006**, 1319–1335.
- (29) Abe, M. Diradicals. *Chem. Rev.* **2013**, *113* (9), 7011–7088.
- (30) Zeng, Z.; Shi, X.; Chi, C.; López Navarrete, J. T.; Casado, J.; Wu, J. Pro-Aromatic and Anti-Aromatic π -Conjugated Molecules: An Irresistible Wish to Be Diradicals. *Chem. Soc. Rev.* **2015**, *44* (18), 6578–6596.
- (31) Shimizu, D.; Oh, J.; Furukawa, K.; Kim, D.; Osuka, A. Meso-Hydroxysubporphyrins: A Cyclic Trimeric Assembly and a Stable Meso-Oxy Radical. *Angew. Chemie - Int. Ed.* **2015**, *54* (22), 6613–6617.
- (32) Yoshida, T.; Zhou, W.; Furuyama, T.; Leznoff, D. B.; Kobayashi, N. An Extremely Air-Stable 19π Porphyrinoid. *J. Am. Chem. Soc.* **2015**, *137* (29), 9258–9261.
- (33) Zeng, W.; Lee, S.; Son, M.; Ishida, M.; Furukawa, K.; Hu, P.; Sun, Z.; Kim, D.; Wu, J. Phenalenyl-Fused Porphyrins with Different Ground States. *Chem. Sci.* **2015**, *6* (4), 2427–2433.
- (34) Satoh, T.; Minoura, M.; Nakano, H.; Furukawa, K.; Matano, Y. Redox-Switchable 20π -, 19π -, and 18π -Electron 5,10,15,20-Tetraaryl-5,15-Diazaporphyrinoid Nickel(II) Complexes. *Angew. Chemie - Int. Ed.* **2016**, *55* (6), 2235–2238.
- (35) Konishi, A.; Hirao, Y.; Nakano, M.; Shimizu, A.; Botek, E.; Champagne, B.; Shiomi, D.; Sato, K.; Takui, T.; Matsumoto, K.; et al. Synthesis and Characterization of Teranthene: A Singlet Biradical Polycyclic Aromatic Hydrocarbon Having Kekulé Structures. *J. Am. Chem. Soc.* **2010**, *132*, 11021–

11023.

- (36) Von Ragué Schleyer, P. Introduction: Aromaticity. *Chem. Rev.* **2001**, *101* (5), 1115–1117.
- (37) Lazzeretti, P. Assessment of Aromaticity via Molecular Response Properties. *Phys. Chem. Chem. Phys.* **2004**, *6* (2), 217–223.
- (38) Shimizu, A.; Hirao, Y.; Matsumoto, K.; Kurata, H.; Kubo, T.; Uruichi, M.; Yakushi, K. Aromaticity and π -Bond Covalency: Prominent Intermolecular Covalent Bonding Interaction of a Kekulé Hydrocarbon with Very Significant Singlet Biradical Character. *Chem. Commun.* **2012**, *48* (45), 5629–5631.
- (39) Kim, K. S.; Yoon, Z. S.; Ricks, A. B.; Shin, J.; Mori, S.; Sankar, J.; Saito, S.; Jung, Y. M.; Wasielewski, M. R.; Osuka, A.; et al. Temperature Dependent Conformational Change of Meso - Hexakis (Pentafluorophenyl) [28]Hexaphyrins(1.1.1.1.1.1) into Möbius Structures. *J. Phys. Chem. A* **2009**, *113*, 4498–4506.
- (40) Section, C.; Ahn, T. K.; Kwon, J. H.; Kim, D. Y.; Cho, D. W.; Jeong, D. H.; Kim, S. K.; Suzuki, M.; Shimizu, S.; Osuka, A.; et al. Comparative Photophysics of [26]- and [28]Hexapyrins(1.1.1.1.1.1): Large Two-Photon Absorption Cross Section of Aromatic [26]Hexapyrin(1.1.1.1.1.1). *J. Am. Chem. Soc.* **2005**, *127*, 12856–12861.
- (41) Oh, J.; Sung, Y. M.; Kim, W.; Mori, S.; Osuka, A.; Kim, D. Aromaticity Reversal in the Lowest Excited Triplet State of Archetypical Möbius Heteroannulenic Systems. *Angew. Chem. Int. Ed.* **2016**, *55* (22), 6487–6491.
- (42) Sung, Y. M.; Oh, J.; Kim, W.; Mori, H.; Osuka, A.; Kim, D. Switching between Aromatic and Antiaromatic 1,3-Phenylene-Strapped [26]- and [28]Hexaphyrins

- upon Passage to the Singlet Excited State. *J. Am. Chem. Soc.* **2015**, *137* (37), 11856–11859.
- (43) Ottosson, H. Organic Photochemistry: Exciting Excited-State Aromaticity. *Nat. Chem.* **2012**, *4* (12), 969–971.
- (44) Aihara, J.-I. Aromaticity-Based Theory of Pericyclic Reactions. *Bull. Chem. Soc. Jpn.* **1978**, *51* (6), 1788.
- (45) Baird, N. C. Quantum Organic Photochemistry. II. Resonance and Aromaticity in the Lowest $3\pi\pi^*$ State of Cyclic Hydrocarbons. *J. Am. Chem. Soc.* **1972**, *94* (14), 4941–4948.
- (46) Félix, V.; Drew, G. B.; Cavaleiro, J. a S. Meso-Substituted Expanded Porphyrins : New and Stable Hexaphyrins. *Chem. Commun.* **1999**, 385–386.
- (47) Fuki, M.; Murai, H.; Tachikawa, T.; Kobori, Y. Time Resolved EPR Study on the Photoinduced Long-Range Charge- Separated State in Protein: Electron Tunneling Mediated by Arginine Residue in Human Serum Albumin. *J. Phys. Chem. B* **2016**, *120*, 4365–4372.
- (48) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98* (7), 5648.
- (49) Peterson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. A Complete Basis Set Model Chemistry. I. The Total Energies of Closed-Shell Atoms and Hydrides of the First-Row Elements. *J. Chem. Phys.* **1988**, *89* (4), 2193–2218.
- (50) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. Results Bbtained with the Correlation Energy Density Functionals of Becke and Lee, Yang and Parr. *Chem. Phys. Lett.* **1989**, *157* (3), 200–206.

- (51) Petersson, G. A.; Al-Laham, M. A. A Complete Basis Set Model Chemistry. II. Open-Shell Systems and the Total Energies of the First-Row Atoms. *J. Chem. Phys.* **1991**, *94* (9), 6081–6090.
- (52) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, J. R.; Cheeseman, J. A.; Montgomery, Jr., T.; Vreven, K. N.; Kudin, J. C.; Burant, J. M.; Millam, S. S.; Iyengar, J.; Tomasi, V.; Barone, B.; Mennucci, M.; Cossi, G.; Scalmani, N.; Rega, G. A.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukui, Y.; Hasegawa, I.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Li, X.; Peveretti, M.; Hrncic, S.; Adamo, C.; Ochterski, J.; Petersson, G. A.; Al-Laham, M. A.; Piquero, J.; Ciofi Alvino, C.; Cossi, M.; Morris, S. M.; Li, S. G.; Piskorz, P.; Chabaux, J.; Reinkens, D.; Gompf, R.; Mennucci, B.; Schlegel, H. B.; Frisch, M. J.; Gaussian 03, Revision D.01. Gaussian, Inc.: Wallingford CT 2004.
- (53) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, J. R.; Cheeseman, J. A.; Montgomery, Jr., T.; Vreven, K. N.; Kudin, J. C.; Burant, J. M.; Millam, S. S.; Iyengar, J.; Tomasi, V.; Barone, B.; Mennucci, M.; Cossi, G.; Scalmani, N.; Rega, G. A.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukui, Y.; Hasegawa, I.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Li, X.; Peveretti, M.; Hrncic, S.; Adamo, C.; Ochterski, J.; Petersson, G. A.; Al-Laham, M. A.; Piquero, J.; Ciofi Alvino, C.; Cossi, M.; Morris, S. M.; Li, S. G.; Piskorz, P.; Chabaux, J.; Reinkens, D.; Gompf, R.; Mennucci, B.; Schlegel, H. B.; Frisch, M. J.; Gaussian 09, Revision B.01. Gaussian, Inc.: Wallingford CT 2009.
- (54) Ridley, J.; Zerner, M. An Intermediate Neglect of Differential Overlap Technique for Spectroscopy: Pyrrole and the Azines. *Theor. Chim. Acta* **1973**, *32* (2), 111–134.
- (55) Bacon, A. D.; Zerner, M. C. An Intermediate Neglect of Differential Overlap Theory for Transition Metal Complexes: Fe, Co and Cu Chlorides. *Theor. Chim. Acta* **1979**, *53* (1), 21–54.
- (56) Neese, F. The ORCA Program System. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2012**, *2* (1), 73.
- (57) Neese, F.; Becker, U.; Ganyushin, G.; Hansen, A.; Izsak, R.; Liakos, D.; Kollmar, C.; Kossmann, S.; Pantazis, D.; Petrenko, T. ORCA: An Ab Initio, DFT, and Semiempirical SCF-MO Package, Version 3.0. *Univ. Bonn* **2012**.

- (58) Foresman, J. B.; Head-Gordon, M.; Pople, J. a. Toward a Systematic Molecular Orbital Theory for Excited States. *J. Phys. Chem.* **1992**, 96, 135–149.
- (59) Woon, D. E.; Dunning, T. H. Gaussian Basis Sets for Use in Correlated Molecular Calculations. III. The Atoms Aluminum through Argon. *J. Chem. Phys.* **1993**, 98 (2), 1358–1371.
- (60) Sinnecker, S.; Neese, F. Spin-Spin Contributions to the Zero-Field Splitting Tensor in Organic Triplets, Carbenes and Biradicals - A Density Functional and Ab Initio Study. *J. Phys. Chem. A* **2006**, 110 (44), 12267–12275.
- (61) McWeeny, R.; Mizuno, Y. In The Density Matrix in Many-Electron Quantum Mechanics II. Separation of Space and Spin Variables; Spin Coupling Problems. *Proc. R. Soc. Lond. A* **1961**, 554–577.
- (62) Shoji, M.; Koizumi, K.; Hamamoto, T.; Taniguchi, T.; Takeda, R.; Kitagawa, Y.; Kawakami, T.; Okumura, M.; Yamanaka, S.; Yamaguchi, K. A Theoretical Study of Zero-Field Splitting of Organic Biradicals. *Polyhedron* **2005**, 24 (16–17), 2708–2715.
- (63) Sugisaki, K.; Toyota, K.; Sato, K.; Shiomi, D.; Kitagawa, M.; Takui, T. Ab Initio Calculations of Spin-Orbit Contribution to the Zero-Field Splitting Tensors of $N\pi^*$ -excited States by the CASSCF Method with MRMP2 Energy Correction. *Chem. Phys. Lett.* **2009**, 477 (4–6), 369–373.
- (64) Tanabe, M.; Matsuoka, H.; Ohba, Y.; Yamauchi, S.; Sugisaki, K.; Toyota, K.; Sato, K.; Takui, T.; Goldberg, I.; Saltsman, I.; et al. Time-Resolved Electron Paramagnetic Resonance and Phosphorescence Studies of the Lowest Excited Triplet States of Rh(III) Corrole Complexes. *J. Phys. Chem. A* **2012**, 116 (39), 9662–9673.

- (65) Yamauchi, S.; Tanabe, M.; Ohba, Y.; Sugisaki, K.; Toyota, K.; Sato, K.; Takui, T.; Saltsman, I. Complete Assignment of Spin Sublevels in the Lowest Excited Triplet State of Corrole Compounds by Time-Resolved EPR Spectroscopy. *Chem. Phys. Lett.* **2012**, 521, 64–68.
- (66) Wolinski, K.; Hinton, J. F.; Pulay, P. Efficient Implementation of the Gauge-Independent Atomic Orbital Method for NMR Chemical Shift Calculations. *J. Am. Chem. Soc.* **1990**, 112 (23), 8251–8260.
- (67) Gauss, J. Effects of Electron Correlation in the Calculation of Nuclear Magnetic Resonance Chemical Shifts. *J. Chem. Phys.* **1993**, 99 (5), 3629–3643.
- (68) Marcos, E.; Anglada, J. M.; Torrent-Sucarrat, M. Theoretical Study of the Switching between Hückel and Möbius Topologies for Expanded Porphyrins. *J. Phys. Chem. C* **2012**, 116 (45), 24358–24366.
- (69) Yamauchi, S.; Takahashi, K.; Islam, S. S. M.; Ohba, Y.; Tarasov, V. Time-Resolved High-Frequency EPR Studies on Magnesium and Zinc Tetraphenylporphines in Their Lowest Excited Triplet States. *J. Phys. Chem. B* **2010**, 114 (45), 14559–14563.
- (70) Gonen, O.; Levanon, H. Line-Shape Analysis of Transient Triplet Electron Paramagnetic Resonance Spectra. Application to Porphyrins and Chlorophylls in Nematic Uniaxial Liquid Crystals. *J. Phys. Chem.* **1984**, 88 (28), 4223–4228.
- (71) Murai, H.; Imamura, T.; Obi, K. Time-Resolved ESR Detection of Benzophenone $N\pi^*$ Triplet State in Glassy Matrices at 77 K. *Chem. Phys. Lett.* **1982**, 87 (3), 295–298.
- (72) Tait, C. E.; Neuhaus, P.; Peeks, M. D.; Anderson, H. L.; Timmel, C. R. Transient EPR Reveals Triplet State Delocalization in a Series of Cyclic and Linear

- π -Conjugated Porphyrin Oligomers. *J. Am. Chem. Soc.* **2015**, *137* (25), 8284–8293.
- (73) Tait, C. E.; Neuhaus, P.; Anderson, H. L.; Timmel, C. R. Triplet State Delocalization in a Conjugated Porphyrin Dimer Probed by Transient Electron Paramagnetic Resonance Techniques. *J. Am. Chem. Soc.* **2015**, *137* (20), 6670–6679.
- (74) Michaeli, S.; Soffer, S.; Levanon, H.; Senge, M. O.; Kalisch, W. W. Triplet Dynamics of Conformationally Distorted Porphyrins in Isotropic Liquids and Liquid Crystals. Time-Resolved Electron Paramagnetic Resonance Study. *J. Phys. Chem. A* **1999**, *103* (13), 1950–1957.
- (75) Di Valentin, M.; Biasibetti, F.; Ceola, S.; Carbonera, D. Identification of the Sites of Chlorophyll Triplet Quenching in Relation to the Structure of LHC-II from Higher Plants. Evidence from EPR Spectroscopy. *J. Phys. Chem. B* **2009**, *113* (39), 13071–13078.
- (76) Salvadori, E.; Di Valentin, M.; Kay, C. W. M.; Pedone, A.; Barone, V.; Carbonera, D. The Electronic Structure of the Lutein Triplet State in Plant Light-Harvesting Complex II. *Phys. Chem. Chem. Phys.* **2012**, *14* (35), 12238–12251.
- (77) Borovykh, I. V.; Klenina, I. B.; Proskuryakov, I. I.; Gast, P.; Hoff, A. J. Magnetophotoselection Study of the Carotenoid Triplet State in Rhodobacter Sphaeroides Reaction Centers. *J. Phys. Chem. B* **2002**, *106* (16), 4305–4312.
- (78) Frank, H. A.; Bolt, J.; Friesner, R.; Sauer, K. Magnetophotoselection of the Triplet State of Reaction Centers from Rhodospseudomonas Sphaeroides R-26. *Biochim. Biophys. Acta* **1979**, *547*, 502–511.

- (79) Thurnauer, M. C.; Norris, J. R. The Ordering of the Zero Field Triplet Spin Sublevels in the Chlorophylls. A Magnetophotoselection Study. *Chem. Phys. Lett.* **1977**, *47* (1), 100–105.
- (80) Borovykh, I. V.; Proskuryakov, I. I.; Klenina, I. B.; Gast, P.; Hoff, A. J. Magnetophotoselection Study of the Lowest Excited Triplet State of the Primary Donor in Photosynthetic Bacteria. *J. Phys. Chem. B* **2000**, *104* (17), 4222–4228.
- (81) Di Valentin, M.; Tait, C.; Salvadori, E.; Ceola, S.; Scheer, H.; Hiller, R. G.; Carbonera, D. Conservation of Spin Polarization during Triplet-Triplet Energy Transfer in Reconstituted Peridinin-Chlorophyll-Protein Complexes. *J. Phys. Chem. B* **2011**, *115* (45), 13371–13380.
- (82) Wasserman, E. ESR of the Triplet States of Randomly Oriented Molecules. *J. Chem. Phys.* **1964**, *41* (6), 1763–1772.
- (83) Wasielewski, M. R.; Johnson, D. G.; Svec, W. A.; Kersey, K. M.; Minsek, D. W. Achieving High Quantum Yield Charge Separation in Porphyrin-Containing Donor-Acceptor Molecules at 10 K. *J. Am. Chem. Soc.* **1988**, *110* (21), 7219–7221.
- (84) Torrent-Sucarrat, M.; Navarro, S.; Cossío, F. P.; Anglada, J. M.; Luis, J. M. Relevance of the DFT Method to Study Expanded Porphyrins with Different Topologies. *J. Comput. Chem.* **2017**, *38* (32), 2819–2828.
- (85) Matsuoka, H.; Retegan, M.; Schmitt, L.; Höger, S.; Neese, F.; Schiemann, O. Time-Resolved Electron Paramagnetic Resonance and Theoretical Investigations of Metal-Free Room-Temperature Triplet Emitters. *J. Am. Chem. Soc.* **2017**, *139* (37), 12968–12975.
- (86) Gouterman, M.; Khalil, G.-E. Porphyrin Free Base Phosphorescence. *J. Mol.*

Spectrosc. **1974**, 53, 88–100.

- (87) Kamata, Y.; Akiyama, K.; Tero-Kubota, S.; Tabata, M. Two-Laser Two-Color Time-Resolved EPR Study on Higher-Excited -State Triplet-Singlet Intersystem Crossing of Porphyrins and Phthalocyanines. *Appl. Magn. Reson.* **2003**, 23 (3–4), 409–420.

Chapter 5

Electronic Structure of Room Temperature Phosphorescent Organic Inclusion Crystals

5.1 Chapter Introduction

Room-temperature phosphorescence (RTP) materials have attracted great research interest because of their long decay lifetimes and high emission quantum-yields. Especially, the metal-free organic RTP compounds are promising for new materials because of flexibilities and low-costs for device applications. The RTP materials have been widely applied to organic light-emitting diodes (OLED), bioimaging, and chemical sensors due to these luminescence features.¹⁻¹⁰ Generally, most RTP materials are inorganic or organometallic complexes including precious metals such as iridium or platinum, because the phosphorescent emission from the organic compound is very limited relative to the inorganic and organometallic materials due to weak spin-orbit coupling.¹⁰⁻¹⁴ The phosphorescence is a spin-forbidden, radiative transition from the lowest triplet excited (T_1) state to the ground (S_0) state. To achieve the efficient RTP, the intersystem crossing (ISC) from the singlet excited (S_1) state to the T_1 state needs to be faster than the $S_1 - S_0$ fluorescence and the nonradiative internal conversion (IC). In particular, the $T_1 - S_0$ radiative transition is required to be faster than the non-radiative deactivation. It has however been quite difficult for the organic materials to cause efficient RTP, because the T_1 state may deactivate non-radiatively due to the molecular vibrations, collisions, and oxygen quenching.^{15,16}

Meanwhile, the organic metal-free pure organic RTP crystals and co-crystals have recently been reported with controlled emission color and lifetime by tuning the

emission properties.^{17–26} These crystals showed the strong emissions while their lifetimes are larger than the millisecond order at room temperature because of crystallization and aggregation. In the supramolecular chemistry and crystal engineering fields, porous crystalline materials such as inclusion crystals are reported to be promising for the solid-state organic materials.^{19,20} In the functional materials including the OLEDs, the triplet state is important from a perspective of exciton formation. Namely, when the charge carriers recombine, triplet exciton is produced up to 75% while singlet exciton formation efficiency is restricted to 25% by the spin statistics.^{27–29} And also, in these systems, the charge transfer (CT) interaction between the donor and the acceptor molecules, and the distance between the guest and the host in the exciplex affect the efficiency of the electron transfer or the energy transfer, and emission properties.^{30–36} However, the magnitudes of the CT interaction are not known in the inclusion crystal for the RTP. In addition, the hybridized excited-state configurations ((n, π^*) and (π , π^*) configurations) are the key factors for archiving the persistent efficient pure organic RTP, with a help of the theoretical calculations.^{37–40} Deeper understanding of the emission mechanism and the electronic structure is required for the future design of these functions.^{37–39,41–47}

In this study, we focused on how the organic inclusion crystals (Figure 5.1 and Figure 5.2) consisting of electron-acceptor host and donor guest molecules⁴⁸ play a role on the electronic structures for the efficient RTP. These crystals show guest-dependent color-tunable emission under UV-light irradiations due to the charge transfer transition.⁴⁸ Very interestingly, the inclusion crystals showed longer-lived emission with higher quantum yield when the guest molecules are halogenated by heavy atoms. We have herein studied the electronic structure and electronic couplings in the excited states

of these compounds (Figure 5.1 and Figure 5.2). The ISC mechanism was also clarified in the present systems by using the TREPR method at room temperature.

5.2 Materials and Methods

5.2.1 Materials and Sample Preparations

Organic inclusion crystals consisting of *N,N'*-bis(pyrid-3-yl)-1,4,5,8-pyromellitic diimide (PMDI) or *N,N'*-bis(pyrid-3-yl)-1,4,5,8-naphthalenediimide (NDI) as an acceptor host molecule; 3-bromo-1-fluorobenzene (3BrF), 4-bromo-1-fluorobenzene (4BrF), 1-fluoro-3-iodobenzene (3IF), or 3-iodo-1-methylbenzene (3IMe) as a donor guest molecule; and tris(pentafluorophenyl)-borane (TPFB), as designed by a multicomponent molecular puzzles.⁴⁸ These organic inclusion crystals and PMDI crystal (powder crystals) were sealed in the quartz EPR sample tubes for emission spectra measurements and time-resolved TREPR measurements at room-temperature. As a model compound of the acceptor molecule, 2-ethylhexyl pyromellitic diimide (2EH-PMDI) and 2-ethylhexyl naphthalenediimide (2EH-NDI) were dissolved in 2-methyltetrahydrofuran (MTHF) and toluene. The solutions were deoxygenated by the freeze-pump-thaw cycle and it was also sealed in the EPR sample tube. MTHF (> 98.0 %), 3BrF (> 98.0 %), 4BrF (> 98.0 %) (EP grade) were purchased from Tokyo Chemical Industry Co., Ltd. Toluene (guaranteed reagent, > 99.5 %) and acetonitrile (super dehydrated, 99.8 %) were purchased from Wako Pure Chemical Industries, Ltd. Silver nitrate (AgNO₃; ACS reagent, ≥ 99.0 %) and tetrabutylammonium hexa-fluorophosphate (TBAPF₆, 98 %) were purchased from Sigma-Aldrich Co. LLC. These compounds were used as received without further purification. For the electrochemical measurement, acetonitrile solutions of TBAPF₆ (0.1 M) and the donor

molecule (3BrF, 4BrF; ca. 1-2 mM) as sample solutions, and acetonitrile solution of TBAPF₆ (0.1 M) and AgNO₃ (0.01 M) as a solution for the reference electrode were prepared. Process of the sythesis are described as below.

PMDI-3BrF system: PMDI (100mg, 1 equiv), TPFB (293 mg, 2.1 equiv) and 3-bromofluorobenzene (15.0 g, excess) were mixed in a sample tube. The mixture was heated up to close to the boiling point, then cooled at 20 °C to obtain colorless crystals (348 mg). **PMDI-3BrF:** [C₇₄H₂₂B₂Br₃F₃₃N₄O₄]. Colorless block (0.10 × 0.15 × 0.40 mm). Triclinic, *P*-1, *a* = 11.2440(11), *b* = 12.3469(12), *c* = 13.5777(13) Å, *α* = 69.822(2), *β* = 72.675(2), *γ* = 86.155(2) °, *V* = 1687.7(3) Å³, *Z* = 1, *T* = 100 K, $\rho_{\chi\alpha\lambda\chi} = 1.886 \text{ g cm}^{-3}$, $\mu = 1.943 \text{ mm}^{-1}$. Of a total of 24954 reflections that were collected, 9048 were unique. Final *R*_I = 0.0484 and *wR*₂ = 0.1245. GOF = 1.009.

PMDI-4BrF system: PMDI (100mg, 1 equiv), TPFB (290 mg, 2.1 equiv) and 4-bromofluorobenzene (15.0 g, excess) were mixed in a sample tube. The mixture was heated up to close to the boiling point, then cooled at 60 °C to obtain colorless crystals (318 mg). **PMDI-4BrF:** [C₇₄H₂₂B₂Br₃F₃₃N₄O₄]. Colorless block (0.25 × 0.25 × 0.40 mm). Triclinic, *P*-1, *a* = 10.7741(7), *b* = 12.6058(8), *c* = 14.2683(9) Å, *α* = 72.1865(10), *β* = 77.6930(10), *γ* = 70.9643(9) °, *V* = 1730.18(19) Å³, *Z* = 1, *T* = 100 K, $\rho_{\chi\alpha\lambda\chi} = 1.842 \text{ g cm}^{-3}$, $\mu = 1.895 \text{ mm}^{-1}$. Of a total of 25567 reflections that were collected, 9278 were unique. Final *R*_I = 0.0469 and *wR*₂ = 0.1366. GOF = 1.044.

PMDI (guest free) system: PMDI (100mg, 1 equiv), TPFB (290 mg, 2.1 equiv) and 1-bromo-3,4-difluorobenzene (15.0 g, excess) were mixed in a sample tube. The

mixture was heated up to close to the boiling point, then cooled at 60 °C to obtain colorless crystals (166 mg). **PMDI (guest free):** [C₅₆H₁₀B₂F₃₀N₄O₄]. Colorless block (0.05 × 0.05 × 0.10 mm). Triclinic, *P*-1, *a* = 10.7352(13), *b* = 10.8684(14), *c* = 21.953(3) Å, α = 102.233(2), β = 94.321(3), γ = 91.008(2) °, *V* = 2492.6(6) Å³, *Z* = 2, *T* = 100 K, $\rho_{\chi\alpha\lambda\chi}$ = 1.858 g cm⁻³, μ = 0.194 mm⁻¹. Of a total of 17436 reflections that were collected, 12237 were unique. Final *R*₁ = 0.0633 and *wR*₂ = 0.1515. GOF = 1.059.

NDI-3IF system: NDI (100mg, 1 equiv), TPFB (250 mg, 2.1 equiv) and 3-iodofluorobenzene (25.0 g, excess) were mixed in a sample tube. The mixture was heated up to close to the boiling point, then cooled at 60 °C to obtain colorless crystals (390 mg). **NDI-3IF:** [C₅₆H₁₀B₂F₃₀N₄O₄]. Colorless block (0.05 × 0.14 × 0.17 mm). Triclinic, *P*-1, *a* = 10.72(4), *b* = 11.69(5), *c* = 13.55(6) Å, α = 90.57(10), β = 103.40(10), γ = 93.59(6) °, *V* = 1648.(12) Å³, *Z* = 1, *T* = 100 K, $\rho_{\chi\alpha\lambda\chi}$ = 1.902 g cm⁻³, μ = 1.102 mm⁻¹. Of a total of 8127 reflections that were collected, 5682 were unique. Final *R*₁ = 0.0854 and *wR*₂ = 0.2391. GOF = 1.020.

NDI-3IMe system: NDI (100mg, 1 equiv), TPFB (250 mg, 2.1 equiv) and 3-iodotoluene (25.0 g, excess) were mixed in a sample tube. The mixture was heated up to close to the boiling point, then cooled at 60 °C to obtain colorless crystals (403 mg). **NDI-3IMe:** [C₁₄₈H₅₂B₄F₆₄I₄N₈O₄]. Pale yellow, block (0.50 × 0.50 × 0.30 mm). Triclinic, *P*-1, *a* = 11.5056(8), *b* = 14.3930(7), *c* = 21.3929(16) Å, α = 101.507(6), β = 97.604(6), γ = 93.927(5) °, *V* = 3424.5(4) Å³, *Z* = 1, *T* = 93 K, $\rho_{\chi\alpha\lambda\chi}$ = 1.829 g cm⁻³, μ = 1.059 mm⁻¹. Of a total of 22176 reflections that were collected, 22176 were unique. Final *R*₁ = 0.0822 and *wR*₂ = 0.2835. GOF = 1.091.

5.2.2 Emission Spectra Measurements

Emission spectra were measured by using a fluorescence spectrometer (JASCO, FP-8300) at room temperature. The excitation wavelength was set to be $\lambda_{\text{exc}} = 340$ nm. UV-vis diffuse reflectance measurements were recorded using a JASCO V-670 spectrometer (JASCO) with an integration sphere attachment. Fluorescence excitation and emission spectra were collected at room temperature on a Hitachi F-7000 fluorescence spectrometer. Emission spectra were collected in the range between 380-720 nm, with a scan speed of 240 nm/min, and the slits were set at 5.0 nm (excitation slit) and 5.0 nm (emission slit). The excitation wavelength is 340 nm for PMDI and 370 nm for NDI. The absolute photoluminescence quantum yields (Φ_{PL}) were determined as a solid state using absolute PL quantum yields measurement system C9920-02 (Hamamatsu photonics) after excitation at 340 nm for PMDI and 370 nm for NDI. Time-resolved photoluminescence lifetimes were carried out by using time-correlated single photon counting lifetime spectroscopy system, Quantaaurus-Tau C11367-02 (Hamamatsu photonics). The decay constants and fitting parameters for transient decays were determined using the embedded software of Quantaaurus-Tau. Fluorescence images were visualized under fluorescence microscope (Carl Zeiss Axio Imager.A2). The excitation source was a xenon lamp equipped with a band-pass filter (330-380 nm), Emission > 420 nm.

5.2.3 Time-resolved EPR Measurements

TREPR spectra were recorded using an X-band continuous wave (CW) EPR spectrometer (Bruker EMX) at room-temperature without magnetic field modulation. For the measurement of sample in frozen solution at 77 K, the EPR sample tube was

placed in a dewer bottle filled with liquid nitrogen installed in the EPR cavity. Detected EPR signals were amplified by a wide-band preamplifier and taken in a digital oscilloscope (Tektronix, DPO 3054). The nanosecond pulsed Nd:YAG laser (Continuum, Minilite; $\lambda = 355$ nm) was utilized to excite the samples. The time-resolved experiments were performed by synchronizing the pulsed laser to the digital oscilloscope. A quartz depolarizer (Sigmakoki, DEQ-1N) was placed between the laser and the hole of the EPR cavity.

5.2.4 Electrochemical Measurements

Electrochemical measurement was carried out by electrochemical analyzer (BAS Inc., ALS, model 608ES) using a standard three-electrode configuration. The cyclic voltammograms of donor molecules (3BrF, 4BrF) were obtained by taking grassy carbon, Pt, and Ag/AgCl as working, counter, and reference electrodes, respectively at room temperature. Sample solutions were deoxygenated by bubbling of Argon gas for 5 minutes prior to the measurement.

5.2.5 Theoretical Calculations

To investigate the excited singlet-state character, the molecular orbital calculations of PMDI were carried out using the density functional theory (DFT) method and time-dependent DFT (TD-DFT) method with the Becke's three parameter hybrid exchange functional and Lee-Yang-Parr correlation functional (B3LYP)⁴⁹⁻⁵¹ with a 6-31G** basis set^{52,53} by Gaussian 09 program package.⁵⁴

5.2.6 X-ray Crystal Structural Analysis

The crystals (**PMDI-3BrF**, **PMDI-4BrF**, **PMDI-guest free** and **NDI-3IF**) were mounted on a loop. Diffraction data for the crystal samples was collected at 100 K on a Bruker SMART APEX CCD detector with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). From the collected data, unit cell, integration, absorption correction, and space group were determined using the Bruker APEX3 software package.⁵⁵ The data frames were integrated using SAINT and merged to give a unique data set for the structure determination. Empirical absorption corrections by SADABS were carried out. A crystal of **NDI-3IMe** was mounted on a loop. Data from X-ray diffraction were collected at 93 K by a Rigaku XtaLAB mini CCD diffractometer equipped with graphite monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å). Collected data were integrated, corrected, and scaled using the program CrysAlisPro.⁵⁶ The structures were refined using SHELXT (Sheldrick, 2015)⁵⁷ Intrinsic Phasing and SHELXL (Sheldrick, 2015).⁵⁸ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at calculated positions and included in the structure factor calculation but were not refined. The program Olex2 was used as a graphical interface.⁵⁹

5.3 Results

5.3.1 Emission Properties of Organic Inclusion Crystals

[Figure 5.3](#) shows emission spectra of organic inclusion crystals including 3BrF and 4BrF as a guest molecule (PMDI-3BrF system and PMDI-4BrF system in [Figure 5.1](#)) under the UV light irradiation at room temperature. These crystals having bromine (Br) atoms showed the emission lifetimes in the order of ms with high quantum yields up to 70%, obtained by using an integrating sphere unit. These lifetimes are significantly

longer (3.94 ms ~ 6.56 ms) (Table 5.1) than the lifetimes (4.2 ns ~ 24.9 ns) in the case of those organic inclusion crystals whose guests do not possess the Br atom, which are composed of the TPFB, NDI as an acceptor, and the guests.⁴⁸ These results indicate the RTP. The PMDI-4BrF system showed red-shifted emission bands relative to the band obtained in the PMDI-3BrF system. The emission spectrum of the phosphorescent PMDI-3BrF system was almost identical with the emission spectrum from the crystal consisting of PMDI and TPFB, which has no guest (Figure 5.4).

Figure 5.5 shows emission spectra of organic inclusion crystals including 3IF and 3IMe as the guest molecules (NDI-3IF system and NDI-3IMe system in Figure 5.2) under UV light irradiation at room temperature. These crystals having iodine (I) atom represent longer emission wavelength than in the case of those including bromine (Br) atom. These crystals having iodine (I) atom exhibited slightly shorter lifetimes and lower quantum yield (for example: 0.48 ms and 9 %, respectively in NDI-3IF system) than those of the systems containing bromine atom. The emission lifetime is longer in the NDI-3IF and NDI-3IMe systems than in the case of those organic inclusion crystals whose guests have no Br and I atoms, which are composed of the TPFB, NDI as an acceptor, and the guests.⁴⁸

5.3.2 Time-resolved EPR Experiments for the Organic Inclusion Crystals

To confirm whether the long-lived emission was attributed to the triplet state or not, we carried out a TREPR measurement for the photo-induced excited state at room temperature. Figure 5.6 and Figure 5.7 represent TREPR spectra of PMDI-3BrF and PMDI-4BrF systems, respectively, observed at room temperature. These spectra exhibit the fine structures by the zero-field splitting (ZFS) interaction. The EPR signals from

220 mT to 480 mT in Figure 5.6, as an example, are caused by $\Delta m_s = \pm 1$ transition, and the strong sharp signals around 160 mT are from $\Delta m_s = \pm 2$ transition of the electron spins between the triplet sublevels. Thus, these spectra (Figure 5.6 and Figure 5.7) were assigned to the excited triplet states.

To confirm whether the room temperature luminescence from the iodine systems was attributed to the triplet state or not, we performed the TREPR measurement as well as the bromine system. Figure 5.8 and Figure 5.9 exhibit TREPR spectra of NDI-3IF and NDI-3IMe systems, respectively, observed at room temperature. These spectra were also assigned to the excited triplet states.

5.4 Discussion

5.4.1 Excited Triplet State of the Organic Inclusion Crystals Observed by TREPR Method at Room Temperature.

To clarify the electronic structure of the room temperature luminescent state, the spin-density distribution in the crystals was evaluated based on the EPR parameters obtained from the line-shape analyses of the TREPR spectra, as shown with the experimental spectra in Figure 5.6 and Figure 5.7.

In the PMDI-3BrF system (Figure 5.6), the ZFS parameters were determined to be $|D| = 118$ mT and $|E| = 38$ mT, as summarized in Table 5.2. These dipolar parameters well agree with those obtained for the guest-free crystal composed of the host PMDI and TPFB obtained at room temperature (Figure 5.10). And also, the line-shape of those TREPR spectra and the ZFS parameters were almost identical with the model compound of the host PMDI (2EH-PMDI) obtained in a frozen solution at 77 K (Figure 5.11). This indicates that the RTP is originating from the host PMDI molecule in the

PMDI-3BrF system. $|D| = 118$ mT is very close to the D value ($= 106$ mT) in the excited triplet state of naphthalene.⁶⁰ This strongly suggests the $^3\pi\pi^*$ character triplet state in PMDI.

To obtain the crucial factor resulting in the long-lived luminescence at room temperature, we characterized the ISC process in the RTP organic inclusion crystals from the line shape analysis. The polarization pattern of the EPR transitions due to the excited triplet state is explained by the ISC mechanism.^{61,62} This denotes that the triplet state is formed by the spin-orbit coupling (SOC) as shown in Figure 5.12a. In the spin-orbit coupling induced ISC (SOC-ISC) mechanism, spin-polarization occurs with selective populations to the zero-field triplet sublevels, resulting in the generation of the spin polarization depending on the direction of the external magnetic field.^{61,62} On the other hand, in the hyperfine coupling induced ISC (HFC-ISC) mechanism, spin-polarization results from the $S-T_0$ mixing. In the present measurements, the line-shape of the TREPR spectrum of the PMDI-3BrF system (Figure 5.6) was reproduced using the SOC-ISC mechanism, as shown by equation (4.5) in chapter 4. Thus, the TREPR spectrum is assigned to the excited triplet state generated via ISC from the S_1 state through SOC, which is similar to the case of the guest-free crystal composed of the host PMDI and TPFB obtained at room temperature (Figure 5.10) and 2EH-PMDI obtained in a frozen solution at 77 K (Figure 5.11). This result is in disagreement with the case of thermally activated delayed fluorescence (TADF) molecules, revealed by the TREPR method⁶³ and by the resonant spin sensitive measurements based EPR.⁶⁴ Thus, the RTP triplet state in the donor-acceptor system is concluded to be formed by the SOC, while the TADF triplet state is due to the HFC mechanism.

The sign of D value cannot be directly determined by the line-shape analysis of the TREPR spectrum. However the sign can be rationalized by anisotropic S_1 - T_1 ISC scheme reflecting the molecular orbitals in the singlet and in the triplet states. In the guest-free PMDI:TPFB system, the spin-polarization pattern of the TREPR spectra obtained at room temperature was reproduced by both positive and negative D value, when the different combination of population ratios P_x , P_y , and P_z in the triplet sublevels are employed, as in the case of the model molecule as a PMDI (2EH-PMDI) in MTHF at 77 K. The sign of the D value was however determined to be positive as in [Figure 5.13a](#), as detailed below. PMDI possess the carbonyl oxygen atoms with the lone-pair electrons. This heavy atom may contribute to the S_1 - T_1 ISC through SOC. Such lone-pair electrons are well known to facilitate the ISC via an allowed transition between $^1n\pi^*$ and $^3\pi\pi^*$ states by the SOC. In the case that the forbidden transition between the two $\pi\pi^*$ states are involved in the ISC, as represented in [Figure 5.14](#), the participation of the $^1n\pi^*$ character by the vibronic coupling may play a role for the ISC. On the basis of the n-orbitals on the carbonyl oxygen group orienting to the X-Y plane of the PMDI molecule, the principal Z-axis is set to be the out-of-plane direction ([Figure 5.15](#) as referred from [Figure 5.19](#)) as well as PMDI in the PMDI-3BrF system as mentioned later. Then $^1n\pi^* \rightarrow ^3\pi\pi^*$ transition via the $^3\pi'\pi^*$ state in [Figure 5.15b](#) to cause the internal conversion (IC) after the S_1 - T_1 ISC process ([Figure 5.14](#)) may generate the triplet sublevels almost equally to the T_x and T_y through the SOC because of the angular momentum changes along the X- and Y-axes during the $^1n\pi^* \rightarrow ^3\pi\pi^*$ transition. This scheme is represented by $P_x \approx P_y \gg P_z$ for $D > 0$. In the case of negative D , overpopulation in the P_z value may explain the observed EPR line shape in [Figure 5.10](#). For the negative D , it is highly anticipated that the triplet PMDI takes on

the $^3n\pi^*$ character. However, the negative D is not coincident with the magnitude of $|D| = 118$ mT which is very close to the D value ($=106$ mT) in the excited triplet state of naphthalene, because $|D| = 118$ mT is well compatible with the $^3\pi\pi^*$ character by the delocalized spin-spin interaction in the π -skelton.

In the case of the PMDI-3BrF system at room temperature, the ZFS parameters and the population ratios P_x , P_y , and P_z in the triplet sublevels were both almost identical with those for the guest-free crystal composed of the host PMDI and TPFB and the 2EH-PMDI at 77 K (Table 5.2). This suggests that the excited triplet state of PMDI has the $^3\pi\pi^*$ character in the PMDI-3BrF system with the positive D as well as the case in the guest-free PMDI:TPFB system. This indicates that 3BrF does not contribute to the RTP triplet character in the PMDI-3BrF system, which was in agreement with the little CT character observed in the emission spectrum.

In the case of PMDI-4BrF system (Figure 5.7), the $|D|$ value ($=108$ mT) is smaller than that in the PMDI-3BrF system. The EPR results suggest the formation of the triplet charge-transfer (CT) state between the host and the guest, as recently characterized by TREPR spectra of a twisted [28]Hexaphyrin, as shown in chapter 4. The intermolecular CT character is also indicated by the red-shifted emission band in the PMDI-4BrF system with respect to the emission band in the PMDI-3BrF system (Figure 5.3). The efficient formation of the triplet state can thus be interpreted in terms of the external heavy-atom effect by the bromine atom in the guest molecule. In this system, relative populations in the triplet sublevels were determined as $P_x \gg P_y > P_z$ when the sign of D is assumed to be positive, as shown in Figure 5.13b.

The electron transition process of the PMDI-4BrF system is discussed, as follows. Two kinds of process are discussed. One is tightly related to the phosphorescent triplet

state of the electron donor acceptor (EDA) complex generated in the iridium(III) compound and tetracene system.⁶⁵ In the present PMDI-4BrF system, the excited triplet state of PMDI ($^3\text{PMDI}^*$) would be formed via the excited singlet state ($^1\text{PMDI}^*$) through ISC after UV light irradiation. After that a rapid electron transfer from the guest to the host may occur, resulting in the formation of the intermolecular triplet CT state in the guest-PMDI system, i.e. $^3(\text{PMDI}^{\delta-} + \text{guest}^{\delta+})$ in contrast to the PMDI-3BrF system. This scheme is however excluded, because the spin polarization pattern (E/A/E/A/E/A) of the EPR spectrum in the PMDI-4BrF system is not reproduced by the electron spin polarization transfer from the sublevel populations of $P_x \approx P_y \gg P_z$ obtained from E/E/E/A/A/A pattern of $^3\text{PMDI}^*$. Thus, it is proposed that the intermolecular triplet CT character between the host and the guest is formed after the photo-excitation by a direct ISC using the bromine atom which can facilitate the $S_1\text{-}T_1$ ISC through SOC.

The TREPR spectrum obtained in the PMDI-4BrF system (Figure 5.7) does not exhibit the symmetric splitting line shape by the ZFS; the center magnetic field position of the inner peaks (330 mT and 370 mT) is apparently shifted in comparison to the center position of the outer-most peaks (250 mT and 450 mT). This reflects the anisotropy in the g values. g values were determined to be $g_z = 2.002$, which is coincident with that of the free-electron and smaller than g_x and g_y , from the line-shape analysis as expressed in Table 5.2. Since the π -electron spin density (p_z character) should be delocalized in the molecular plane, then the principal Z-axis providing the largest dipolar splitting can be set to be the out-of-plane direction with respect to the PMDI and the 4BrF (Figure 5.17). This results in $D > 0$.

Next, to determine the ISC mechanism in the PMDI-4BrF system, the triplet sublevels are assigned as follows. Here, ZFS axes of PMDI-4BrF system are assumed

that X- and Y-axes are along the short and long molecular axes with respect to the PMDI. In this situation, sign of the E value is defined to be positive ($E > 0$). In terms of 4BrF, Y-axis is along the molecular axis connecting bromine and fluorine. In this case, n-orbital on the bromine atom is perpendicular to the Y-axis (Figure 5.17c as referred from Figure 5.20), thus, the T_y sublevel is expected to be most populated due to SOC around the Y-axis, because the rotation of the n-orbital on the bromine atom around the Y-axis leads to the π' in Figure 5.17d. This is not consistent with the results of $P_x \gg P_y$. In contrast, when the contribution of σ -orbital on the bromine atom is considered (Figure 17e), $P_x \gg P_y$ can be explained by the SOC around the X-axis because the rotation of the σ -orbital on the bromine atom around the X-axis leads to the π' .

To verify the influence of the orbitals to the ISC due to SOC, their orbital energies were checked. Figure 5.21 and Figure 5.22 represent the energies of the molecular orbitals in the system of the unit of PMDI and 3BrF or 4BrF, respectively, whose orientation was taken from the X-ray structures as exhibited in Figure 5.23 and Figure 5.24. Energy difference between n-orbital (#126 in Figure 5.19a) and π -orbital (#134 in Figure 5.19a) of 3BrF as a guest (pointed in Figure 5.21) is large (1.2683 eV; obtained from Table 5.4), indicating that it is difficult for n-orbital of 3BrF (guest) to participate in the transition between $^1n\pi^*$ and $^3\pi\pi^*$ states by vibronic coupling in the PMDI-3BrF system. In contrast, in the PMDI-4BrF system, energy difference between n-orbital (#127 in Figure 5.20a) and π -orbital (#133 in Figure 5.20a) of 4BrF as a guest (pointed in Figure 5.22) is relatively small (0.9143 eV; obtained from Table 5.5), suggesting that n-orbital of 4BrF (guest) can participate in the transition between $^1n\pi^*$ and $^3\pi\pi^*$ states by the vibronic coupling in the PMDI-4BrF system. Moreover, the σ -orbital is seen in deeper HOMOs (#118, #117, and #116 in Figure 5.20b). This would explain that the

σ -orbital of 4BrF attend the transition between $^1\sigma\pi^*$ and $^3\pi\pi^*$ states by the vibronic coupling in the PMDI-4BrF system. Notably, these orbitals of #118, #117, and #116 are explained by the hybridizations between the σ characters in 4BrF and the π -orbitals in PMDI, while such a hybridization effect is absent in the n-orbital character in #127. The participation of the π orbitals in PMDI in the σ characters may induce the generation of the locally excited triplet state character ($^3\pi_{\text{host}}\pi^*_{\text{host}}$) in PMDI by the SOC from the L_x , while the L_y in the n-orbital character in #127 may induce the triplet CT character ($^3\pi'_{\text{guest}}\pi^*_{\text{host}}$) by the SOC. If the contribution of the locally excited state character is dominant in the triplet state, $P_x \gg P_y$ can be explained by the preferential contribution of the ISC from the $^1\sigma\pi^*_{\text{host}}$ state.

5.4.2 Contribution of the Triplet CT Character to the RTP Organic Inclusion Crystals.

To clarify the effect of the donor guest on the shift of the emission bands and to assess the degree of the contribution of the triplet CT character to the RTP, intermolecular interaction between the host and the guest molecules were confirmed from the X-ray structure. Figure 5.23 and 5.24 show the crystal structure of PMDI-3BrF and PMDI-4BrF systems. X-ray structure of the PMDI-3BrF system exhibits that the guest and host molecules are perpendicularly oriented in the crystal (Figure 5.23), as described above. On the other hand, PMDI-4BrF system shows that guest molecule is oriented parallel to the host molecule (Figure 5.24, which results in the larger π - π interaction between the guest and the host molecules because of the π -stacking. These insights suggest that degree of the CT character depends on the orientation of the guest and the host molecules in the organic inclusion crystal. Note that, a major cause of the

observed RTP emission and the TREPR spectra came from the PMDI molecule whose molecular motion is restricted in the crystal even at room temperature, as well as the case of guest-free PMDI crystal (Figure 5.25).

To investigate the origin of the red-shifted emission band of PMDI-4BrF system relative to the PMDI-3BrF system, we evaluated the degree of the triplet CT character based on the D values, as follows. We evaluated the degree of the triplet CT character based on the equation explained by linear combination as $D_{T1} = a^2 D_{CT} + b^2 D_{LE}$, where $a^2 + b^2 = 1$,⁶⁶ D_{T1} is an experimentally observed D -value, D_{CT} is a D -value due to the triplet CT state between the guest and the host molecules, D_{LE} is a D -value due to excited triplet state of the host molecule, and “a” and “b” are the coefficient reflecting the contribution of the D_{CT} and D_{LE} , respectively in our case. This equation represents that D_{T1} decreases with increase in the contribution of the triplet CT character, and it illustrates the experimental results, as shown in Figure 5.26. In addition, we also considered that ZFS parameter (D_{T1}) is contributed by not only spin-spin coupling (D_{SS}) but also by the spin-orbit coupling (D_{SO}) due to bromine atom. This effect was clarified in duroquinone-*N,N*-dimethylaniline derivative systems by intrinsic enhancement factors by the SOC mechanism polarization.⁶⁷

In the PMDI-4BrF system, when D (D_{T1}) value is contributed by the spin-spin coupling, Tz sublevel energy in the pure CT (100% CT) character was estimated to be $D_{SS} = -43$ mT (< 0) by a distance between host and guest molecules (4 Å) by considering the X-ray structure (Figure 5.24). Moreover, when D (D_{T1}) value is contributed by SOC, Tz sublevel energy in the pure CT (100% CT) character was estimated to be $D_{T1} = 21$ mT ($=D_{SS} + D_{SO}$) (> 0) due to bromine atom.⁶⁷ On the other hand, Tz sublevel energy in the pure LE (0 % CT) character was estimated to be $D_{T1} =$

118 mT (> 0), which is determined by the PMDI-3BrF system and the guest-free PMDI crystal. Thus, from the TREPR analysis, the CT character was estimated to be 13% for the PMDI-4BrF system. The E -value is decreased with the decrease in the D -value (D_{T1} -value), supporting the increase of the contribution of the triplet CT character with the decrease in D .

To characterize the reason why the second sublevel (Tx sublevel) was most populated in the PMDI-4BrF system (Figure 5.13b), the influence by the SOC to the triplet sublevel energies is discussed. If the CT character is not contributed to the triplet state, the same parameters such as ZFS parameters and combinations of P_x , P_y , and P_z values had been obtained as well as the guest-free PMDI and TPFB crystal. In that case, the triplet sublevels are assigned as represented in Figure 5.27a, which was determined by the TREPR results of the guest-free crystal composed of PMDI and TPFB similar to 2EH-PMDI. Given that D (D_{T1}) value is determined by only spin-spin coupling, negative D (D_{SS}) was obtained in the pure CT (100% CT) in the PMDI-4BrF system as described above, in which Tz sublevel is the highest (Figure 5.24b and Figure 5. 24d).

However, when n-orbital on the bromine atom participates in the ISC due to SOC around the Y-axis, in which the n-orbital on the bromine atom rotates around the Y-axis, Tz and Tx sublevels are more stabilized.⁶⁸ This would results in that Tz sublevel is close to the Ty sublevel and that Tx sublevel is separated from Ty sublevel. In the PMDI-4BrF system, Tz sublevel was 64 mT stabilized due to the SOC ($21 \text{ mT} (=D_{SS} + D_{SO}) + 43 \text{ mT} (=D_{SS})$, as mentioned above), which induce that Tx and Tz sublevels were reversed resulting in positive D in appearance (Figure 5.24c). In the same way, when σ -orbital on the bromine atom participates in the ISC due to SOC around the X-axis, where the σ -orbital on the bromine atom rotates around the X-axis, Ty and Tz sublevels are more

stabilized. This leads that Tz and Tx sublevels were reversed and that Ty sublevel was separated from Tx sublevel, which also induce positive D in appearance (Figure 24e). Therefore, the ZFS axes are defined as represented in Figure 5.24, and positive D was obtained in the condition of 13% CT character.

To gain the further information about degree of the contribution of the triplet CT character to the RTP, the oxidation potentials of the guests and the reduction potential of the host were investigated. Figure 5.28 and Figure 5.29 show cyclic voltammogram of the host (model molecule: 2EH-PMDI) and the guest molecules (3BrF and 4BrF), respectively. The reduction potential of 2EH-PMDI is 1.16 V (vs. Fc/Fc⁺), and the oxidation potential of 3BrF and 4BrF are 2.44 and 2.16 V (vs. Fc/Fc⁺), respectively. The results of the electro-chemical measurement explain the oxidation potential of the donor molecules decrease in order of 3BrF > 4BrF. Figure 5.30 demonstrates the difference between the reduction potential (E_{red}) of 2EH-PMDI and the oxidation potential (E_{ox}) of 3BrF or 4BrF. Therefore, the larger intermolecular interaction in the triplet CT state on the RTP estimated by the TREPR results is in good agreement with the longer emission wavelength and the lower oxidation potential of the guest molecules. These results share the view that CT character is more dominant when the donor molecule possess a relatively lower oxidation potential,^{69,70} and that exciplexes exhibit tunable contribution of the CT character.⁷⁰ And also, the energetic stability of the triplet CT state evaluated by the TREPR results is supported by the oxidation potential of a donor molecule. This is because the energy of a charge separated (CS) state of a donor-acceptor complex is lowered by increasing of the HOMO level of a donor and decreasing of the LUMO level of an acceptor.⁷¹

Moreover, to analyze the intermolecular charge-transfer (CT) interaction, we

determined the electronic coupling between the host and the guest. The excited triplet state of the PMDI-4BrF system has a contribution of the LE and the CT states as mentioned above. The wavefunction of the T_1 state (Φ_{T1}) is given by the linear combination of the wavefunctions for the pure LE state (Φ_{LE}) and the pure CT state (Φ_{CT}) as $|\Phi_{T1}\rangle = C_{LE}|\Phi_{LE}\rangle + C_{CT}|\Phi_{CT}\rangle$ where C_{LE} and C_{CT} are the mixing coefficients of the LE and the CT states. Then, the electronic coupling between the host and the guest in the T_1 state (V_{HG}) was determined to be 0.17 eV by solving the secular equation of the T_1 state as follows.

Figure 5.31 shows schematic energy diagram of the local excitation (LE) state and the intermolecular charge-transfer (CT) state in the system of the PMDI as a host and the 4BrF as a guest. The electronic coupling between the host and the guest in the T_1 state (V_{HG}) was determined as following. The wavefunction of the T_1 state (Φ_{T1}) is given by the linear combination of the wavefunctions for the pure LE state (Φ_{LE}) and the pure CT state (Φ_{CT}) as

$$|\Phi_{T1}\rangle = C_{LE}|\Phi_{LE}\rangle + C_{CT}|\Phi_{CT}\rangle \quad (5.1)$$

where C_{LE} and C_{CT} are the mixing coefficients of the LE and the CT states.

The secular equation is given as

$$\begin{vmatrix} E_{LE} - E & V_{HG} \\ V_{HG} & E_{CT} - E \end{vmatrix} = 0 \quad (5.2)$$

from the following equations obtained by solving the Schrödinger equation of the T_1 state using the Hückel approximation;

$$C_{LE} E_{LE} + C_{CT} V_{HG} = C_{LE} E \quad (5.3)$$

$$C_{LE} V_{HG} + C_{CT} E_{CT} = C_{CT} E \quad (5.4)$$

where E_{LE} , E_{CT} , and E are the energies of the pure LE, the pure CT, and the mixed states, respectively. Here E_{LE} is 2.88 eV, which was obtained by the emission spectrum

of the system of the PMDI as a host and the 3BrF as a guest at room temperature (Figure 5.3). E_{CT} is 3.32 eV, which was the difference between the reduction potential of the 2EH-PMDI and the oxidation potential of the 4BrF. Note that the E_{LE} and the E_{CT} are the experimentally estimated values, and they also correspond to the T_1 energy of the pure LE state and the pure CT state, respectively. The sets of E can be defined as E_1 and E_2 ($E_1 < E_2$), then E_1 is acquired as 2.82 eV, which was obtained by the emission spectrum of the system of the PMDI as a host and the 4BrF as a guest at room temperature (Figure 5.3). In that case, the energy difference between the E_{LE} and the E_1 (ΔE) is given as 0.06 eV, and the energy difference between the E_2 and the E_{CT} is estimated as also 0.06 eV, and thus E_2 is lead to 3.38 eV. Thus, the V_{HG} can be obtained to be 0.17 eV using the E_1 or the E_2 by the equation (5.2).

However, since the reduction potential of the 2EH-PMDI and the oxidation potential of the 4BrF were measured in acetonitrile, the effect of the solvent needs to be corrected. The reorganization energy for the CT state (λ_s) was estimated as following.⁷²

$$\lambda_s = \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{2r_H} + \frac{1}{2r_G} - \frac{1}{r_{CC}} \right) \left(\frac{1}{n^2} - \frac{1}{\epsilon_s} \right) \quad (5.5)$$

where r_H and r_G are the radius of the host and the guest molecules, respectively. r_{CC} is the distance between the host and the guest molecules. n and ϵ_s are the refractive index and the dielectric constant of the solvent, respectively. Assuming that r_H = 84 nm, r_G = 30 nm, r_{CC} = 40 nm based on the X-ray structure of the system of the PMDI as a host and the 4BrF as a guest (Figure 5.24), n = 1.34 (293 K) and ϵ_s = 37.5 (293 K) of acetonitrile, λ_s was estimated to be -0.0017 eV. With taking account that estimated E_{CT} is 0.0017 eV stabilized by the solvent, actual E_{CT} ($E_{CT,eff}$) is estimated to be 3.3183 eV, thus, the V_{HG} that was considered with a solvent effect can be obtained as 0.17 eV. This is reasonable because the V_{HG} value is consistent with that of the Mulliken-type CT complexes

formed in the DNA hairpin systems whose π - π distances are similar to that of PMDI-4BrF system.^{73,74}

Then, $C_{CT}^2 = 0.11$ was obtained, indicating the CT character was estimated to be 11 % for the PMDI-4BrF system based on the results of the emission spectra and the CV measurements. This result is in good agreement with the degree of the CT character estimated by the analyses of the TREPR results. Note that, the energy of the CT character should be stabilized by Coulombic interaction, which estimated to be 3.59 eV based on the distance between the host and the guest. However, the energy of the CT character would be destabilized by surrounding environment. In fact, the CV data of the hosts and the guests were measured in acetonitrile as a solvent but the hosts and the guests are not surrounded by the solvent in the solid crystals, thus the stabilization energy due to the Coulombic interaction is possible to be cancelled by the destabilization energy such as reorganization energy due to surrounding molecules and molecular motion.

Therefore, the excited triplet state of the PMDI-4BrF system has an intermolecular CT character between the host and the guest at 13 %, namely, the LE character results from the triplet state of the host is dominant in the triplet state at 87 %. This means that the CT character contributes to the S_1 - T_1 ISC in a small proportion of 13 %, indicating that $P_x \gg P_y$ can be demonstrated by the preferential contribution of the ISC from the $^1((\sigma_g\pi_h)\pi^*_h)$ state having a σ - π conjugation, as exhibited in [Figure 5.32](#). This suggest that the hybridizations between the σ -orbitals in 4BrF and the π -orbitals in PMDI induce efficient ISC to increase the emission quantum-yield in comparison to that in the PMDI-3BrF system that has little CT character.

5.4.3 Triplet CT Character in the Organic Inclusion Crystals Including Iodine Atom in the Guests.

Interestingly and importantly, the contribution of the triplet CT character to the RTP in the organic inclusion crystals including heavier halogen (bromine) atom was revealed. In addition, the ISC mechanism was characterized in the system of bromine that forms the triplet CT state. Then, to verify the emission properties and the intermolecular CT character in other systems, we focused on the organic inclusion crystals including heavier iodine atom (Figure 5.2).

In the NDI-3IF system (Figure 5.8), the ZFS parameters were determined to be $|D| = 89$ mT and $|E| = 12$ mT, which were smaller than those obtained in the PMDI-3BrF and PMDI-4BrF systems. The ZFS parameters of the NDI-3IMe system ($|D| = 86$ mT and $|E| = 10$ mT) (Figure 5.9), similarly, are smaller than those obtained in the PMDI-3BrF and PMDI-4BrF systems. These smaller $|D|$ were assumed to be caused by the SOC due to iodine atom.⁶⁷ However, these $|D|$ were larger than that of a model compound of the host NDI (2EH-NDI) obtained in a frozen solution at 77 K (Figure 5.33), in contrast to the PMDI-3BrF and PMDI-4BrF systems. This indicates that there is a contribution of the CT character to the excited triplet states of the NDI-3IF and NDI-3IMe systems in addition to the contribution of the large SOC to the $|D|$ because of iodine atom. Figure 5.34 represents relative populations in the triplet sublevels, which determined as $P_y \gg P_x > P_z$ when the sign of D in the NDI-3IF and the NDI-3IMe systems. In these systems, X- and Y- axes of the ZFS should be more indistinguishable than the case of the PMDI-3BrF and PMDI-4BrF systems because of the smaller $|E|$.

To determine the ISC mechanism in NDI-3IF system, triplet sublevels were assigned as following. Here, ZFS axes of NDI-3IF system were assumed that X- and Y-axes were

along the short and long molecular axes with respect to the NDI. In this case, sign of the E value was defined to be positive ($E > 0$). Given that 3BrF is parallel to the NDI like stacking orientation, n-orbital and σ -orbital on the iodine atom exist in the X-Y-plane, thus, the T_x and T_y sublevels expected to be more populated than T_z sublevel due to SOC around the X- and Y-axes, in which the n-orbital and σ -orbital on the iodine atom rotate around the X- and Y-axes. The contribution of the n-orbital and σ -orbital depends on the orientation of the guest in the crystal although $P_y \gg P_x$, and $g_z (= 2.002) \ll g_x$ and g_y .

Next, degree of the CT character in the NDI-3IF was estimated considering the contribution of the SOC to the ZFS parameter. T_z sublevel energy in the pure CT (100% CT) state is supposed to be $D_{SS} = -43$ mT (< 0) due to the spin-spin coupling by a distance between host and guest molecules ($4 \text{ \AA}$) as well as the PMDI-4BrF system. Moreover, when D (D_{T1}) value is contributed by the SOC, T_z sublevel energy in the pure CT (100% CT) state was supposed as $D_{T1} = 21$ mT ($=D_{SS} + D_{SO}$) (> 0) due to bromine atom.⁶⁷ This means D_{SO} is 64 mT in the bromine system, then D_{SO} of the iodine system is given as following. The SOC constants (ζ) of bromine and iodine are 2456 cm^{-1} and 5069 cm^{-1} , respectively.⁷⁵ D_{SO} is proportional to $(\zeta_I/\zeta_{Br})^2$,⁶⁷ thus D_{SO} of the iodine system is given as 273 mT in the iodine system and T_z sublevel energy in the pure CT (100% CT) state was supposed as $D_{T1} = 230$ mT ($=D_{SS} + D_{SO}$) (> 0) due to iodine atom, as represented in (Figure 5.35). On the other hand, T_z sublevel energy in the pure LE (0% CT) state was supposed to be $D_{T1} = 78$ mT (> 0), which is determined by the host model molecule (2EH-NDI) at 77 K. Thus, from the TREPR analysis, the CT character was estimated to be 9% for the NDI-3IF system.

4.5 Conclusion

In conclusion, the electronic structures and the ISC mechanism of the RTP organic inclusion crystals have been studied. The T_1 state of the crystals was observed by using TREPR method at room temperature. In the PMDI-3BrF system whose guest is oriented perpendicular to the host molecule, there is little CT character in the RTP triplet state. On the other hand, the PMDI-4BrF system whose guest is oriented parallel to the host molecule represents the CT character in the RTP triplet state. The contribution of the triplet CT character was estimated to be PMDI-3BrF < PMDI-4BrF systems, which result in the color-tunable RTP emissions. The S_1 - T_1 ISC mechanism has been demonstrated that n-orbitals on the carbonyl oxygen in the host PMDI participate in the ISC in the PMDI-3BrF system having little CT character. In contrast, in the PMDI-4BrF system which shows triplet CT character, n-orbital and σ -orbital on the bromine atom in the guest participates in the ISC. This can form the triplet CT state through an allowed transition between $n\pi^*$ and $\pi\pi^*$ states and between $\sigma\pi^*$ and $\pi\pi^*$ states by vibronic coupling. In the NDI-3IF and the NDI-3IME systems whose guests have iodine atom, the S_1 - T_1 ISC mechanism can be demonstrated as well as the PMDI-4BrF system. However, $|D|$ of the NDI-3IF and the NDI-3IME systems is larger than that of the host model molecule (2EH-NDI). This is not in agreement with the tendency of the bromine systems (PMDI-3BrF and PMDI-4BrF systems), which can be explained by considering the larger contribution of the SOC to $|D|$ rather than bromine systems. This would be a first report on the electronic structure of the pure organic RTP triplet state at room temperature in the donor-acceptor system. These results would help us to develop the practical organic light emitting devices by controlling the triplet CT interaction in the organic donor-acceptor systems depending on the guest or host molecules.

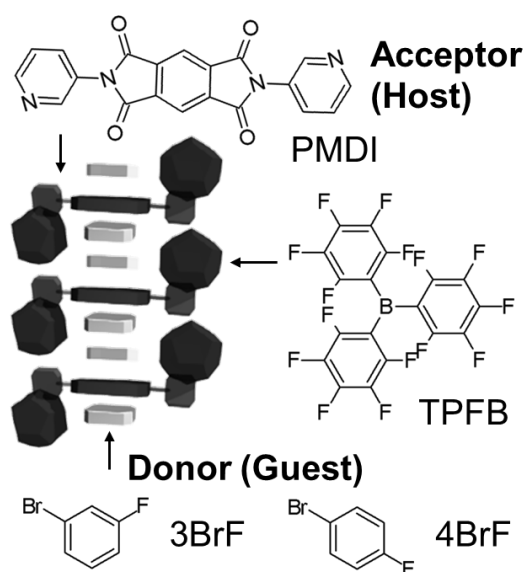


Figure 5.1. Schematic illustration of the crystal structure of the organic inclusion crystals and chemical structure of the constituent molecules including bromine atom in the guests used in this study.

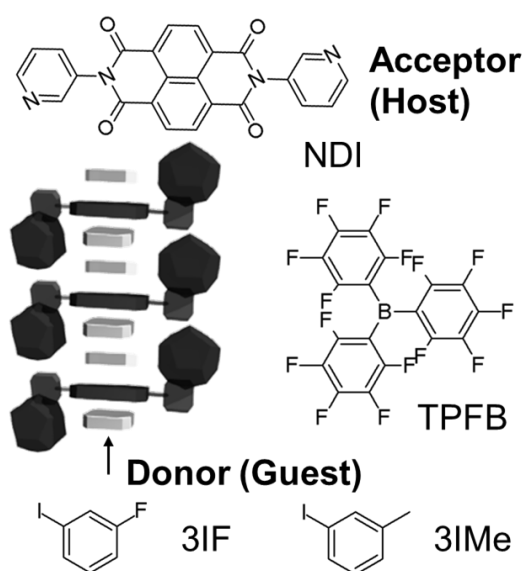


Figure 5.2. Schematic illustration of the crystal structure of the organic inclusion crystals and chemical structure of the constituent molecules including iodine atom in the guests used in this study.

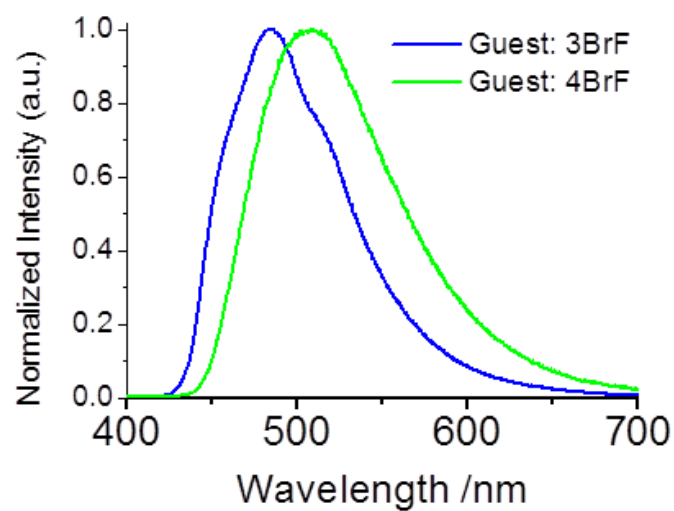


Figure 5.3. Normalized emission spectra of organic inclusion crystals consisting of PMDI as a host; 3BrF or 4BrF as a guest, and TPFB, under 340 nm light excitation at room temperature, which were measured by phosphorescence mode.

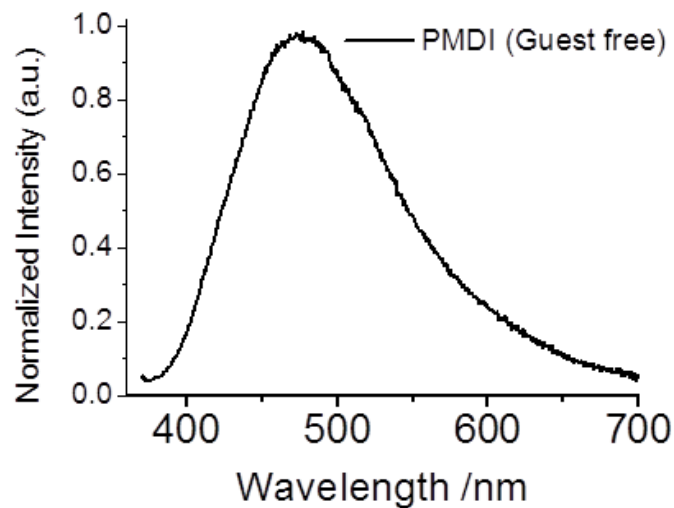


Figure 5.4. Normalized emission spectra of organic crystal consisting of PMDI and TPFB without guest molecule, under 340 nm light excitation at room temperature, which were measured by phosphorescence mode.

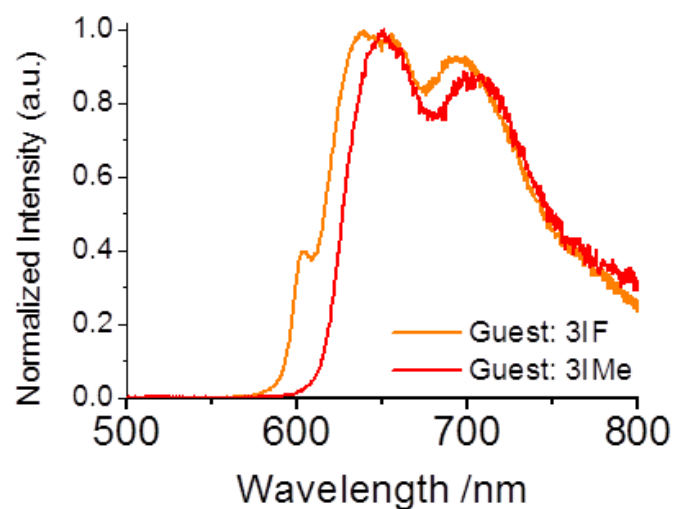


Figure 5.5. (a) Normalized emission spectra of organic inclusion crystals consisting of NDI as a host; 3IF or 3IMe as a guest, and TPFB, under 405 nm light excitation for 3IF and 3IMe systems, respectively, at room temperature, which were measured by phosphorescence mode.

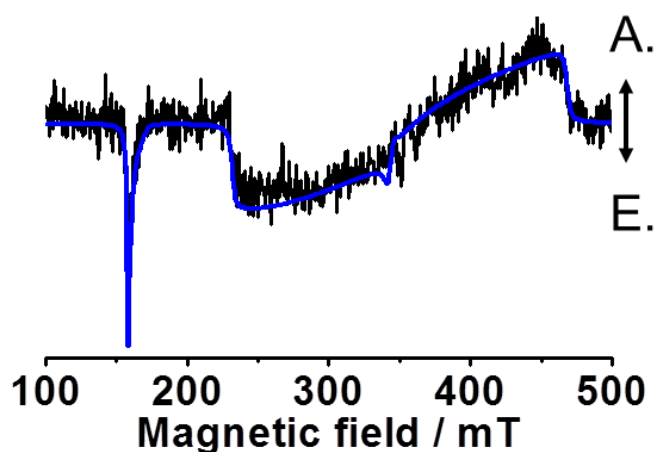


Figure 5.6. Experimental (black) and simulated (blue) TREPR spectra of organic inclusion crystals consisting of TPFB, PMDI and 3BrF observed at 0.5 μ s after the 355 nm laser irradiation at room temperature. “A” and “E” show absorption and emission of microwave, respectively.

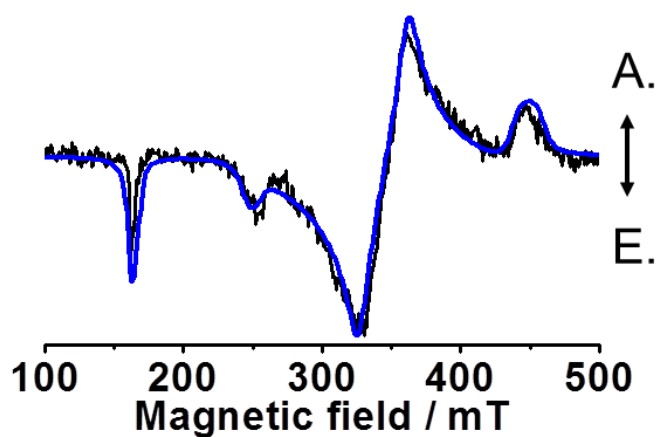


Figure 5.7. Experimental (black) and simulated (blue) TREPR spectra of organic inclusion crystals consisting of TPFB, PMDI and 4BrF observed at 0.5 μ s after the 355 nm laser irradiation at room temperature. “A” and “E” show absorption and emission of microwave, respectively.

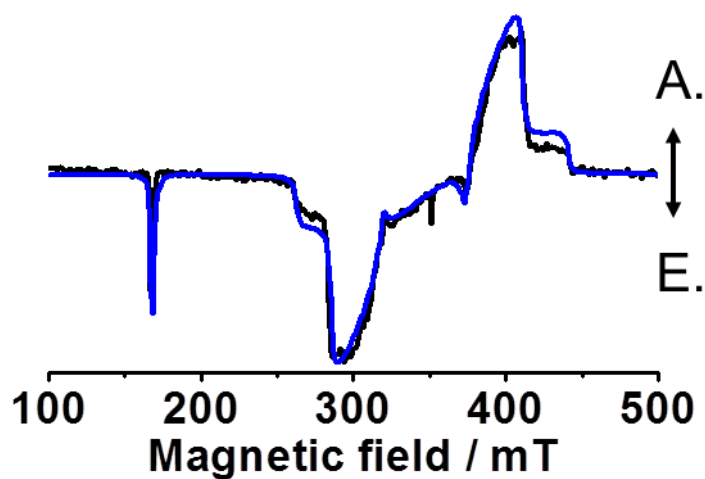


Figure 5.8. Experimental (black) and simulated (blue) TREPR spectra of organic inclusion crystals consisting of TPFB, PMDI and 3IF observed at 0.5 μ s after the 355 nm laser irradiation at room temperature. “A” and “E” show absorption and emission of microwave, respectively.

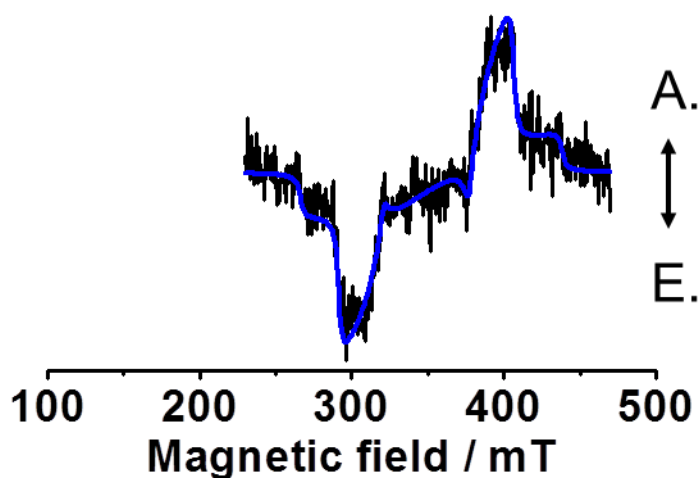


Figure 5.9. Experimental (black) and simulated (blue) TREPR spectra of organic inclusion crystals consisting of TPFB, PMDI and 3IMe observed at 0.5 μ s after the 355 nm laser irradiation at room temperature. “A” and “E” show absorption and emission of microwave, respectively.

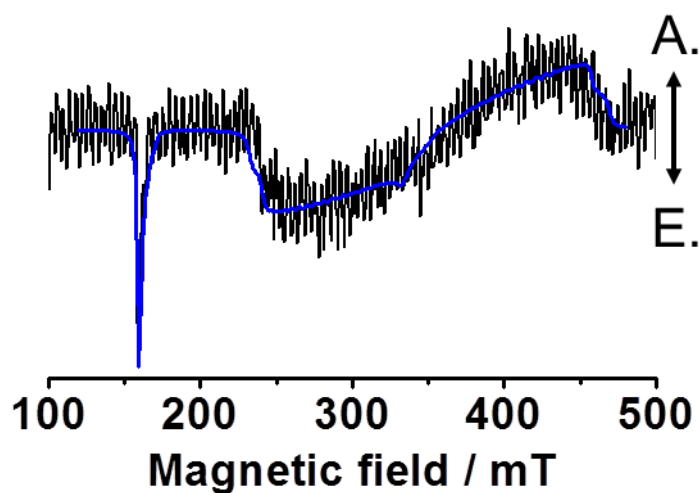


Figure 5.10. Experimental (black) and simulated (blue) TREPR spectra of guest-free organic crystal consisting of TPFB and PMDI observed at room temperature at 0.5 μ s after the 355 nm laser irradiation. “A” and “E” show absorption and emission of microwave, respectively.

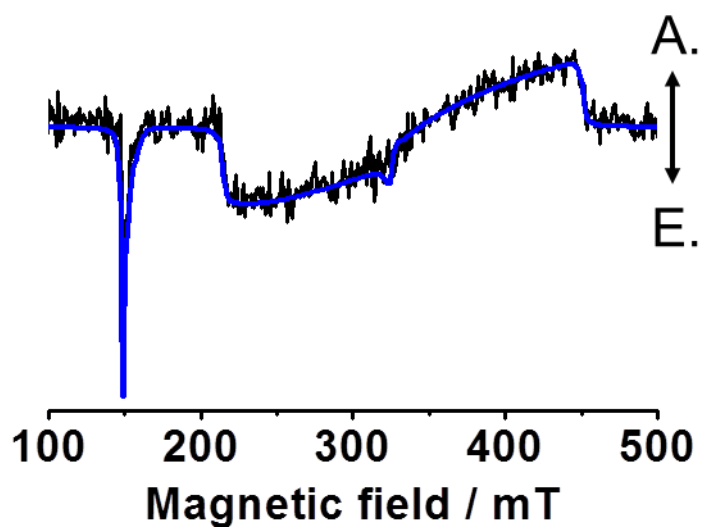


Figure 5.11. Experimental (black) and simulated (blue) TREPR spectra of 2EH-PMDI observed in 2-methyltetrahydrofuran at 77 K at 0.5 μ s after the 355 nm laser irradiation. “A” and “E” show absorption and emission of microwave, respectively.

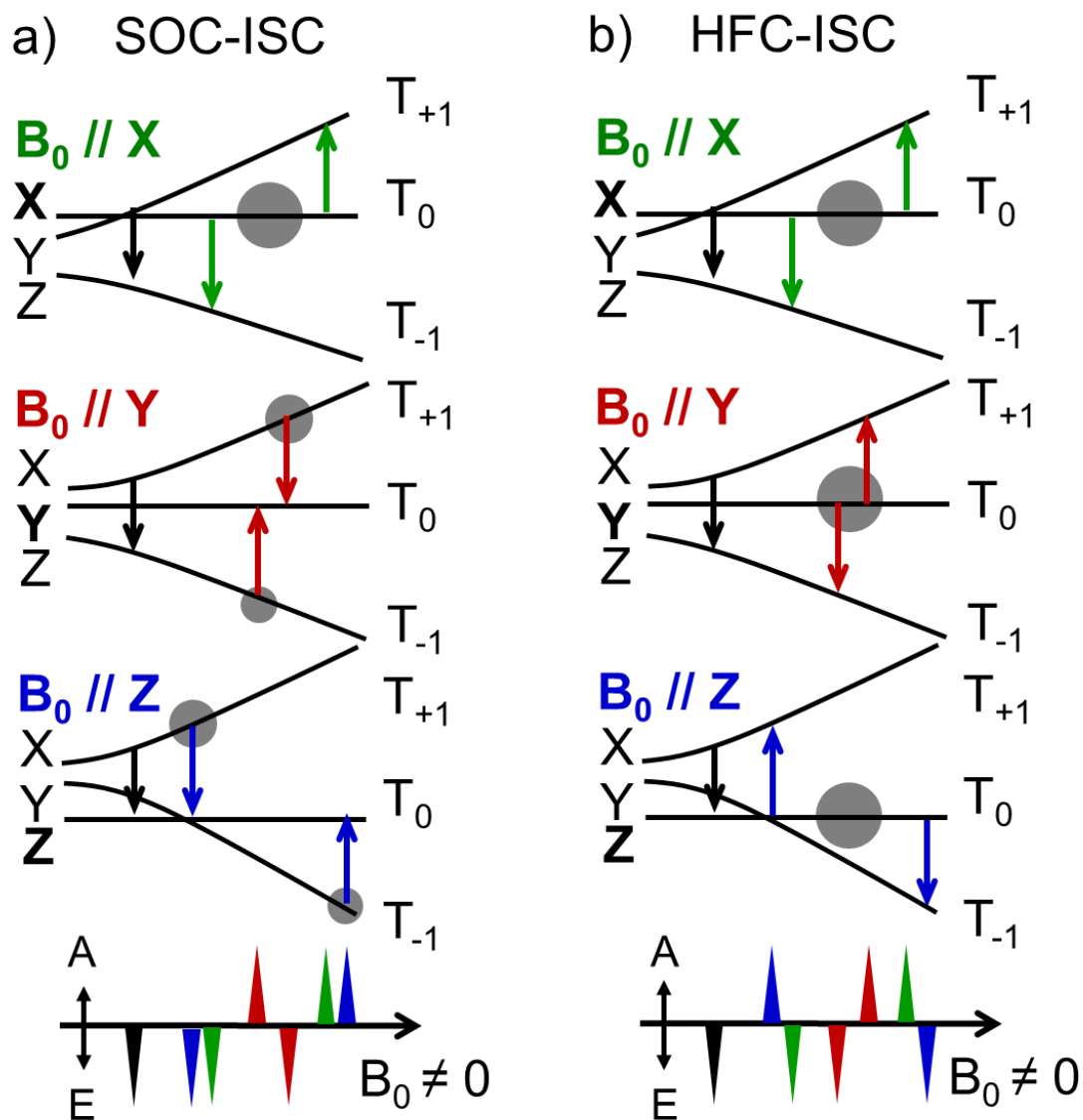


Figure 5.12. Energy sublevels (in the case of $D > 0$, $E < 0$) and the EPR transition due to the spin polarization for the T_1 state based on the (a) spin-orbit coupling induced ISC (in the case of $P_x \gg P_y, P_z$) and (b) hyperfine coupling with S- T_0 mixing induced ISC from the S_1 state in the presence of external magnetic field along the X, Y, and Z axes of the molecule.

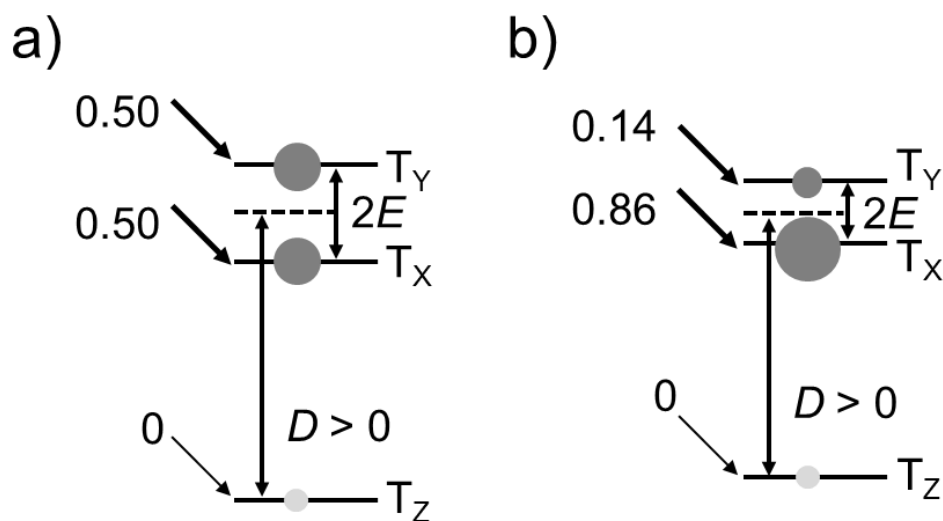


Figure 5.13. Triplet sublevels and relative populations through spin-orbit coupling for organic inclusion crystals consisting of TPFB, PMDI and 3BrF in (a) or 4BrF in (b), respectively.

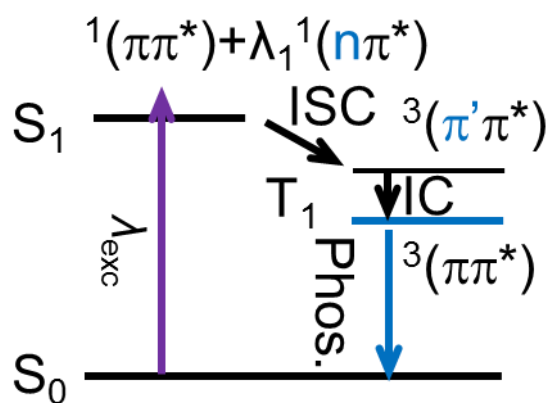


Figure 5.14. Schematic representation of the S_1 - T_1 ISC in the organic inclusion crystals consisting of PMDI and TPFB.

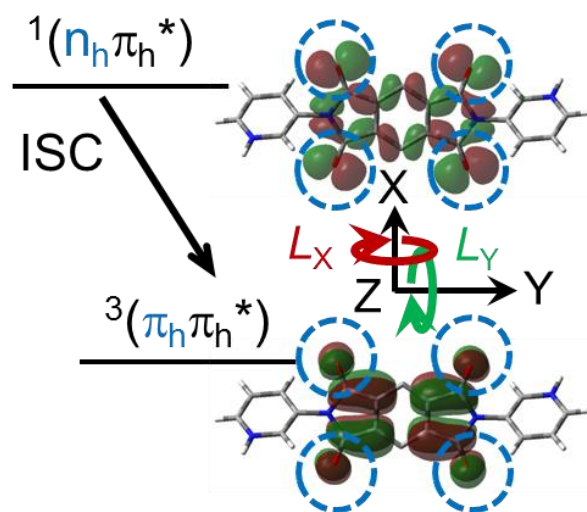


Figure 5.15. (a) n-Orbital character and (b) π' -orbital characters including the $^1n\pi^* \rightarrow ^3\pi'\pi^*$ ISC, which induces the angular momentum changes along the X- and Y-axes in the organic inclusion crystals consisting of TPFB, PMDI and 3BrF.

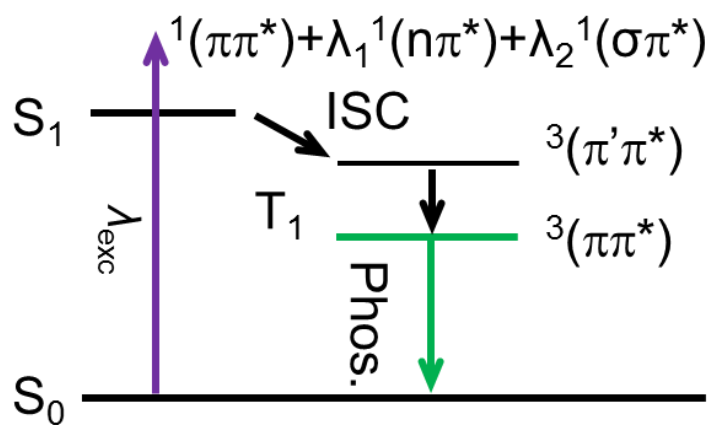


Figure 5.16. Schematic representation of the S_1 - T_1 ISC in the organic inclusion crystals consisting of PMDI, 4BrF and TPFB.

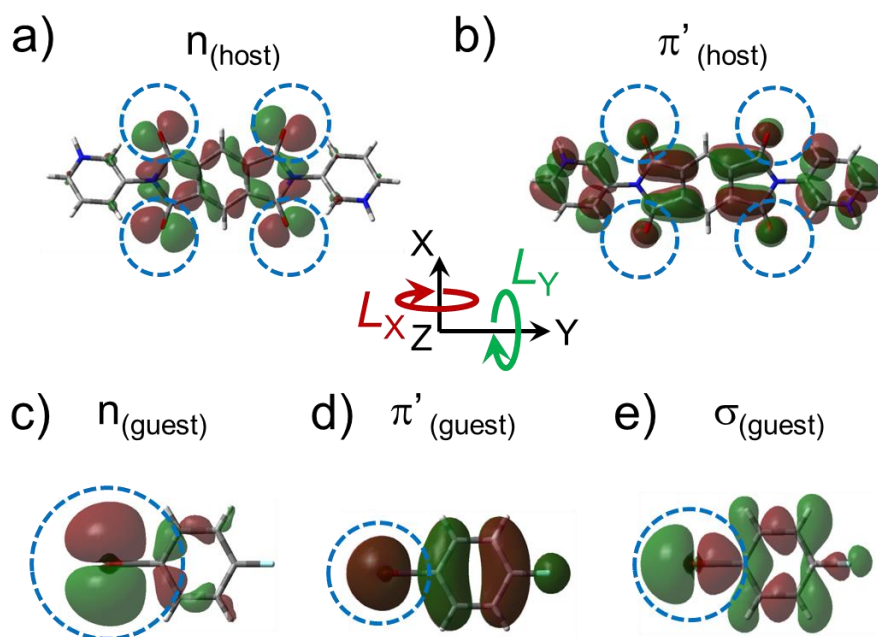


Figure 5.17. (a) n-Orbital character and (b) π' -orbital characters including the ${}^1n\pi^* \rightarrow {}^3\pi'\pi^*$ ISC, which induces the angular momentum changes along the X- and Y-axes in the organic inclusion crystals consisting of TPFB, PMDI and 4BrF.

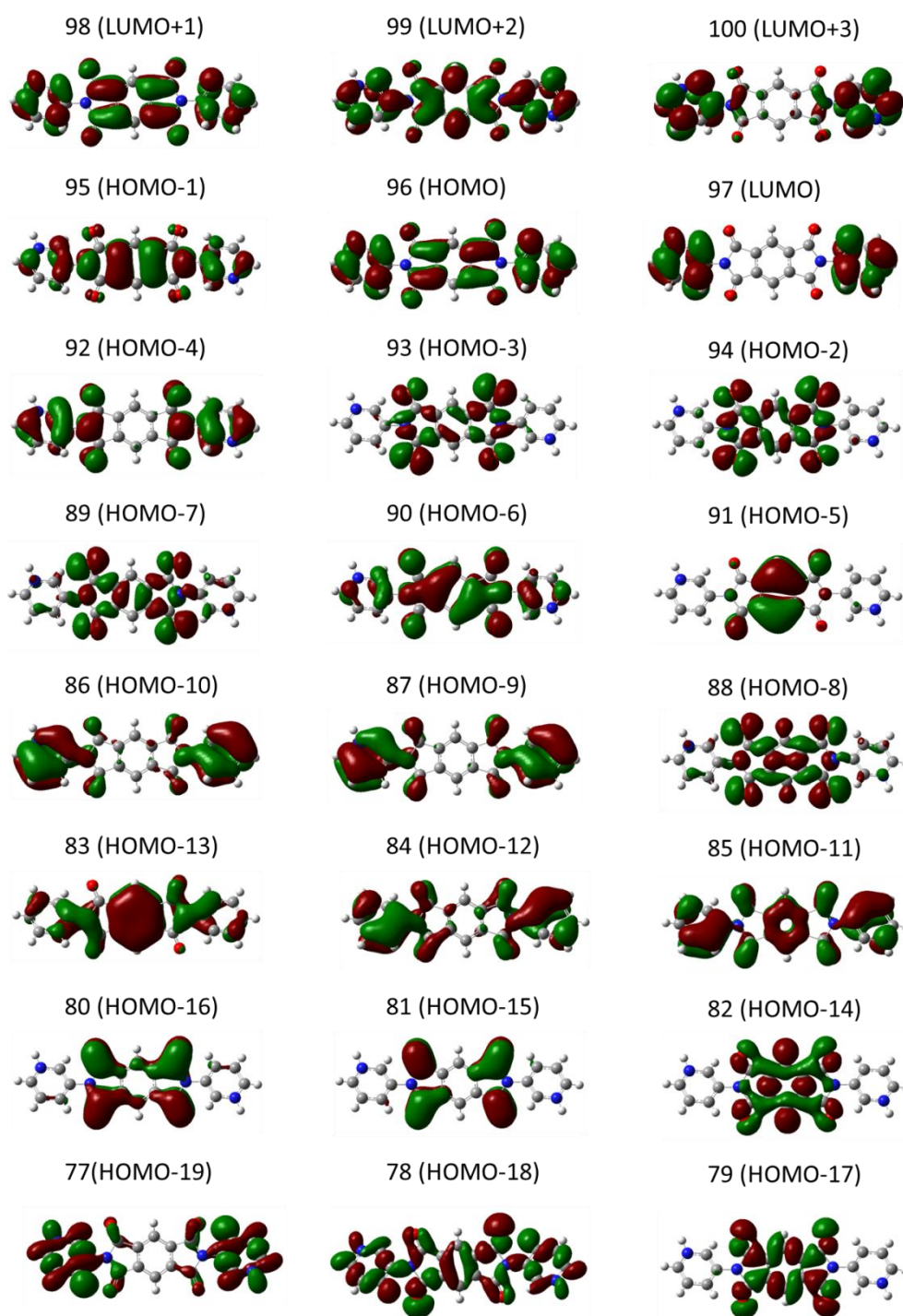


Figure 5.18. Molecular orbitals of the singlet state of the **PMDI** calculated by the DFT method at the RB3LYP/6-31G** level.

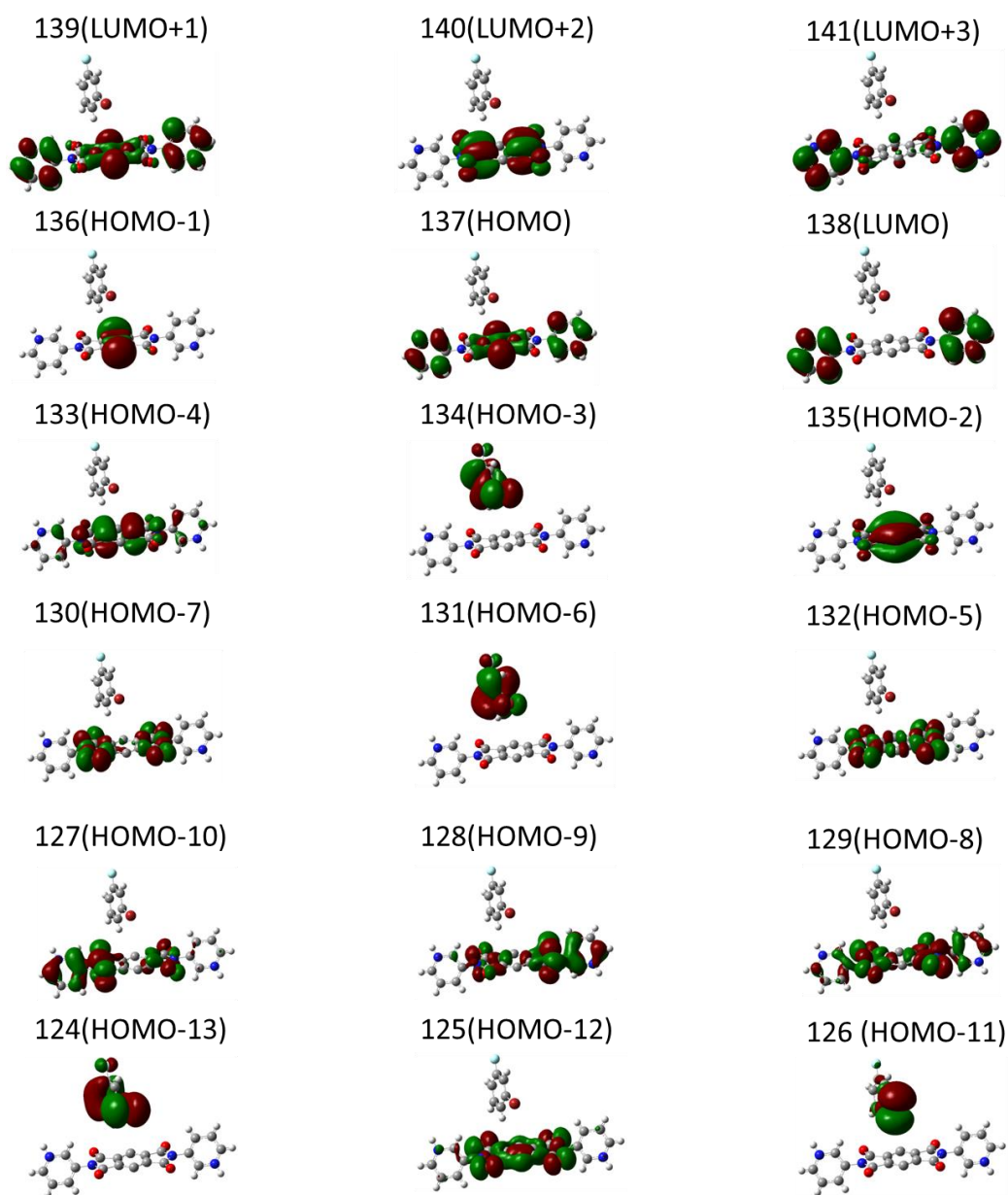


Figure 5.19a. Molecular orbitals of the singlet state of the system (from HOMO-13 to LUMO+3) of the PMDI as a host and the 3BrF as a guest calculated by the DFT method at the RB3LYP/6-31G** level.

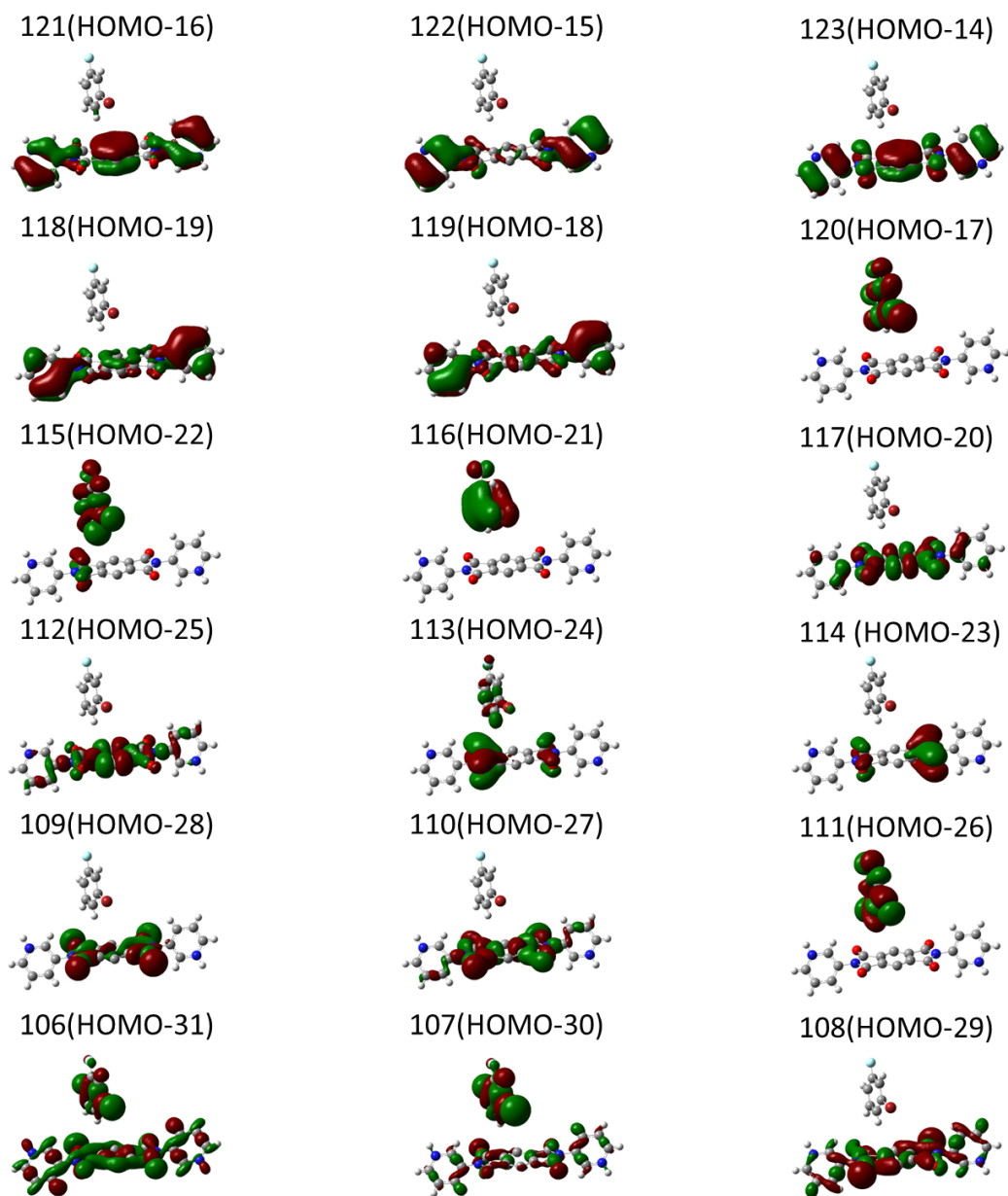


Figure 5.19b. Molecular orbitals of the singlet state of the system (from HOMO-31 to HOMO-14) of the PMDI as a host and the 3BrF as a guest calculated by the DFT method at the RB3LYP/6-31G** level.

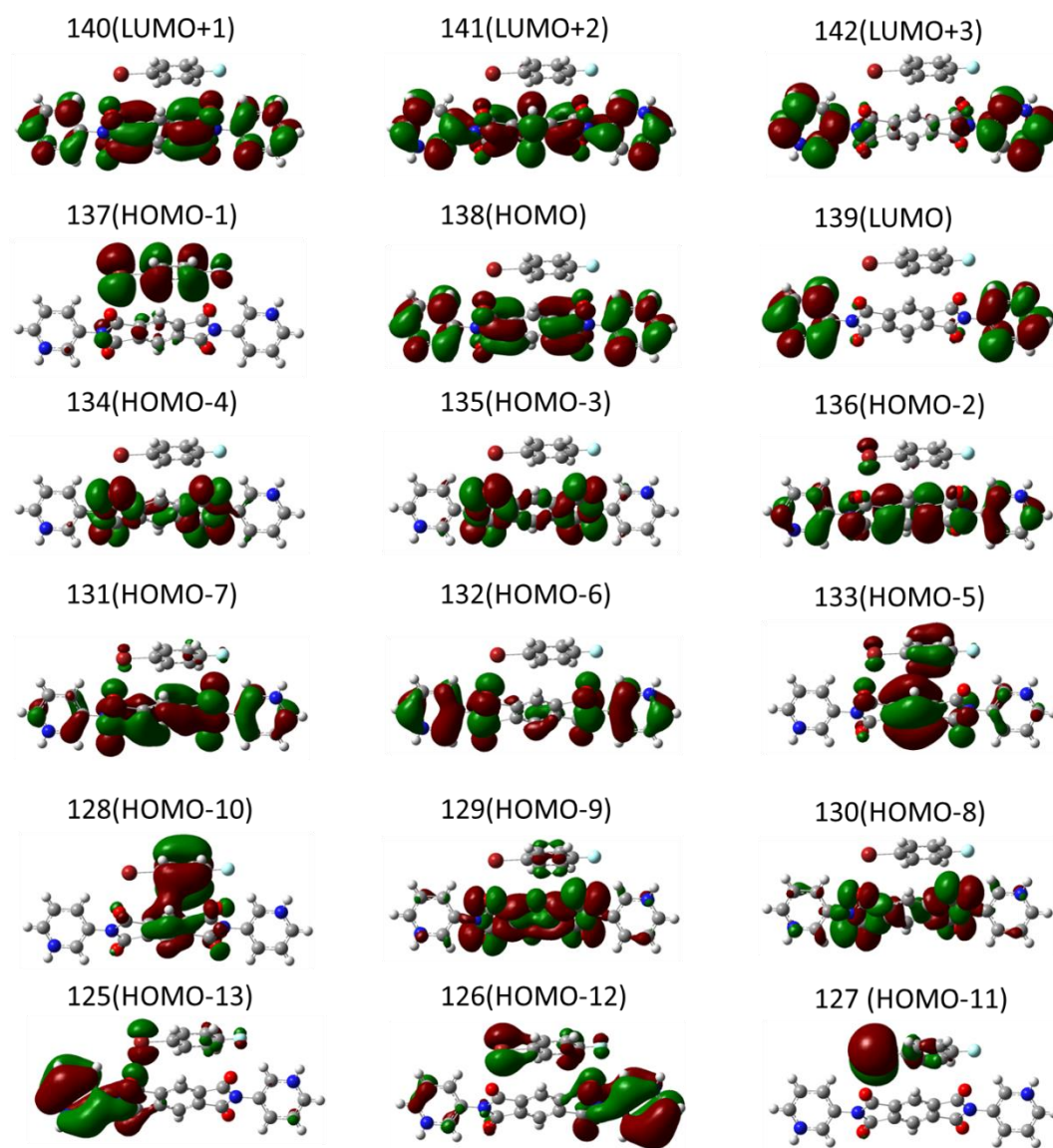


Figure 5.20a. Molecular orbitals of the singlet state of the system (from HOMO-13 to LUMO+3) of the PMDI as a host and the 4BrF as a guest calculated by the DFT method at the RB3LYP/6-31G** level.

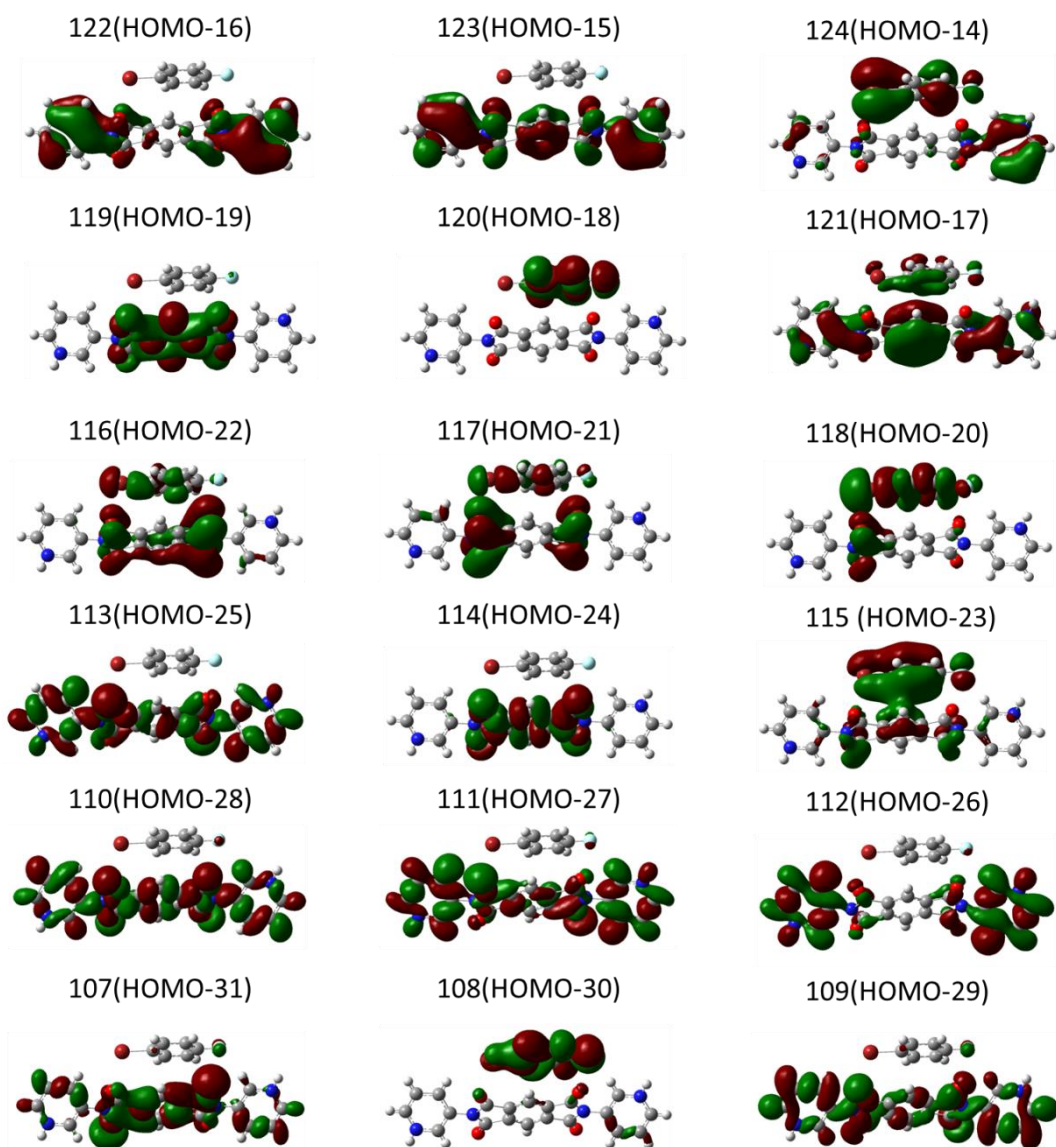


Figure 5.20b. Molecular orbitals of the singlet state of the system (from HOMO-31 to HOMO-14) of the PMDI as a host and the 4BrF as a guest calculated by the DFT method at the RB3LYP/6-31G** level.

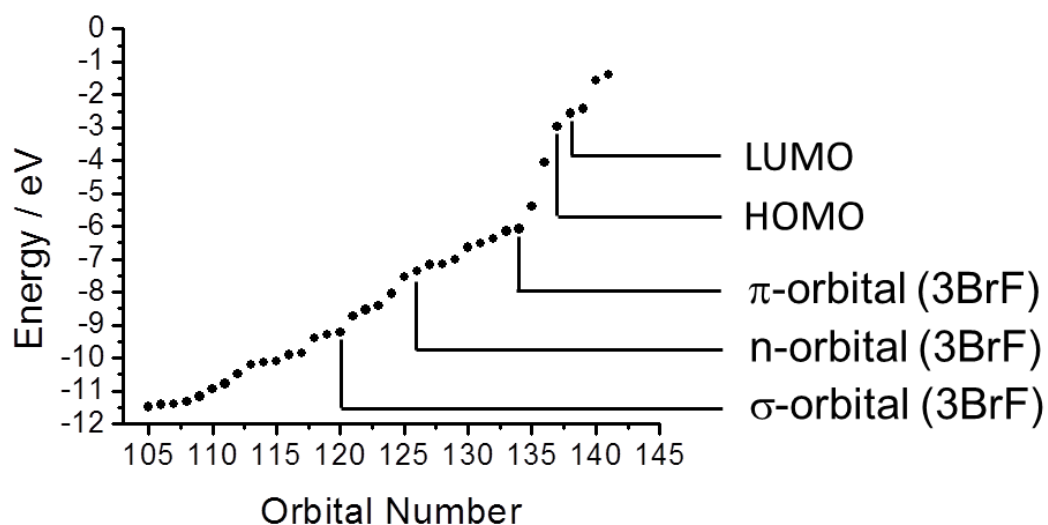


Figure 5.21. Plots of orbital energies in the PMDI:3BrF complex in [Figure 5.19](#) calculated by the DFT method at the RB3LYP/6-31G** level

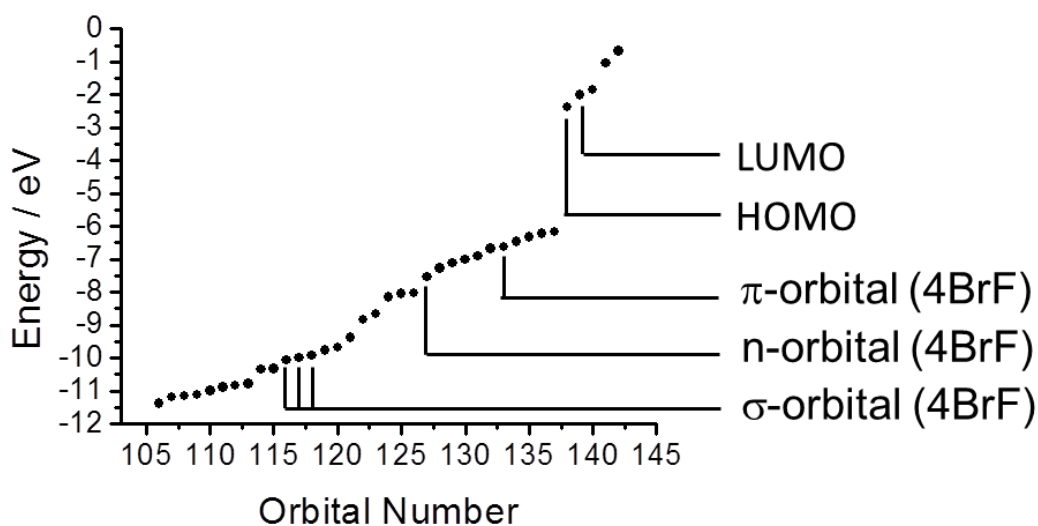


Figure 5.22. Plots of orbital energies in the PMDI:4BrF complex in [Figure 5.20](#) calculated by the DFT method at the RB3LYP/6-31G** level

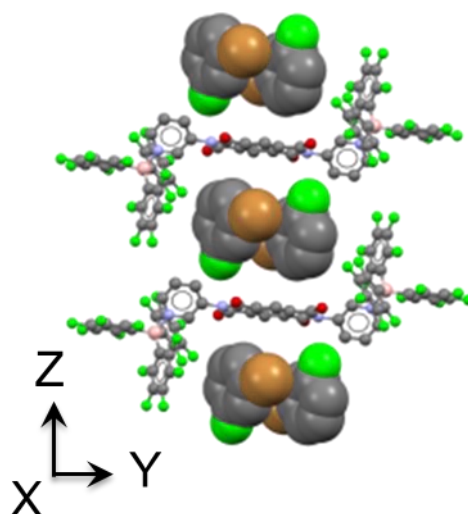


Figure 5.23. Crystal structure of organic inclusion crystals consisting of PMDI, TPFB, and 3BrF determined by single crystal X-ray diffraction measurement, with principal ZFS axes. Green and Orange atoms in the guest molecules represent the fluorine (F) and the bromine (Br) atoms, respectively.

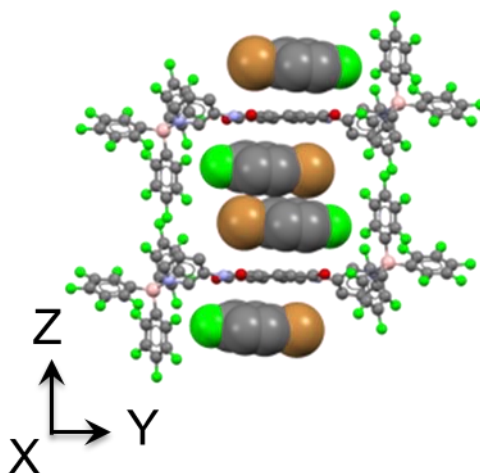


Figure 5.24. Crystal structure of organic inclusion crystals consisting of PMDI, TPFB, and 4BrF determined by single crystal X-ray diffraction measurement, with principal ZFS axes. Green and Orange atoms in the guest molecules represent the fluorine (F) and the bromine (Br) atoms, respectively.

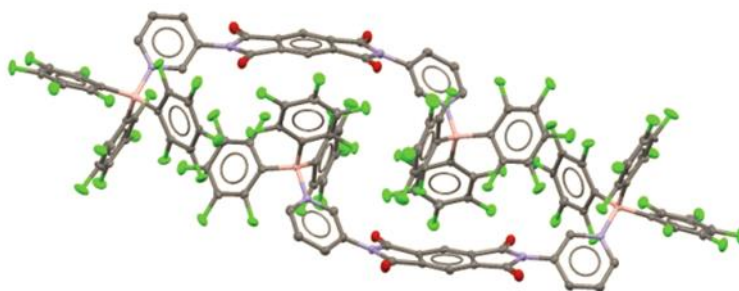


Figure 5.25. Crystal structure of guest-free organic crystal consisting of PMDI and TPFB, determined by single crystal X-ray diffraction measurement.

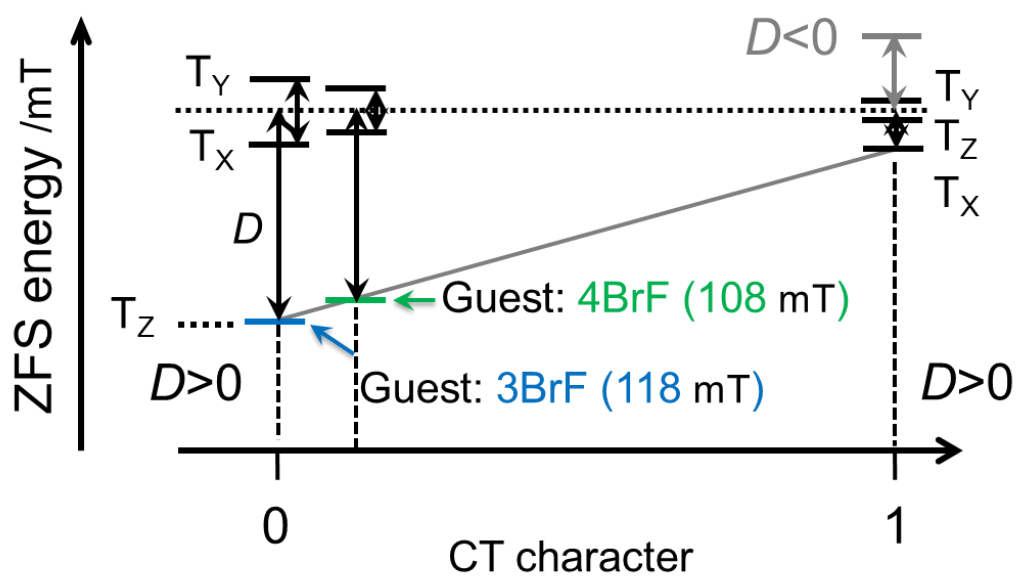


Figure 5.26. Schematic illustration of the spin-orbit coupling between the singlet CT state and the triplet CT state.

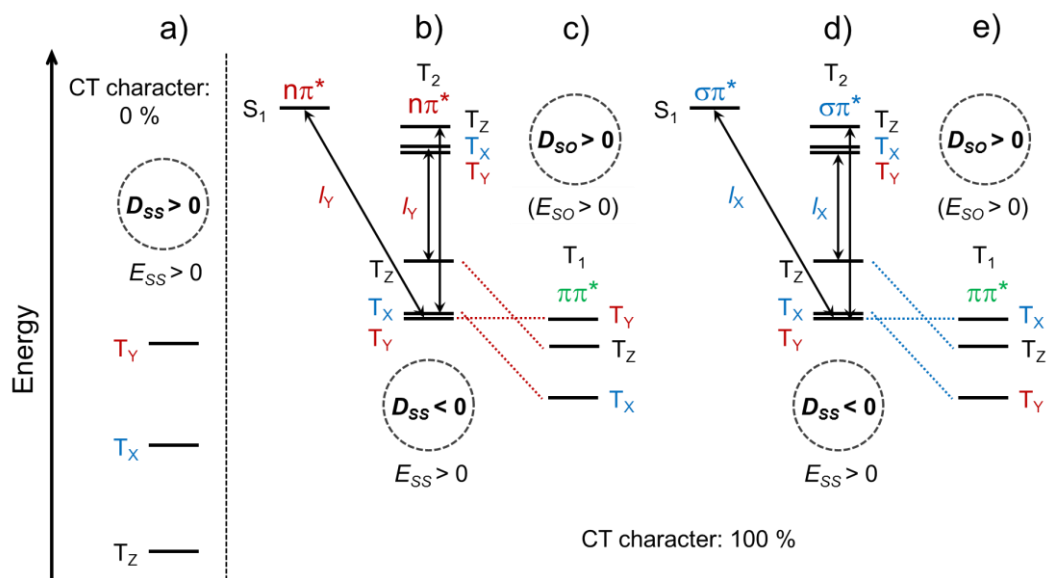


Figure 5.27. Schematic representation of the contribution of the intermolecular charge transfer character in the T_1 state of the organic inclusion crystals consisting of the TPFB, PMDI and 4BrF₆, which is estimated by the TREPR results.

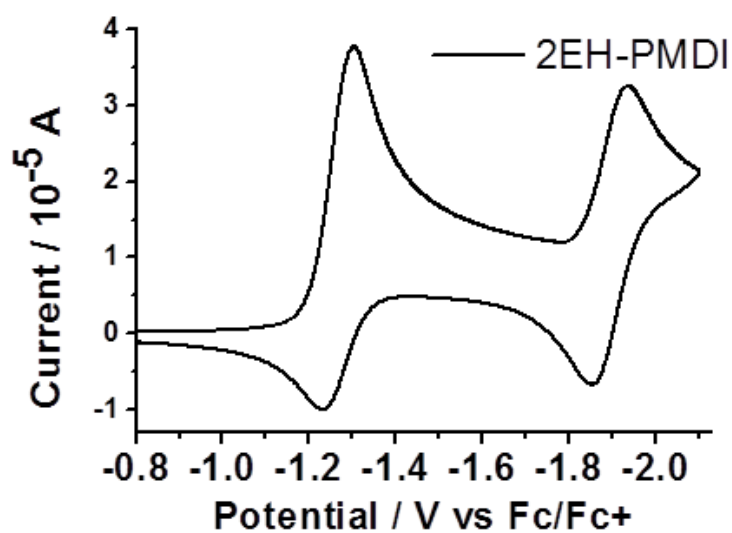


Figure 5.28. Cyclic voltammogram (V vs. Fc/Fc⁺) of 2EH-PMDI in acetonitrile.

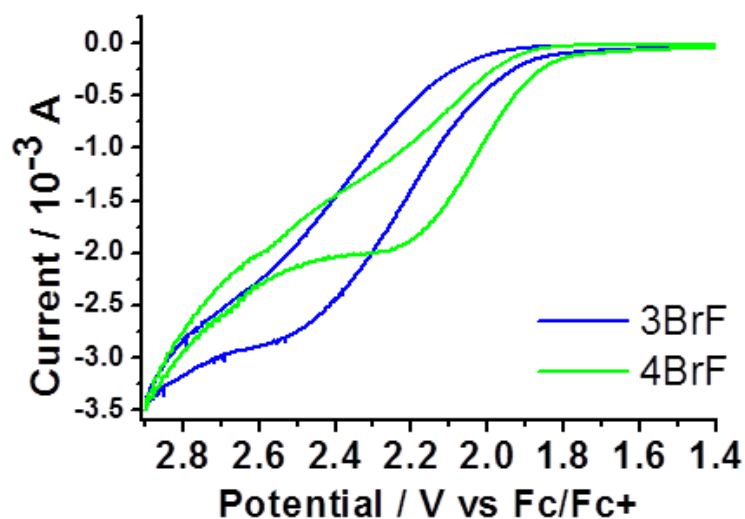


Figure 5.29. Cyclic voltammogram (V vs. Fc/Fc+) of 3BrF and 4BrF in acetonitrile.

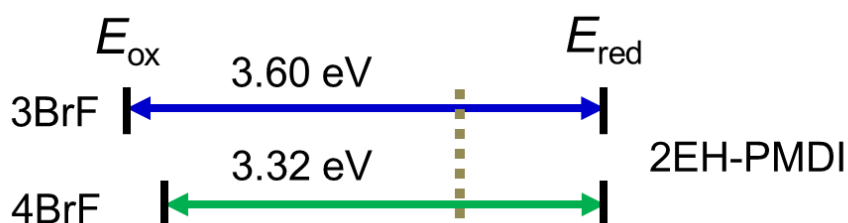


Figure 5.30. Schematic view of the difference between the reduction potential (E_{red}) of 2EH-PMDI and the oxidation potential (E_{ox}) of 3BrF and 4BrF, respectively. Dashed line shows the V=0.

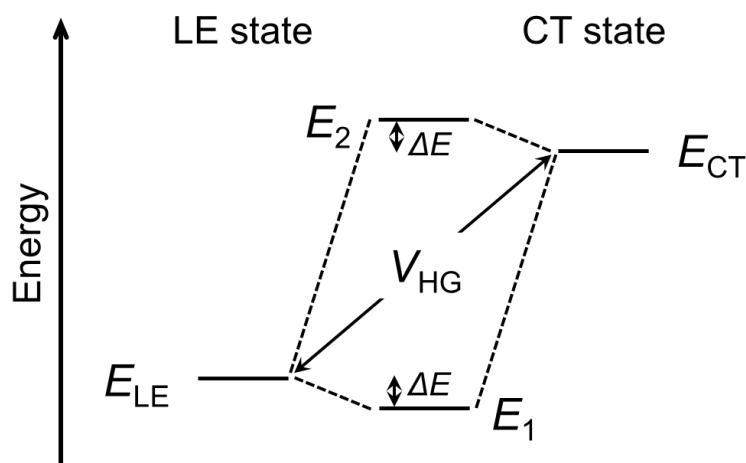


Figure 5.31. Schematic representation of the energy diagram of the local excitation (LE) state and the intermolecular charge-transfer (CT) state in the T_1 state in the system of the PMDI as a host and the 4BrF as a guest.

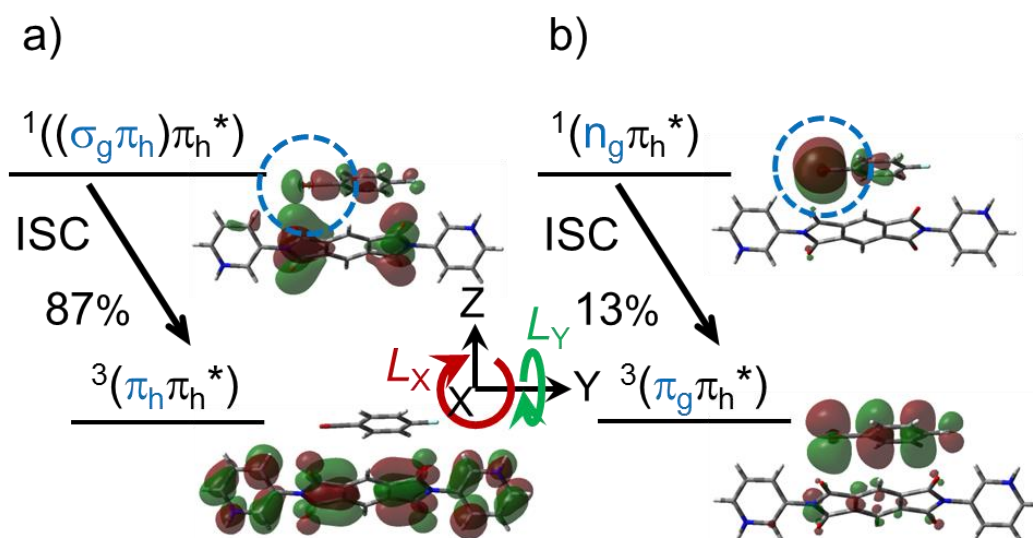


Figure 5.32. σ -Orbital character, n-orbital character, and π -orbital character of the 4BrF (g: guest), and π -orbital character of the PMDI (h: host) including the $^1\sigma\pi^* \rightarrow ^3\pi'\pi^*$ ISC and $^1n\pi^* \rightarrow ^3\pi'\pi^*$ ISC, which induces the angular momentum changes along the (a) X- and (b) Y-axes in the organic inclusion crystals consisting of TPFB, PMDI and 4BrF.

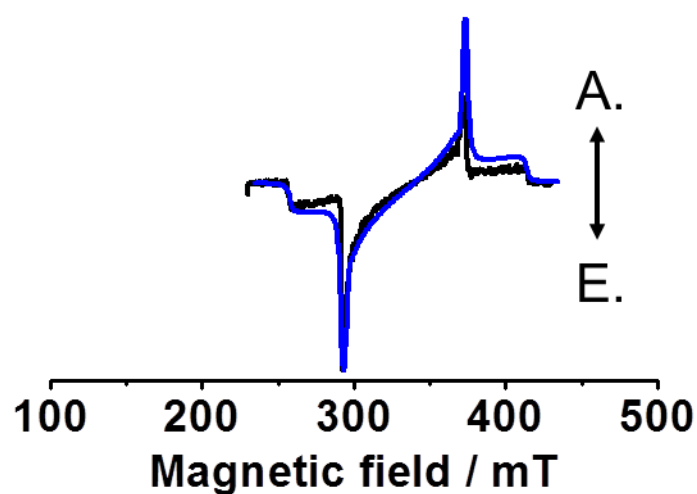


Figure 5.33. Experimental (black) and simulated (blue) TREPR spectra of 2EH-NDI observed in 2-methyltetrahydrofuran at 77 K, at 0.5 μ s after the 355 nm laser irradiation. “A” and “E” show absorption and emission of microwave, respectively.

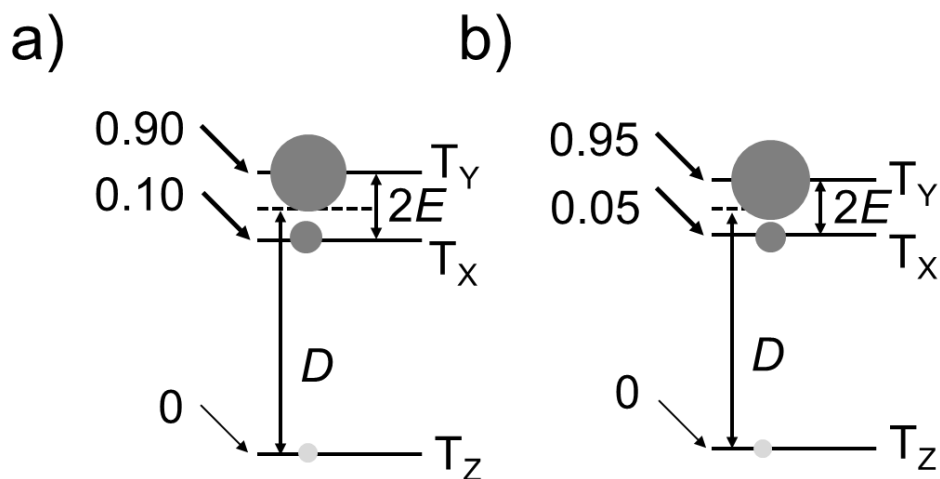


Figure 5.34. Relative populations in the triplet sublevels at 0.5 μ s after laser irradiation of (a) TPFB, NDI and 3IF and (b) TPFB, NDI and 3IMe, respectively.

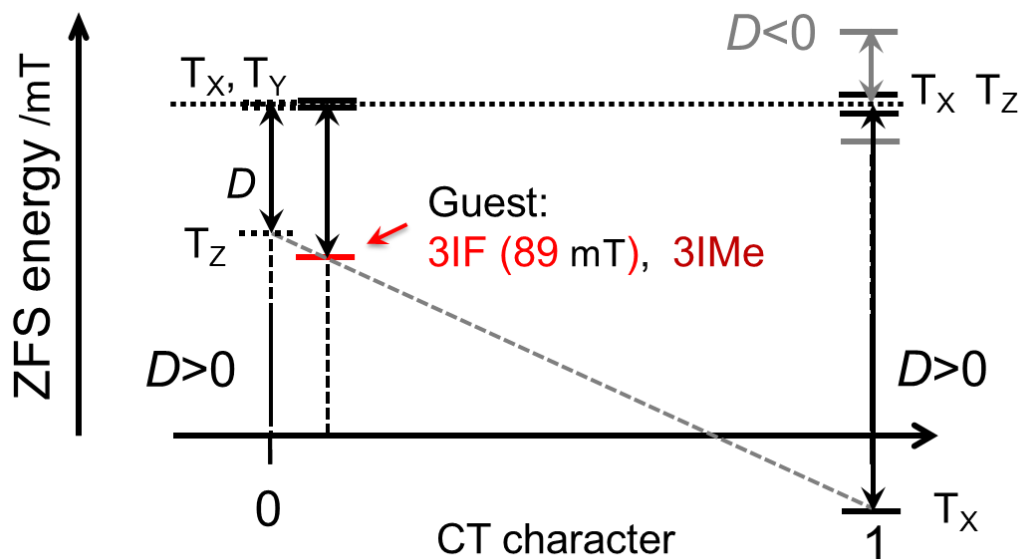


Figure 5.35. Schematic representation of the contribution of the intermolecular charge transfer character in the T_1 state of the organic inclusion crystals consisting of the TPFB, PMDI and 3IF, which is estimated by the TREPR results.

Table 5.1. Emission lifetime and quantum yield of organic inclusion crystals consisting of PMDI as a host; 3BrF or 4BrF as a guest, and TPFB, obtained at room temperature.

Host	Guest	τ_{av} / ms	Φ_{PL} / %
PMDI	3BrF	6.56	28.0
PMDI	4BrF	3.94	70.6

Table 5.2. ZFS parameters (D and E) and anisotropies ($P_x : P_y : P_z$) of the populations at the zero-field sublevels in organic inclusion crystals consisting of PMDI as a host; 3BrF or 4BrF as a guest, and TPFB, obtained at room temperature.

Host	Guest	D / mT ^a	E / mT ^b	$ E/D $	$P_x : P_y : P_z$	$g_x : g_y : g_z$
PMDI	3BrF	118	38	0.322	0.50:0.50:0.00	2.002:2.002:2.002
PMDI	4BrF	108	24	0.222	0.86:0.14:0.00	2.005:2.005:2.002
PMDI	free	118	32	0.271	0.40:0.60:0.00	2.002:2.002:2.002
2EH- PMDI ^c		118 ^d	38 ^d	0.322 ^d	0.50:0.50:0.00 ^d	2.002:2.002:2.002

^a ± 1 , ^b ± 0.5 , ^c host model molecule, ^d obtained in 2-methyltetrahydrofuran at 77 K

Table 5.3. ZFS parameters (D and E) and anisotropies ($P_x : P_y : P_z$) of the populations at the zero-field sublevels in organic inclusion crystals consisting of NDI as a host; 3IF or 3IMe as a guest, and TPFB, obtained at room temperature.

Host	Guest	D / mT ^a	E / mT ^b	$ E/D $	$P_x : P_y : P_z$	$g_x : g_y : g_z$
NDI	3IF	89	12	0.135	0.10:0.90:0.00	2.005:2.005:2.002
NDI	3IMe	86	10	0.116	0.05:0.95:0.00	2.002:2.002:2.002
2EH- NDI ^c		78 ^d	1.0 ^d	0.0133 ^d	0.00:1.00:0.00 ^d	2.002:2.002:2.002

^a ± 1 , ^b ± 0.5 , ^c host model molecule, ^d obtained in 2-methyltetrahydrofuran at 77 K

Table 5.4. Orbital energies in the unit of PMDI and 3BrF based on the X-ray structure, calculated by the DFT method at the RB3LYP/6-31G** level.

Orbital	Number	Energy / hartree	Energy / eV
LUMO+5	143	-0.0002	-0.00544228
LUMO+4	142	-0.04811	-1.309140454
LUMO+3	141	-0.05118	-1.392679452
LUMO+2	140	-0.05721	-1.556764194
LUMO+1	139	-0.08942	-2.433243388
LUMO	138	-0.0944	-2.56875616
HOMO	137	-0.10935	-2.97556659
HOMO-1	136	-0.14898	-4.053954372
HOMO-2	135	-0.19798	-5.387312972
HOMO-3	134	-0.22368	-6.086645952
HOMO-4	133	-0.22614	-6.153585996
HOMO-5	132	-0.23426	-6.374542564
HOMO-6	131	-0.23967	-6.521756238
HOMO-7	130	-0.24391	-6.637132574
HOMO-8	129	-0.25804	-7.021629656
HOMO-9	128	-0.26259	-7.145441526
HOMO-10	127	-0.26364	-7.174013496
HOMO-11	126	-0.27029	-7.354969306
HOMO-12	125	-0.27675	-7.53075495
HOMO-13	124	-0.29579	-8.048860006

HOMO-14	123	-0.30907	-8.410227398
HOMO-15	122	-0.31385	-8.54029789
HOMO-16	121	-0.3207	-8.72669598
HOMO-17	120	-0.33904	-9.225753056
HOMO-18	119	-0.34175	-9.29949595
HOMO-19	118	-0.34524	-9.394463736
HOMO-20	117	-0.36189	-9.847533546
HOMO-21	116	-0.36436	-9.914745704
HOMO-22	115	-0.37103	-10.09624574
HOMO-23	114	-0.3722	-10.12808308
HOMO-24	113	-0.37499	-10.20400289
HOMO-25	112	-0.38566	-10.49434852
HOMO-26	111	-0.39647	-10.78850376
HOMO-27	110	-0.40233	-10.94796256
HOMO-28	109	-0.41087	-11.18034792
HOMO-29	108	-0.41612	-11.32320777
HOMO-30	107	-0.41934	-11.41082848
HOMO-31	106	-0.41944	-11.41354962
HOMO-32	105	-0.42232	-11.49191845

Table 5.5. Orbital energies in the unit of PMDI and 4BrF based on the X-ray structure, calculated by the DFT method at the RB3LYP/6-31G** level.

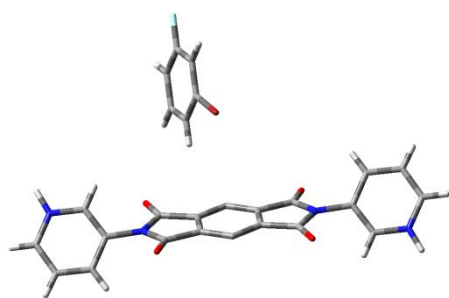
Orbital	Number	Energy / hartree	Energy / eV
LUMO+5	144	-0.00721	-0.196194194
LUMO+4	143	-0.0129	-0.35102706
LUMO+3	142	-0.02449	-0.666407186
LUMO+2	141	-0.03801	-1.034305314
LUMO+1	140	-0.06796	-1.849286744
LUMO	139	-0.07377	-2.007384978
HOMO	138	-0.08727	-2.374738878
HOMO-1	137	-0.22652	-6.163926328
HOMO-2	136	-0.22843	-6.215900102
HOMO-3	135	-0.23238	-6.323385132
HOMO-4	134	-0.23752	-6.463251728
HOMO-5	133	-0.24324	-6.618900936
HOMO-6	132	-0.24545	-6.67903813
HOMO-7	131	-0.25364	-6.901899496
HOMO-8	130	-0.25755	-7.00829607
HOMO-9	129	-0.26126	-7.109250364
HOMO-10	128	-0.26733	-7.274423562
HOMO-11	127	-0.27684	-7.533203976
HOMO-12	126	-0.29528	-8.034982192
HOMO-13	125	-0.29581	-8.049404234

HOMO-14	124	-0.29948	-8.149270072
HOMO-15	123	-0.31846	-8.665742444
HOMO-16	122	-0.32456	-8.831731984
HOMO-17	121	-0.34473	-9.380585922
HOMO-18	120	-0.35616	-9.691612224
HOMO-19	119	-0.35917	-9.773518538
HOMO-20	118	-0.36492	-9.929984088
HOMO-21	117	-0.36711	-9.989577054
HOMO-22	116	-0.36962	-10.05787767
HOMO-23	115	-0.37943	-10.3248215
HOMO-24	114	-0.38066	-10.35829152
HOMO-25	113	-0.39637	-10.78578262
HOMO-26	112	-0.39831	-10.83857273
HOMO-27	111	-0.40021	-10.89027439
HOMO-28	110	-0.40425	-11.00020845
HOMO-29	109	-0.40859	-11.11830593
HOMO-30	108	-0.41026	-11.16374896
HOMO-31	107	-0.41103	-11.18470174
HOMO-32	106	-0.41829	-11.38225651

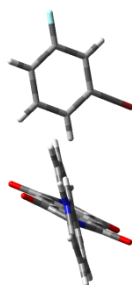
Table 5.6. Cartesian coordinate of the geometry of the unit of PMDI and 3BrF based on the X-ray structure.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	35	0	1.323000	2.046000	0.908000
2	6	0	6.476000	1.282000	2.380000
3	6	0	6.071000	0.733000	1.055000
4	8	0	6.850000	2.385000	2.670000
5	6	0	0.903000	0.405000	1.712000
6	7	0	6.306000	0.217000	3.286000
7	6	0	5.635000	-0.572000	1.227000
8	6	0	6.079000	1.364000	-0.183000
9	6	0	-0.412000	0.068000	2.010000
10	6	0	1.934000	-0.478000	2.016000
11	6	0	5.741000	-0.923000	2.676000
12	6	0	6.652000	0.250000	4.669000
13	6	0	5.165000	-1.364000	0.183000
14	6	0	5.609000	0.572000	-1.227000
15	6	0	-0.697000	-1.152000	2.613000
16	1	0	-1.116000	0.671000	1.802000
17	6	0	1.648000	-1.698000	2.620000
18	1	0	2.832000	-0.247000	1.813000
19	8	0	5.410000	-1.924000	3.246000
20	6	0	5.710000	-0.148000	5.587000
21	6	0	7.924000	0.609000	5.094000
22	6	0	5.173000	-0.733000	-1.055000
23	6	0	5.503000	0.923000	-2.676000
24	9	0	-1.947000	-1.470000	2.891000
25	6	0	0.332000	-2.034000	2.918000
26	1	0	2.352000	-2.301000	2.828000
27	1	0	4.833000	-0.361000	5.288000
28	7	0	5.999000	-0.243000	6.903000
29	6	0	8.208000	0.513000	6.445000

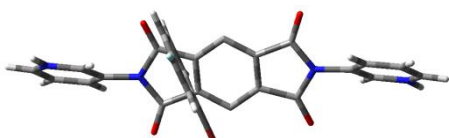
30	1	0	8.578000	0.911000	4.475000
31	6	0	4.768000	-1.282000	-2.380000
32	7	0	4.938000	-0.217000	-3.286000
33	8	0	5.834000	1.924000	-3.246000
34	1	0	0.138000	-2.867000	3.331000
35	6	0	7.233000	0.061000	7.322000
36	1	0	9.067000	0.756000	6.771000
37	8	0	4.394000	-2.385000	-2.670000
38	6	0	4.592000	-0.250000	-4.669000
39	1	0	7.447000	-0.036000	8.242000
40	6	0	3.320000	-0.609000	-5.094000
41	6	0	5.534000	0.148000	-5.587000
42	1	0	2.666000	-0.911000	-4.475000
43	6	0	3.036000	-0.513000	-6.445000
44	7	0	5.245000	0.243000	-6.903000
45	1	0	6.411000	0.361000	-5.288000
46	1	0	2.177000	-0.756000	-6.771000
47	6	0	4.011000	-0.060000	-7.322000
48	1	0	3.797000	0.036000	-8.242000
49	1	0	5.251304	-0.580136	7.475092
50	1	0	5.992696	0.580136	-7.475092



Longside view



Shortside view

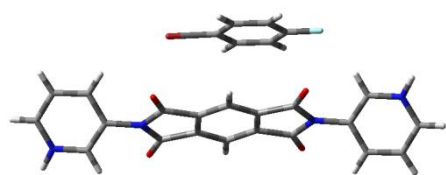


Top view

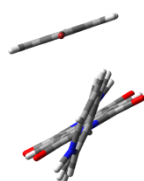
Table 5.7. Cartesian coordinate of the geometry of the unit of PMDI and 3BrF based on the X-ray structure.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	35	0	-2.273780	2.328540	-0.611843
2	6	0	-1.099649	-0.767371	0.915057
3	6	0	-2.492160	-0.571723	1.398680
4	6	0	0.086323	-0.367999	1.509617
5	1	0	0.117360	0.085120	2.344769
6	6	0	-5.415041	0.082458	0.786430
7	1	0	-4.942583	0.828985	1.139345
8	6	0	-6.797478	0.113120	0.651662
9	1	0	-7.288359	0.872117	0.942113
10	6	0	-0.375567	2.415720	-0.558776
11	6	0	0.241125	2.821975	0.614344
12	1	0	-0.276861	3.073210	1.369786
13	1	0	2.066433	3.121898	1.462266
14	8	0	-2.875035	-0.060907	2.417860
15	6	0	-1.143061	-1.431257	-0.313286
16	7	0	-3.326615	-1.152348	0.412823
17	6	0	1.220646	-0.682124	0.785719
18	6	0	-4.741734	-1.066479	0.391801
19	6	0	-7.453247	-0.969292	0.095892
20	6	0	0.347879	2.068253	-1.681313
21	6	0	1.618934	2.854881	0.667732
22	6	0	-2.572355	-1.716745	-0.643672
23	6	0	-0.009387	-1.746565	-1.037605
24	6	0	2.650002	-0.397602	1.116354
25	6	0	1.176585	-1.347193	-0.443045
26	6	0	-5.453752	-2.135703	-0.107153
27	7	0	-6.792211	-2.071483	-0.282980
28	1	0	-8.395171	-0.930736	-0.023095
29	1	0	-0.100330	1.801019	-2.476517

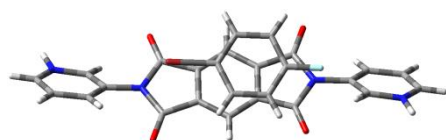
30	6	0	1.719257	2.109959	-1.640383
31	6	0	2.326764	2.497348	-0.449922
32	8	0	-3.022302	-2.303354	-1.585731
33	1	0	-0.040423	-2.199685	-1.872757
34	7	0	3.403552	-0.962217	0.059189
35	8	0	3.099948	0.189007	2.058414
36	6	0	2.569096	-1.542841	-0.926668
37	1	0	-4.993174	-2.935758	-0.332781
38	1	0	2.237954	1.880546	-2.403653
39	9	0	3.663437	2.555145	-0.398332
40	6	0	4.819380	-1.047868	0.080881
41	8	0	2.951972	-2.053658	-1.945848
42	6	0	5.531398	0.021355	0.579836
43	6	0	5.491978	-2.197022	-0.314418
44	1	0	5.070050	0.822160	0.804545
45	7	0	6.869147	-0.043082	0.754992
46	1	0	5.020168	-2.942366	-0.666912
47	6	0	6.874414	-2.227685	-0.179650
48	6	0	7.530893	-1.145056	0.376790
49	1	0	7.366006	-2.986465	-0.469431
50	1	0	8.472046	-1.182862	0.494858
51	1	0	7.254226	0.689410	1.316392
52	1	0	-7.177211	-2.803857	-0.844587



Longside view



Shortside view



Top view

References

- (1) Shao, Y.; Yang, Y. Efficient Organic Heterojunction Photovoltaic Cells Based on Triplet Materials. *Adv. Mater.* **2005**, *17* (23), 2841–2844.
- (2) Gong, Y.; Chen, G.; Peng, Q.; Yuan, W. Z.; Xie, Y.; Li, S.; Zhang, Y.; Tang, B. Z. Achieving Persistent Room Temperature Phosphorescence and Remarkable Mechanochromism from Pure Organic Luminogens. *Adv. Mater.* **2015**, *27* (40), 6195–6201.
- (3) Li, C.; Tang, X.; Zhang, L.; Li, C.; Liu, Z.; Bo, Z.; Dong, Y. Q.; Tian, Y. H.; Dong, Y.; Tang, B. Z. Reversible Luminescence Switching of an Organic Solid: Controllable On-Off Persistent Room Temperature Phosphorescence and Stimulated Multiple Fluorescence Conversion. *Adv. Opt. Mater.* **2015**, *3* (9), 1184–1190.
- (4) Mao, Z.; Yang, Z.; Mu, Y.; Zhang, Y.; Wang, Y. F.; Chi, Z.; Lo, C. C.; Liu, S.; Lien, A.; Xu, J. Linearly Tunable Emission Colors Obtained from a Fluorescent-Phosphorescent Dual-Emission Compound by Mechanical Stimuli. *Angew. Chem. Int. Ed.* **2015**, *54* (21), 6270–6273.
- (5) Xue, P.; Sun, J.; Chen, P.; Wang, P.; Yao, B.; Gong, P.; Zhang, Z.; Lu, R. Luminescence Switching of a Persistent Room-Temperature Phosphorescent Pure Organic Molecule in Response to External Stimuli. *Chem. Commun.* **2015**, *51* (52), 10381–10384.
- (6) Chen, H.; Yao, X.; Ma, X.; Tian, H. Amorphous, Efficient, Room-Temperature Phosphorescent Metal-Free Polymers and Their Applications as Encryption Ink. *Adv. Opt. Mater.* **2016**, *4* (9), 1397–1401.

- (7) Kabe, R.; Notsuka, N.; Yoshida, K.; Adachi, C. Afterglow Organic Light-Emitting Diode. *Adv. Mater.* **2016**, 28 (4), 655–660.
- (8) Kanosue, K.; Ando, S. Polyimides with Heavy Halogens Exhibiting Room-Temperature Phosphorescence with Very Large Stokes Shifts. *ACS Macro Lett.* **2016**, 5, 1301–1305.
- (9) Wang, C. R.; Gong, Y. Y.; Yuan, W. Z.; Zhang, Y. M. Crystallization-Induced Phosphorescence of Pure Organic Luminogens. *Chinese Chem. Lett.* **2016**, 27 (8), 1184–1192.
- (10) Baroncini, M.; Bergamini, G.; Ceroni, P. Rigidification or Interaction-Induced Phosphorescence of Organic Molecules. *Chem. Commun.* **2017**, 53, 2081–2093.
- (11) Yan, D.; Evans, D. G. Molecular Crystalline Materials with Tunable Luminescent Properties: From Polymorphs to Multi-Component Solids. *Mater. Horizons* **2014**, 1 (1), 46–57.
- (12) Yang, X.; Yan, D. Strongly Enhanced Long-Lived Persistent Room Temperature Phosphorescence Based on the Formation of Metal–Organic Hybrids. *Adv. Opt. Mater.* **2016**, 4 (6), 897–905.
- (13) You, Y.; Cho, S.; Nam, W. Cyclometalated Iridium(III) Complexes for Phosphorescence Sensing of Biological Metal Ions. *Inorg. Chem.* **2014**, 53 (4), 1804–1815.
- (14) Zhao, J.; Wu, W.; Sun, J.; Guo, S. Triplet Photosensitizers: From Molecular Design to Applications. *Chem. Soc. Rev.* **2013**, 42 (12), 5323–5351.
- (15) Kwon, M. S.; Yu, Y.; Coburn, C.; Phillips, A. W.; Chung, K.; Shanker, A.; Jung, J.; Kim, G.; Pipe, K.; Forrest, S. R.; et al. Suppressing Molecular Motions for Enhanced Room-Temperature Phosphorescence of Metal-Free Organic Materials.

Nat. Commun. **2015**, *6*, 8947.

- (16) Shimizu, M.; Shigitani, R.; Nakatani, M.; Kuwabara, K.; Miyake, Y.; Tajima, K.; Sakai, H.; Hasobe, T. Siloxy Group-Induced Highly Efficient Room Temperature Phosphorescence with Long Lifetime. *J. Phys. Chem. C* **2016**, *120* (21), 11631–11639.
- (17) Yuan, W. Z.; Shen, X. Y.; Zhao, H.; Lam, J. W. Y.; Tang, L.; Lu, P.; Wang, C.; Liu, Y.; Wang, Z.; Zheng, Q.; et al. Crystallization-Induced Phosphorescence of Pure Organic Luminogens at Room Temperature. *J. Phys. Chem. C* **2010**, *114*, 6090–6099.
- (18) Bolton, O.; Lee, K.; Kim, H.-J.; Lin, K. Y.; Kim, J. Activating Efficient Phosphorescence from Purely Organic Materials by Crystal Design. *Nat. Chem.* **2011**, *3* (3), 205–210.
- (19) Hirata, S.; Totani, K.; Zhang, J.; Yamashita, T.; Hironori, K.; Marder, S. R.; Watanabe, T.; Adachi, C. Efficient Persistent Room Temperature Phosphorescence in Organic Amorphous Materials under Ambient Conditions. *Adv. Funct. Mater.* **2013**, *23* (27), 3386–3397.
- (20) Hirata, S.; Totani, K.; Kaji, H.; Vacha, M.; Watanabe, T.; Adachi, C. Reversible Thermal Recording Media Using Time-Dependent Persistent Room Temperature Phosphorescence. *Adv. Opt. Mater.* **2013**, *1* (6), 438–442.
- (21) An, Z.; Zheng, C.; Tao, Y.; Chen, R.; Shi, H.; Chen, T.; Wang, Z.; Li, H.; Deng, R.; Liu, X.; et al. Stabilizing Triplet Excited States for Ultralong Organic Phosphorescence. *Nat. Mater.* **2015**, *14* (7), 685–690.
- (22) Ventura, B.; Bertocco, A.; Braga, D.; Catalano, L.; D’Agostino, S.; Grepioni, F.; Taddei, P. Luminescence Properties of 1,8-Naphthalimide Derivatives in

- Solution, in Their Crystals, and in Co-Crystals: Toward Room-Temperature Phosphorescence from Organic Materials. *J. Phys. Chem. C* **2014**, *118* (32), 18646–18658.
- (23) Maity, S.; Mazumdar, P.; Shyamal, M.; Sahoo, G. P.; Misra, A. Crystal Induced Phosphorescence from Benz(a)Anthracene Microcrystals at Room Temperature. *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2016**, *157*, 61–68.
- (24) Shimizu, M.; Kimura, A.; Sakaguchi, H. Room-Temperature Phosphorescence of Crystalline 1,4-Bis(Aroyl)-2,5-Dibromobenzenes. *European J. Org. Chem.* **2016**, *2016* (3), 467–473.
- (25) Li, Q.; Li, Z. The Strong Light-Emission Materials in the Aggregated State: What Happens from a Single Molecule to the Collective Group. *Adv. Sci.* **2017**, 1600484.
- (26) Mei, J.; Hong, Y.; Lam, J. W. Y.; Qin, A.; Tang, Y.; Tang, B. Z. Aggregation-Induced Emission: The Whole Is More Brilliant than the Parts. *Adv. Mater.* **2014**, *26* (31), 5429–5479.
- (27) Baldo, M. A.; O'brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. Highly Efficient Phosphorescent Emission from Organic Electroluminescent Devices. *Nature* **1998**, *395*, 151–154.
- (28) Baldo, M. A.; Thompson, M. E.; Forrest, S. R. High-Efficiency Fluorescent Organic Light-Emitting Devices Using a Phosphorescent Sensitizer. *Nature* **2000**, *403* (6771), 750–753.
- (29) Furukawa, T.; Nakanotani, H.; Inoue, M.; Adachi, C. Dual Enhancement of Electroluminescence Efficiency and Operational Stability by Rapid Upconversion of Triplet Excitons in OLEDs. *Sci. Rep.* **2015**, *5*, 8429.

- (30) Zhang, Q.; Li, B.; Huang, S.; Nomura, H.; Tanaka, H.; Adachi, C. Efficient Blue Organic Light-Emitting Diodes Employing Thermally Activated Delayed Fluorescence. *Nat. Photonics* **2014**, *8*, 326–332.
- (31) Zhou, D.; Siboni, H. Z.; Wang, Q.; Liao, L.; Aziz, H. Host to Guest Energy Transfer Mechanism in Phosphorescent and Fluorescent Organic Light-Emitting Devices Utilizing Exciplex-Forming Hosts. *J. Phys. Chem. C* **2014**, *118*, 24006–24012.
- (32) Hontz, E.; Chang, W.; Congreve, D. N.; Bulović, V.; Baldo, M. A.; Van Voorhis, T. The Role of Electron-Hole Separation in Thermally Activated Delayed Fluorescence in Donor-Acceptor Blends. *J. Phys. Chem. C* **2015**, *119* (45), 25591–25597.
- (33) Zhu, W.; Zheng, R.; Zhen, Y.; Yu, Z.; Dong, H.; Fu, H.; Shi, Q.; Hu, W. Rational Design of Charge-Transfer Interactions in Halogen-Bonded Co-Crystals toward Versatile Solid-State Optoelectronics. *J. Am. Chem. Soc.* **2015**, *137* (34), 11038–11046.
- (34) Nishikitani, Y.; Inokuchi, N.; Nishide, H.; Uchida, S.; Shibamura, T.; Nishimura, S. Effect of π -Conjugated Polyelectrolyte on Performance of White Polymer Light-Emitting Diodes Based on Excitons and Exciplexes Having Long Intermolecular Distances. *J. Phys. Chem. C* **2016**, *120* (26), 13976–13986.
- (35) Subeesh, M. S.; Shanmugasundaram, K.; Sunesh, C. D.; Chitumalla, R. K.; Jang, J.; Choe, Y. Host-Dopant System to Generate Bright Electroluminescence from Small Organic Molecule Functionalized Light-Emitting Electrochemical Cells. *J. Phys. Chem. C* **2016**, *120* (22), 12207–12217.
- (36) Nakanotani, H.; Furukawa, T.; Morimoto, K.; Adachi, C. Long-Range Coupling

- of Electron-Hole Pairs in Spatially Separated Organic Donor-Acceptor Layers. *Sci. Adv.* **2016**, 2 (2), e1501470.
- (37) Ma, H.; Shi, W.; Ren, J.; Li, W.; Peng, Q.; Shuai, Z. Electrostatic Interaction-Induced Room-Temperature Phosphorescence in Pure Organic Molecules from QM/MM Calculations. *J. Phys. Chem. Lett.* **2016**, 7 (15), 2893–2898.
- (38) Yang, Z.; Mao, Z.; Zhang, X.; Ou, D.; Mu, Y.; Zhang, Y.; Zhao, C.; Liu, S.; Chi, Z.; Xu, J.; et al. Intermolecular Electronic Coupling of Organic Units for Efficient Persistent Room-Temperature Phosphorescence. *Angew. Chem. Int. Ed.* **2016**, 55 (6), 2181–2185.
- (39) Zhao, W.; He, Z.; Lam, J. W. Y.; Peng, Q.; Ma, H.; Shuai, Z.; Bai, G.; Hao, J.; Tang, B. Z. Rational Molecular Design for Achieving Persistent and Efficient Pure Organic Room-Temperature Phosphorescence. *Chem* **2016**, 1 (4), 592–602.
- (40) Duan, Y.; Wen, L.-L.; Gao, Y.; Wu, Y.; Zhao, L.; Geng, Y.; Shan, G.-G.; Zhang, M.; Su, Z.-M. Fluorescence, Phosphorescence, or Delayed Fluorescence? – A Theoretical Exploration on the Reason Why a Series of Similar Organic Molecules Exhibit Different Luminescence Types. *J. Phys. Chem. C* **2018**, 122 (40), 23091–23101.
- (41) Mani, T.; Tanabe, M.; Yamauchi, S.; Tkachenko, N. V.; Vinogradov, S. A. Modulation of Visible Room Temperature Phosphorescence by Weak Magnetic Fields. *J. Phys. Chem. Lett.* **2012**, 3 (21), 3115–3119.
- (42) Reineke, S.; Baldo, M. A. Room Temperature Triplet State Spectroscopy of Organic Semiconductors. *Sci. Rep.* **2014**, 4, 3797.
- (43) Katsurada, Y.; Hirata, S.; Totani, K.; Watanabe, T.; Vacha, M. Photoreversible

- On-Off Recording of Persistent Room-Temperature Phosphorescence. *Adv. Opt. Mater.* **2015**, 3 (12), 1726–1737.
- (44) Kuno, S.; Akeno, H.; Ohtani, H.; Yuasa, H. Visible Room-Temperature Phosphorescence of Pure Organic Crystals via a Radical-Ion-Pair Mechanism. *Phys. Chem. Chem. Phys.* **2015**, 17 (24), 15989–15995.
- (45) Chen, X.; Xu, C.; Wang, T.; Zhou, C.; Du, J.; Wang, Z.; Xu, H.; Xie, T.; Bi, G.; Jiang, J.; et al. Versatile Room-Temperature-Phosphorescent Materials Prepared from N-Substituted Naphthalimides: Emission Enhancement and Chemical Conjugation. *Angew. Chem. Int. Ed.* **2016**, 55 (34), 9872–9876.
- (46) Hirata, S.; Vacha, M. Circularly Polarized Persistent Room-Temperature Phosphorescence from Metal-Free Chiral Aromatics in Air. *J. Phys. Chem. Lett.* **2016**, 7 (8), 1539–1545.
- (47) Wu, H.; Zhao, P.; Li, X.; Chen, W.; Ågren, H.; Zhang, Q.; Zhu, L. Tuning for Visible Fluorescence and Near-Infrared Phosphorescence on a Unimolecular Mechanically Sensitive Platform via Adjustable CH– π Interaction. *ACS Appl. Mater. Interfaces* **2017**, 9 (4), 3865–3872.
- (48) Ono, T.; Sugimoto, M.; Hisaeda, Y. Multicomponent Molecular Puzzles for Photofunction Design: Emission Color Variation in Lewis Acid-Base Pair Crystals Coupled with Guest-to-Host Charge Transfer Excitation. *J. Am. Chem. Soc.* **2015**, 137 (30), 9519–9522.
- (49) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, 98 (7), 5648.
- (50) Weitaoyang, R. G. P. C. L. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev.*

- B* **1988**, 37 (2), 785–789.
- (51) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. Results Bbtained with the Correlation Energy Density Functionals of Becke and Lee, Yang and Parr. *Chem. Phys. Lett.* **1989**, 157 (3), 200–206.
- (52) Petersson, G. A.; Al-Laham, M. A. A Complete Basis Set Model Chemistry. II. Open-Shell Systems and the Total Energies of the First-Row Atoms. *J. Chem. Phys.* **1991**, 94 (9), 6081–6090.
- (53) Peterson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. A Complete Basis Set Model Chemistry. I. The Total Energies of Closed-Shell Atoms and Hydrides of the First-Row Elements. *J. Chem. Phys.* **1988**, 89 (4), 2193–2218.
- (54) Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenb, D. J. Gaussian 09, Revision D.01. Gaussian, Inc.: Wallingford CT 2013.
- (55) Bruker, A.; SADABS, S. and. Bruker APEX3 Software Package. Bulker AXS Inc.: Wisconsin, USA 2016.
- (56) C., R. CrysAlisPro. Tokyo 2015.
- (57) Sheldrick, G. M. SHELXT - Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr. Sect. A Found. Crystallogr.* **2015**, 71 (1), 3–8.
- (58) Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, 71, 3–8.
- (59) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H.

- OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, *42* (2), 339–341.
- (60) Brandon, R. W.; Gerkin, R. E.; Hutchison, C. A. Electron Magnetic Resonance of Triplet States and the Detection of Energy Transfer in Crystals. *J. Chem. Phys.* **1962**, *37* (2), 447–448.
- (61) Dance, Z. E. X.; Mi, Q.; McCamant, D. W.; Ahrens, M. J.; Ratner, M. A.; Wasielewski, M. R. Time-Resolved EPR Studies of Photogenerated Radical Ion Pairs Separated by p-Phenyleneoligomers and of Triplet States Resulting from Charge Recombination. *J. Phys. Chem. B* **2006**, *110* (50), 25163–25173.
- (62) Dance, Z. E. X.; Mickley, S. M.; Wilson, T. M.; Ricks, A. B.; Scott, A. M.; Ratner, M. A.; Wasielewski, M. R. Intersystem Crossing Mediated by Photoinduced Intramolecular Charge Transfer: Julolidine-Anthracene Molecules with Perpendicular π Systems. *J. Phys. Chem. A* **2008**, *112* (18), 4194–4201.
- (63) Ogiwara, T.; Wakikawa, Y.; Ikoma, T. Mechanism of Intersystem Crossing of Thermally Activated Delayed Fluorescence Molecules. *J. Phys. Chem. A* **2015**, *119* (14), 3415–3418.
- (64) V  th, S.; Tvingstedt, K.; Auth, M.; Sperlich, A.; Dabulien  , A.; Grazulevicius, J. V.; Stakhira, P.; Cherpak, V.; Dyakonov, V. Direct Observation of Spin States Involved in Organic Electroluminescence Based on Thermally Activated Delayed Fluorescence. *Adv. Opt. Mater.* **2017**, *5*, 1600926.
- (65) Zhebin, F.; Shuhei, Y.; Hisao, M. Time-Resolved EPR Study on the Photoexcited Triplet State of the Electron-Donor-Acceptor Complex Formed in the System of Fac-Tris[2-(4-Octyl-Phenyl) Pyridine] Iridium(III) and Tetracene. *J. Phys. Chem. A* **2014**, *118* (1), 89–93.

- (66) Hirota, N.; Yamauchi, S. Short-Lived Excited Triplet States Studied by Time-Resolved EPR Spectroscopy. *J. Photochem. Photobiol. C Photochem. Rev.* **2003**, *4* (2), 109–124.
- (67) Sasaki, S.; Kobori, Y.; Akiyama, K.; Tero-Kubota, S. Intrinsic Enhancement Factors of the Spin–Orbit Coupling Mechanism Polarization in the Duroquinone– *N*, *N* -Dimethylaniline Derivative Systems. *J. Phys. Chem. A* **1998**, *102* (42), 8078–8083.
- (68) Tanabe, M.; Matsuoka, H.; Ohba, Y.; Yamauchi, S.; Sugisaki, K.; Toyota, K.; Sato, K.; Takui, T.; Goldberg, I.; Saltsman, I.; et al. Time-Resolved Electron Paramagnetic Resonance and Phosphorescence Studies of the Lowest Excited Triplet States of Rh(III) Corrole Complexes. *J. Phys. Chem. A* **2012**, *116* (39), 9662–9673.
- (69) Hasebe, N.; Deguchi, Y.; Murayama, S.; Yoshihara, T.; Horiuchi, H.; Okutsu, T.; Tobita, S. Phosphorescence Quenching of Neutral and Cationic Iridium(III) Complexes by Molecular Oxygen and Aromatic Electron Acceptors. *J. Photochem. Photobiol. A Chem.* **2016**, *324*, 134–144.
- (70) Young, R. H.; Feinberg, A. M.; Dinnocenzo, J. P.; Farid, S. Transition from Charge-Transfer to Largely Locally Excited Exciplexes, from Structureless to Vibrationally Structured Emissions. *Photochem. Photobiol.* **2015**, *91* (3), 624–636.
- (71) Kamimura, T.; Ohkubo, K.; Kawashima, Y.; Ozako, S.; Sakaguchi, K. I.; Fukuzumi, S.; Tani, F. Long-Lived Photoinduced Charge Separation in Inclusion Complexes Composed of a Phenothiazine-Bridged Cyclic Porphyrin Dimer and Fullerenes. *J. Phys. Chem. C* **2015**, *119* (45), 25634–25650.

- (72) Marcus, R. A.; Sutin, N. Electron Transfers in Chemistry and Biology. *BBA Rev. Bioenerg.* **1985**, *811* (3), 265–322.
- (73) Lewis, F. D.; Letsinger, R. L.; Wasielewski, M. R. Dynamics of Photoinduced Charge Transfer and Hole Transport in Synthetic DNA Hairpins. *Acc. Chem. Res.* **2001**, *34* (2), 159–170.
- (74) Lewis, F. D.; Kalgutkar, R. S.; Wu, Y.; Liu, X.; Liu, J.; Hayes, R. T.; Miller, S. E.; Wasielewski, M. R. Driving Force Dependence of Electron Transfer Dynamics in Synthetic DNA Hairpins. *J. Am. Chem. Soc.* **2000**, *122* (49), 12346–12351.
- (75) Downs, A. J.; Adams, C. J. *The Chemistry of Chlorine, Bromine, Iodine, and Astatine*; Elsevier Ltd.: Amsterdam, 1973.

Chapter 6

Concluding Remarks

Organic compounds and self-assemblies such as π -conjugated and supramolecular materials are attracted attention for the photofunctional solid-state materials that can absorb and emit wide range of photon energy similar to solar energy. In the energy migration, energy transfer, and electron transfer processes, excited triplet state plays a critical role in the view of controlling their quantum yields and lifetimes. In the present thesis, the author focused on photoinduced functionality of the excited triplet states in the π -conjugated systems such as expanded porphyrins and the organic crystals. These systems show interesting behavior, for example, absorption and emission property, and energetically stability/instability, and so on, in the excited triplet state. Then, these photoinduced functionalities were explored by using a TREPR spectroscopy.

In Chapter 4, the electronic character of the T_1 state of a Möbius aromatic [28]hexaphyrin was clarified by employing a TREPR method with applied magnetophotoselection measurements at 77 K. In the twisted Möbius [28]hexaphyrin, the T_1 state possesses intramolecular CT character together with local excitation character residing at one side in the Möbius strip ring. The CT character between orthogonal unpaired orbitals triggers triplet deactivation quickly by SOC. This deactivation can be an important barometer to demonstrate the “antiaromaticity” because of a connection between the orthogonal CT character and instability by a weakened spin-spin exchange coupling in the T_1 state.

In Chapter 5, the electronic structures and the ISC mechanism of the RTP organic inclusion crystals were revealed. The T_1 state of the crystals was observed by using

TREPR method at room temperature. In the PMDI-3BrF system in which the guest is perpendicularly oriented to the host represented little CT character in the RTP triplet state. In contrast, the PMDI-4BrF system where the guest is parallel to the host exhibited the CT character in the RTP triplet state. In the S_1 - T_1 ISC, n-orbitals on the carbonyl oxygen in the host PMDI are attended in the PMDI-3BrF system having little CT character. On the other hand, in the PMDI-4BrF system exhibiting the triplet CT character, n-orbital and σ -orbital on the bromine atom in the guest participate in the S_1 - T_1 ISC, which generates the triplet CT state via an allowed transition between $n\pi^*$ and $\pi\pi^*$ states and between $\sigma\pi^*$ and $\pi\pi^*$ states by vibronic coupling.

In the PMDI-4BrF system, the CT and LE characters were determined to be 13% and 87%, respectively, in the excited triplet state. This indicates that the S_1 - T_1 ISC can be explained by the hybridizations between the σ -orbitals in 4BrF and the π -orbitals in PMDI, namely $^1((\sigma_g\pi_h)\pi^*_h)$ state, which rationalizes $P_x \gg P_y$. Thus, these results demonstrate that the σ - π conjugation between the 4BrF and the PMDI accelerate the ISC resulting in the increasing of the emission quantum-yield. In the NDI-3IF and the NDI-3IMe systems whose guests have iodine atom, the S_1 - T_1 ISC mechanism can be demonstrated as well as the PMDI-4BrF system.

In summary, the formation of the triplet CT state was confirmed by a TREPR method. The degree of intramolecular or intermolecular CT character in the T_1 state was estimated based on the configuration interaction. ZFS axes and the sign of D value were determined based on the S_1 - T_1 ISC mechanism through SOC because of anisotropic ISC rate. In the S_1 - T_1 ISC process, allowed transitions between $n\pi^*$ and $\pi\pi^*$ states and between $\sigma\pi^*$ and $\pi\pi^*$ states play important role by vibronic coupling with a change of the angular momenta around the specific axes due to the SOC. This induce anisotropic

ISC rate to the each triplet sublevel reflecting the initial populations in these triplet sublevels. Especially, in the systems including heavier bromine and iodine atoms represented apparent g -anisotropies depend on the degree of the intermolecular CT character. In addition, triplet sublevels were stabilized because of the SOC due to the heavier bromine and iodine atoms, which results in the reverse of the triplet sublevels with reverse of the sign of the D value in the triplet CT state. The present study would lead to further development of the photofunctional materials for efficient conversion and storage of light energy and electrical energy such as a practical organic light emitting devices by controlling the triplet CT interaction in the organic donor-acceptor systems.

Acknowledgements

I would like to express my deepest gratitude to Prof. Yasuhiro Kobori for his helpful advices and kind encouragement. I could not have completed this study without his support. I also wish to express my gratitude to Prof. Takashi Tachikawa for his helpful discussions and kind support. I would appreciate Prof. Hisao Murai (Shizuoka University) for his helpful suggestions and kind encouragement. For the study on hexaphyrins, especially, I am grateful to Prof. Atsuhiko Osuka, Prof. Shohei Saito, and Dr. Tomoki Yoneda (Kyoto University) for sample preparation and useful discussions. I am also grateful Prof. Takeji Takui, Prof. Kazunobu Sato, and Dr. Kenji Sugisaki (Osaka City University) for useful discussions and theoretical calculations. I thank Prof. Seigo Yamauchi and Dr. Mana Tanabe (Tohoku University) for EPR experiments as a pioneer. I also thank Prof. Seiji Akimoto (Kobe University) for UV-vis absorption measurements at low temperature and kind support. For the study on organic inclusion crystals, especially, I appreciate Dr. Toshikazu Ono, Prof. Hisaeda Yoshio, and Mr. Yuki Fukuda (Kyusyu University) for sample preparation and useful discussions. I am also appreciate collaborators; Prof. Masaki Shimizu, Mr. Ryosuke Shigitani, Mr. Takumi Kinoshita, Prof. Kunihiro Tajima, and Dr. Yusuke Miyake (Kyoto Institute of technology); Prof. Masaaki Mitsui and Dr. Yoshiki Niihori (Rikkyo University); Prof. Kazutaka Hirakawa (Shizuoka University); Prof. Ryosuke Matsubara (Kobe University) for sample preparations and fruitful discussions. I am grateful to Prof. Hitoshi Ohta (Kobe University) and members of the Society of Electron Spin Science and Technology (SEST) for kind encouragements. I greatly thank to Prof. Keisuke Tominaga, Ms. Natsu Mogi who is the clerk of department of chemistry and all members of the laboratory for various supports. Finally, I appreciate my family and friends for many helpful supports.

