Reversible transformation between ionic liquids and coordination polymers by application of light and heat

Funasako, Yusuke
Mori, Shotaro
Mochida, Tomoyuki

(Citation)
Chemical Communications,52(37):6277-6279

(Issue Date)
2016-05-07

(Resource Type)
journal article

(Version)
Accepted Manuscript

(URL)
https://hdl.handle.net/20.500.14094/90003484

Chemical Communications

COMMUNICATION

Reversible transformation between ionic liquids and coordination polymers by application of light and heat

,

Yusuke Funasako,[ab] Shotaro Mori,[a] and Tomoyuki Mochida*[a]

DOI: 10.1039/x0xx00000x

www.rsc.org/

Reversible transformation between an ionic liquid and a coordination polymer by application of light and heat has been achieved. Ultraviolet light irradiation transforms the transparent liquid to a yellow solid; a reverse reaction occurs due to the application of heat. The transformation accompanies drastic switching of intra- and intermolecular coordination bonds of a ruthenium complex. This is a novel material conversion methodology that connects the fields of ionic liquids and coordination polymers.

Ionic liquids, which are salts with melting points below 100 °C, have attracted much attention in this decade because of their excellent performance as green solvents.[1] While most ionic liquids comprise organic cations and various anions, metal-containing ionic liquids have also been recently developed.[2] In particular, we have previously demonstrated that cationic organometallic sandwich complexes with fluorine-containing anions such as $(FSO_2)_2N^-$ (abbreviated as FSA) produce functional ionic liquids.[3] On the other hand, coordination polymers are crystalline or non-crystalline solids formed by self-assembly of metal ions and polydentate ligands. Coodination polymers show various functions such as magnetism[4b] and gas storage properties.[4c] Both coordination polymers and ionic liquids have been extensively investigated. However, interdisciplinary studies involving both of these major fields have been rare. Recent studies showing that coordination polymers melt at high temperatures to give liquid salts provides an intriguing example of such research.[5]

In this study, we report a ruthenium-containing organometallic ionic liquid that exhibits a reversible conversion between an ionic liquid and a coordination polymer driven by application of light and heat. Ultraviolet (UV) light irradiation of the $[Ru(C_5H_5)(benzene)]^+$ sandwich complex in acetonitrile is known to eliminate benzene ligand to produce a half-sandwich complex $[Ru(C_5H_5)(MeCN)_3]^+$, with the reverse reaction taking place due to thermal heating (Fig. 1).[6] Based on this mechanism, in the present study, we designed a ruthenium-based ionic liquid ([**1**]X, X = FSA, bottom left in Fig. 2) bearing a trisubstituted arene ligand $1,3,5\text{-}C_6H_3(OC_6H_{12}CN)_3$ (**L**). Incorporation of two different coordination sites of the ligand, the arene and nitrile moieties, is the key feature of this molecular design.

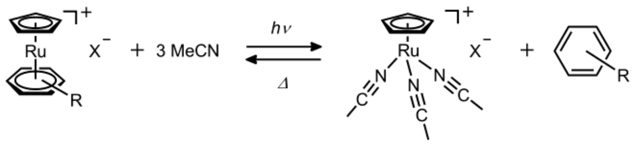


Fig. 1 Photochemical reaction of cyclopentadienyl arene-ruthenium complexes in acetonitrile solution.[6b]

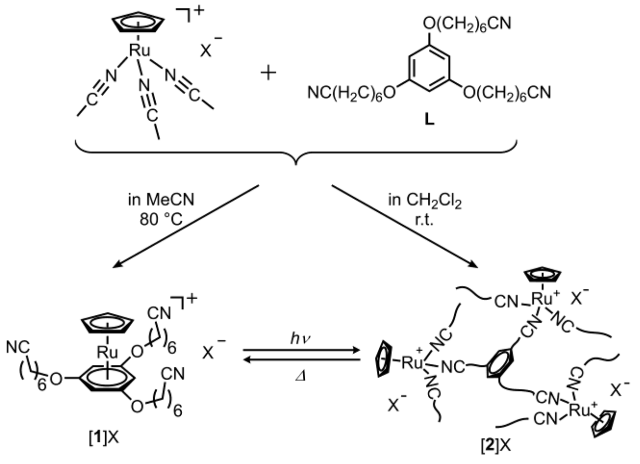


Fig. 2 Reactions of $[Ru(C_5H_5)(MeCN)_3]X$ (X = FSA, PF_6) and **L**. Conversion between [**1**]X and [**2**]X occurs for X = FSA.

Depending on the reaction conditions, the reactions of $[Ru(C_5H_5)(MeCN)_3]X$ (X = FSA or PF_6) and the ligand **L** selectively afforded either the sandwich complex [**1**]X or coordination polymer [**2**]X with nitrile coordination (Fig. 2).

---

[a] Department of Chemistry, Graduate School of Science, Kobe University, Kobe, Hyogo 657-8501, Japan

[b] Department of Applied Chemistry, Faculty of Engineering, Tokyo University of Science, Yamaguchi, Sanyo-Onoda, Yamaguchi, 756-0884, Japan

†Electronic Supplementary Information (ESI) available: Synthesis procedures, UV–Vis spectra, IR spectra, and NMR spectra. See DOI: 10.1039/x0xx00000x

The sandwich complex [**1**]FSA, a colorless viscous ionic liquid, was synthesized with a 60% yield by heating [Ru(C_5H_5)(MeCN)$_3$]PF$_6$ and **L** in acetonitrile at 90 °C, followed by anion exchange using KFSA. The ionic liquid can also be obtained by reacting [Ru(C_5H_5)(MeCN)$_3$]FSA and **L**. This ionic liquid exhibited a glass transition at −53 °C, showing no crystallization at low temperatures. In contrast, the reaction of [Ru(C_5H_5)(MeCN)$_3$]FSA and **L** in dichloromethane for 30 min at room temperature, followed by evaporation, quantitatively afforded yellow films of an amorphous coordination polymer [**2**]FSA ([Ru(C_5H_5)(**L**)]$_n$·nFSA). While the coordination polymer was insoluble in most organic solvents, it was soluble in acetonitrile to produce [Ru(C_5H_5)(MeCN)$_3$]FSA; this feature is useful for recycling the material. The nitrile-coordinated coordination polymer and sandwich complex are the kinetic and the thermodynamic products, respectively, enabling the selective synthesis of [**1**]FSA and [**2**]FSA.

The UV–Vis spectra of [**1**]FSA exhibited only one absorption maximum at approximately λ_{max} = 311 nm and showed no absorption in the visible region, while [**2**]FSA exhibited two absorption maxima at approximately 312 nm and 370 nm (Fig. S1, ESI†). In the IR spectra, the CN stretching vibrations in [**1**]FSA and [**2**]FSA were observed at approximately 2245 and 2274 cm^{-1}, respectively; the C=C stretching vibrations were observed at approximately 1530 and 1590 cm^{-1}, respectively (Fig. S2, ESI†). The UV–Vis and IR spectra of [**2**]FSA were similar to those of [Ru(C_5H_5)(MeCN)$_3$]PF$_6$ (UV(λ_{max}): 314 and 373 nm, IR(ν_{CN}): 2280 cm^{-1}),[6b] in accordance with the nitrile coordination in the complex.

UV light irradiation of the liquid [**1**]FSA sandwiched between quartz plates generated the yellow coordination polymer [**2**]FSA (Fig. 2, bottom). As seen in the UV–Vis spectra (Fig. 3), the intensities of the absorption bands increased upon irradiation, and the reaction was conducted for 5 h. The change of the coordination structure was also confirmed by the shifts of ν_{CN} and $\nu_{\text{C=C}}$ peak in the IR spectra (Fig. 4a–b). UV–Vis, IR, and NMR spectra revealed that approximately 20% of [**1**]FSA remains unreacted (Figs. S3–4, ESI†); these molecules are most likely incorporated in the network structure of the photogenerated coordination polymer via coordination bonds.[7]

Since the nitrile coordinated complex is a kinetic product, a thermal transformation to the thermodynamical product of the sandwich complex is expected. Indeed, heating the coordination polymer [**2**]FSA for 1 min at 130 °C quantitatively recovered the ionic liquid [**1**]FSA (Figs. 4c and Figs. S4–5, ESI†). The reaction took a longer time (within 30 min) at 90 °C. The thermal conversion to the sandwich complex was also observed by differential scanning calorimetry (DSC) measurements (Fig. 5). Upon heating [**2**]FSA, a glass transition of the coordination polymer was observed at around 0 °C. This is consistent with the physical forms of the coordination polymer: brittle below 0 °C but flexible at room temperature. Upon further heating, a broad endothermic peak was observed at around 80 °C, which corresponds to the conversion reaction to the liquid [**1**]FSA (ΔH = 5.2 kJ mol^{-1}). Upon cooling the liquid, a glass transition was observed at −53 °C. These results clearly demonstrate that the transformation is reversible.

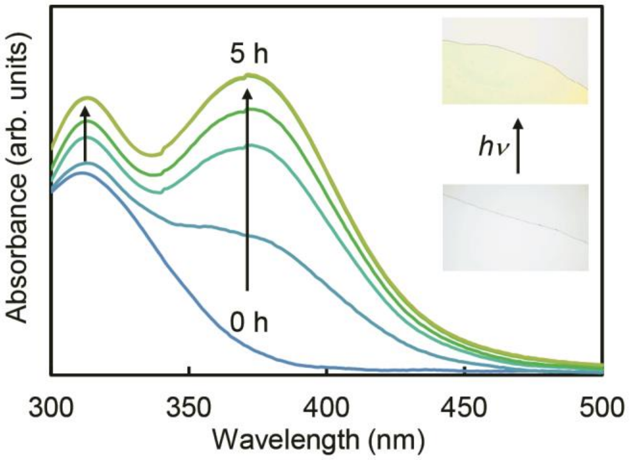


Fig. 3 Changes in UV–Vis absorption spectra of neat [**1**]FSA during photoirradiation taken at 1 h intervals. Note that the spectra obtained at 4 h and 5 h overlapped. The inset shows the images of [**1**]FSA before and after photoirradiation.

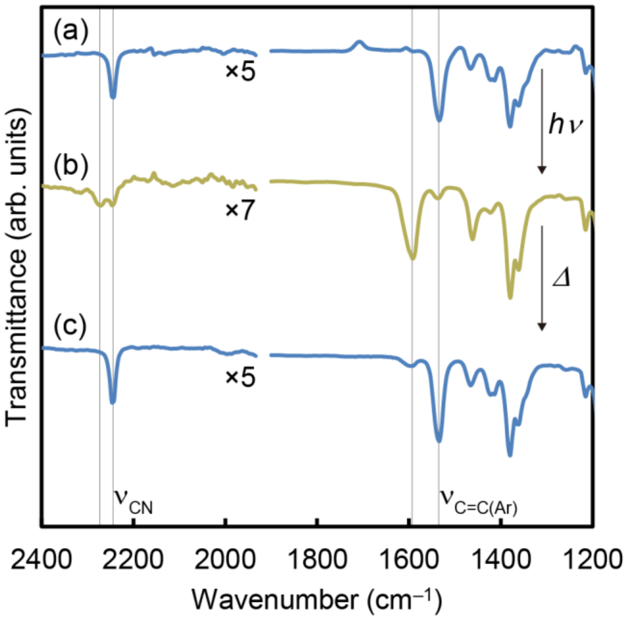


Fig. 4 IR spectra of [**1**]FSA (a) before and (b) after photoirradiation for 10 h, and (c) [**1**]FSA generated from the coordination polymer by heating at 90 °C for 30 min.

Photocured materials are important for industrial applications,[8] wherein for the current materials, the photocuring processes are mostly irreversible due to the formation of intermolecular covalent bonds. However, in the present study, a reversible reaction has been achieved based on the formation of coordination bonds by application of heat and light. This adds the ability to dynamically change the structure and properties of the material by application of light and heat; this capability will lead to a wider use of these materials due to their reversible response and reusability. Although several ionic materials[9] and molecular materials[10] are known to exhibit reversible solid–liquid transformations driven

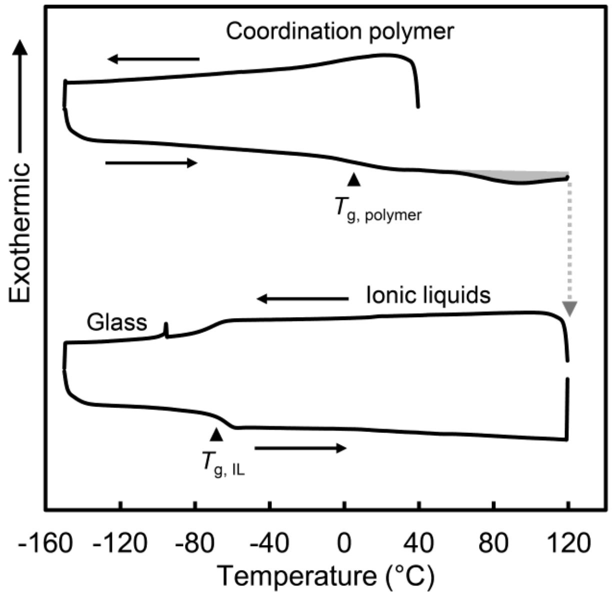


Fig. 5. DSC traces of [**2**]FSA, showing thermal conversion to [**1**]FSA. The broad endothermic peak shown in gray is ascribed to the conversion reaction.

by the application of light and heat, most of these are based on the mechanism of melting point change by photoisomerization. In the present system, the structures were changed largely based on the formation or dissociation of coordination bonds accompanied by drastic changes of properties. A somewhat related intriguing phenomenon of light-triggered crystallization of the host–guest complex solution based on coordination bonds has been reported.[11] Previously, we reported a reversible intramolecular conversion between arene- and chelate-coordination of the ruthenium complexes in solutions.[12] In this study, we have successfully extended the mechanism of coordination bond formation and dissociation to intermolecular transformation based on suitable ligand design for the first time.

In conclusion, we designed a ruthenium-containing ionic liquid that reversibly transforms to a coordination polymer by application of light and heat. This is a novel material conversion methodology that connects the fields of ionic liquids and coordination polymers. Furthermore, due to advantageous features of ionic liquids such as low-volatility and ionic conductivity, the developed ionic liquid will be useful for various current applications; they will serve as a prototype for further development of materials for future uses in applications such as advanced adhesives, unconventional photoresist, electrode catalysts, and for patterning of ruthenium-containing thin films. Further molecular design studies aimed at improving the response characteristics and expanding the reactivity of these materials are currently in progress in our laboratory.

This work was financially supported by JSPS KAKENHI (grant number No. 26620046).

Notes and references

1 A. Stark and K. R. Seddon in *Kirk-Othmer Encyclopedia of Chemical Technology*, Wiley-Interscience, New York, 5th ed., 2007, Vol. 26, pp. 836–919.

2 (*a*) J. Klingele, *Coord. Chem. Rev.* 2015, **292**, 15–29; (*b*) Y. Yoshida and G. Saito, Progress in Paramagnetic Ionic Liquids in *Ionic Liquids: Theory, Properties, New Approaches*, ed. A. Kokorin, InTech, 2011, pp. 723–738; (*c*) N. R. Brooks, S. Schaltin, K. Van Hecke, L. Van Meervelt, K. Binnemans and J. Fransaer, *Chem. – Eur. J.*, 2011, **17**, 5054–5059.

3 (*a*) T. Inagaki, T. Mochida, M. Takahashi, C. Kanadani, T. Saito and D. Kuwahara, *Chem. – Eur. J.* 2012, **18**, 6795–6804; (*b*) A. Komurasaki, Y. Funasako and T. Mochida, *Dalton. Trans.* 2015, **44**, 7595–7605.

4 (*a*) S. R. Batten, N. R. Champness, X.-M. Chen, J. Garcia-Martinez, S. Kitagawa, L. Öhrström, M. O'Keeffe, M. P. Suh and J. Reedijk, *CrystEngComm* 2012, **14**, 3001–3004; (*b*) D. R. Talham and M. W. Meisel, *Chem. Soc. Rev.* 2011, **40**, 3356–3365; (*c*) S. Kitagawa, R. Kitaura and S.-i. Noro, *Angew. Chem. Int. Ed*. 2004, **43**, 2334–2375.

5 (*a*) D. Umeyama, S. Horike, M. Inukai, T. Itakura and S. Kitagawa, *J. Am. Chem. Soc.* 2015, **137**, 864–870; (*b*) E. T. Spielberg, E. Edengeiser, B. Mallick, M. Havenith and A. V. Mudring, *Chem. – Eur. J.* 2014, **20**, 5338–5345.

6 (*a*) B. M. Trost and C. M. Older, *Organometallics* 2002, **21**, 2544–2546; (*b*) T. P. Gill and K. R. Mann, *Organometallics* 1982, **1**, 485–488.

7 We also investigated the reactivity of an ionic liquid with shorter substituents, $[Ru(C_5H_5)\{1,3,5\text{-}C_6H_3(OC_3H_6CN)_3\}]$. This salt was obtained as a solid (T_m = 84 °C), but once melted, it maintained the liquid state at r.t. (T_g = −28 °C). Photoirradiation of the liquid also produced the amorphous coordination polymer, as investigated by UV-vis, IR, NMR and XRD measurements. However, the reaction rate was much smaller than that of [**1**]FSA probably owing to its higher viscosity.

8 A Tiwari and A. Polykarpov, *Photocured Materials (RSC Smart Materials)*, Royal Society of Chemistry: Cambridge, UK, 2014.

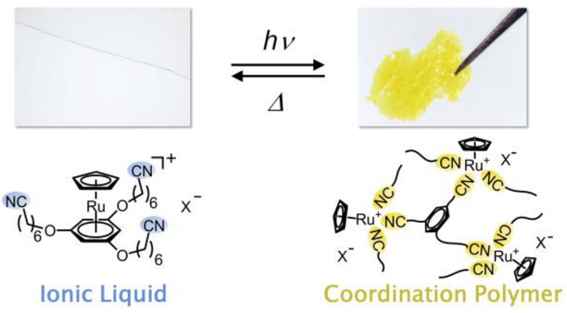
9 (*a*) H. Tamura, Y. Shinohara and T. Arai, *Chem. Lett.* 2011, **40**, 129–131; (*b*) K. Ishiba, M. Morikawa, C. Chikara, T. Yamada, K. Iwase, M. Kawakita and N. Kimizuka, *Angew. Chem. Int. Ed.* 2015, **54**, 1532–1536; (*c*) S. Hisamitsu, N. Yanai, S. Fujikawa and N. Kimizuka, *Chem. Lett.* 2015, **44**, 908–910.

10 (*a*) Y. Norikane, Y. Hirai and M. Yoshida, *Chem. Commun.* 2011, **47**, 1770–1772; (*b*) Y. Okui and M. Han, *Chem. Commun.* 2012, **48**, 11763–11765; (*c*) R. Reuter and H. A. Wegner, *Chem. Commun.* 2013, **49**, 146–148.

11 G. H. Clever, S. Tashiro and M. Shionoya, *J. Am. Chem. Soc*. 2010, **132**, 9973–9975.

12 S. Mori and T. Mochida, *Organometallics* 2013, **32**, 283–288.

Table of contents entry



Reversible transformation between ionic liquids and coordination polymers by application of light and heat has been achieved.

Electronic Supplementary Information (ESI)

Reversible Transformation between Ionic Liquids and Coordination Polymers by Application of Light and Heat

Yusuke Funasako,[a,b] Shotaro Mori,[a] and Tomoyuki Mochida*[a]

[a]*Department of Chemistry, Graduate School of Science, Kobe University, Kobe, Hyogo 657-8501, Japan*

[b]*Department of Applied Chemistry, Faculty of Engineering, Tokyo University of Science, Yamaguchi, Sanyo-Onoda, Yamaguchi, 756-0884, Japan*

Experimental procedures

General. $[Ru(C_5H_5)(\eta^6\text{-benzene})]PF_6$ and $[Ru(C_5H_5)(MeCN)_3]PF_6$ were prepared according to literature methods[S1] and other chemicals were commercially available. All reactions were performed under a nitrogen atmosphere. ^1H NMR spectra were recorded using a JEOL JNM-ECL-400 spectrometer. UV–Vis spectra were recorded using a JASCO V-570 UV/VIS/NIR spectrophotometer. FT-IR spectra were acquired via attenuated total reflectance (ATR) using a Thermo Scientific Nicolet iS5 spectrometer. Powder X-Ray diffraction data were recorded on a Rigaku SmartLab diffractometer using CuKα radiation. DSC measurements were performed using a TA Q100 differential scanning calorimeter from −150 °C to 100 °C at a scan rate of 10 K min^{-1}. Light irradiation was carried out with a deep UV lamp (250 W) using USHIO SP-9 SPOT CURE. During the light irradiation, the temperature of the sample was maintained at 0 °C with the temperature control of the samples performed using a Linkam LTS350 hot stage.

1,3,5-Tri(6-cyanohexyloxy)benzene (L). A mixture of phloroglucinol (416 mg, 3.3 mmol), K_2CO_3 (4.15 g, 30 mmol), tetrabutylammonium chloride (140 mg, 0.5 mmol), and 7-bromoheptanenitrile (2.1 g, 11 mmol) in acetonitrile (30 mL) was heated at 90 °C for 24 h. The mixture was cooled to room temperature and filtered. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, eluents: toluene/dichloromethane, gradient from 1:0 to 1:3) and then dried in vacuo at 60 °C for 7 h. The obtained colorless liquid was solidified over several days at room temperature in a nitrogen atmosphere. White solids. Yield 43%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.51 (m, 12H), 1.70 (m, 6H), 1.78 (m, 6H), 2.36 (t, J = 7.2 Hz, 6H), 4.04 (t, J = 6.2 Hz, 6H), 6.05 (s, 3H).

[Ru(C_5H_5)(η^6-L)]PF_6 ([1]PF_6). L (181 mg, 0.40 mmol) was added to a solution of [Ru(C_5H_5)($MeCN$)$_3$]PF_6 (165 mg, 0.38 mmol) in acetonitrile (1 mL) and the mixture was heated at 90 °C for 24 h. After the solvent was removed under reduced pressure, the crude product was purified by column chromatography (activated alumina, eluent: chloroform), then repeatedly washed with toluene and dried under vacuum at 25 °C. Colorless liquid. Yield 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.48–1.56 (m, 12H), 1.70 (quint, J = 7.3 Hz, 6H), 1.77 (quint, J = 6.8 Hz, 6H), 2.39 (t, J = 7.0 Hz, 6H), 3.96 (t, J = 6.2 Hz, 6H), 5.23 (s, 5H), 5.99 (s, 3H). FT-IR (ATR, cm^{-1}): 556, 667, 831 (PF_6), 1030, 1174, 1533 (Ar, C–C), 2244 (CN). Anal. Calcd for $C_{32}H_{44}F_6N_3O_3PRu$ (764.74): C, 50.26; H, 5.80; N, 5.49. Found: C, 50.44; H, 5.89; N, 5.40.

[Ru(C_5H_5)(η^6-L)]FSA ([1]FSA). An aqueous solution (10 mL) of KFSA (76.7 mg, 0.35 mmol) was added to a solution of [**1**]PF_6 (200 mg, 0.26 mmol) in acetone (10 mL). After stirring, the acetone was removed by evaporation, and the resulting suspension was extracted with dichloromethane (20 mL, 3 times). The organic layer was dried over $MgSO_4$ and evaporated. The crude product was purified by column chromatography (activated alumina, eluents: dichloromethane/acetonitrile, gradient from 1:0 to 0:l) and dried in vacuum at 70 °C for 1 day. Colorless liquid. Yield 60%. ^{1}H NMR (400 MHz, CD_3CN): δ = 1.43–1.51 (m, 12H), 1.64 (quint, J = 7.1 Hz, 6H), 1.72 (quint, J = 6.8 Hz, 6H), 2.40 (t, J = 7.0 Hz, 6H), 3.90 (t, J = 6.6 Hz, 6H), 5.19 (s, 5H), 6.00 (s, 3H). FT-IR (ATR, cm^{-1}): 569, 739 (S–F), 825, 1031, 1175 (SO_2), 1362 (SO_2), 1380 (SO_2), 1533 (Ar, C–C), 2245 (CN). Anal. Calcd for $C_{32}H_{44}F_2N_4O_7RuS_2$ (799.91): C, 48.05; H, 5.54; N, 7.00. Found: C, 48.29; H, 5.70; N, 6.82.

[Ru(C_5H_5)(η^6-benzene)]FSA. An aqueous solution (10 mL) of KFSA (329 mg, 1.5 mmol) was added to a solution of [Ru(C_5H_5)(η^6-benzene)]PF_6 (389 mg, 1.0 mmol) in acetone (10 mL). The acetone was removed by evaporation, and the resulting suspension was extracted with dichloromethane (20 mL, 3 times). The organic layer was dried over $MgSO_4$ and evaporated. The obtained white solids were recrystallized from MeOH at −45 °C and were obtained in quantitative yield. ^{1}H NMR (400 MHz, CD_3CN): δ = 5.33 (s, 5H), 6.08 (s, 6H).

[Ru(C_5H_5)(MeCN)$_3$]FSA. UV irradiation of a solution of [Ru(C_5H_5)(η^6-benzene)]FSA (101 mg, 0.24 mmol) in acetonitrile was performed for 3 days followed by the evaporation of acetonitrile under reduced pressure produced [Ru(C_5H_5)(CH_3CN)$_3$]FSA as a yellow powder. Yield 98%. ^{1}H NMR (400 MHz, CD_3CN): δ = 1.93 (s, 9H), 4.24 (s, 5H). This salt was immediately used for the next step.

[Ru(C_5H_5)(L)]$_n$•nFSA ([2]FSA). [Ru(C_5H_5)(MeCN)$_3$]FSA (109 mg, 0.23 mmol) was added to a dichloromethane (3 mL) solution of **L** (105 mg, 0.23 mmol) and stirred at room temperature for 30 min. The solvent was removed under reduced pressure and dried in vacuum at 25 °C for 24 h. Yellow air-sensitive solids were obtained in quantitative yield. In the ^{1}H NMR spectrum in CD_3CN, the peaks corresponding to [Ru(C_5H_5)(CD_3CN)$_3$]$^+$ and free ligand (**L**) were observed in a ratio of 1:1. FT-IR (ATR, cm^{-1}): 556, 730, 823, 1057, 1177 (SO_2), 1361 (SO_2), 1379 (SO_2), 1590 (Ar, C–C), 2273 (CN).

Coordination transformation. The photochemical and thermal conversions of the complexes were investigated between two quartz plates. Photochemical conversion was carried out by UV light irradiation of ionic liquid [**1**]FSA (1.0 mg) for 1–10 h. Conversion of the photoreaction was determined from ^{1}H NMR spectra of the CD_3CN solution of the resulting yellow solid [**2**]FSA. Thermal conversion was carried out by heating [**2**]FSA (1.0 mg) at 90 °C, 130 °C or 150 °C for 30 min, 1 min, or 10 s, respectively. The sandwich complex [**1**]FSA (ionic liquids) was obtained in quantitative yield.

References

(S1) B. M. Trost and C. M. Older, *Organometallics* 2002, **21**, 2544–2546.

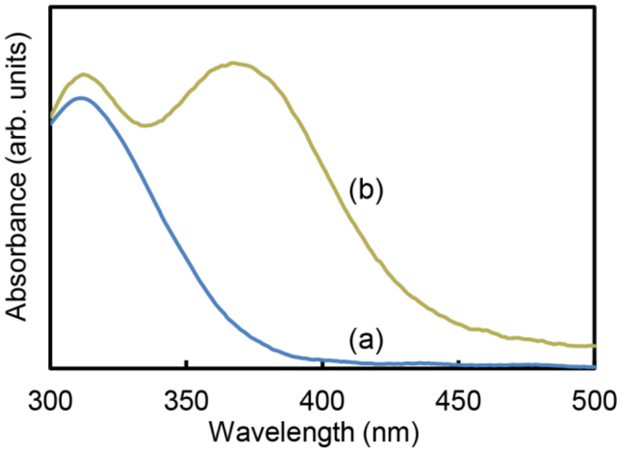


Fig. S1 UV–Vis absorption spectra of (a) [**1**]FSA and (b) [**2**]FSA.

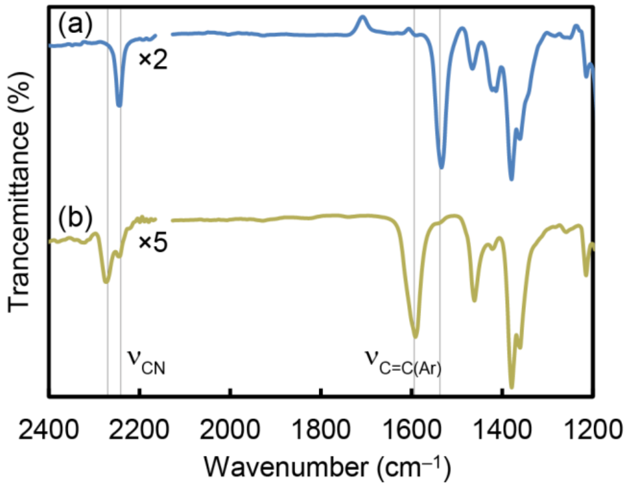


Fig. S2 IR absorption spectra of (a) [**1**]FSA and (b) [**2**]FSA.

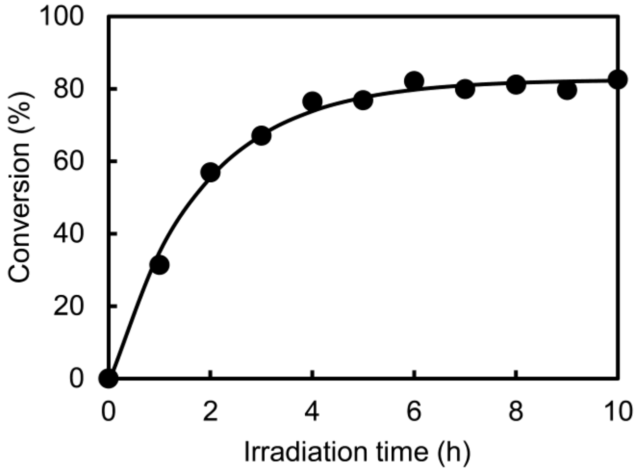


Fig. S3 Time evolution of the molar ratio of the tricyano-coordinated species generated during photoirradiation of [**1**]FSA.

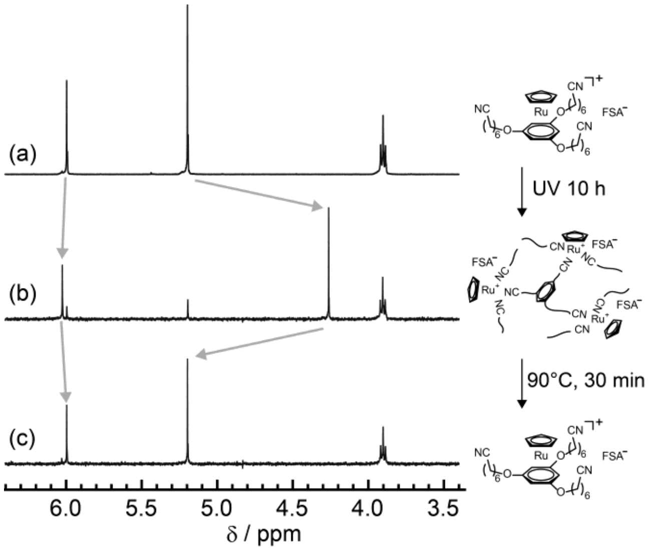


Fig. S4 ^{1}H NMR spectra (400 MHz, CD_3CN, room temperature) of [**1**]FSA (a) before and (b) after photoirradiation for 10 h, and (c) [**1**]FSA generated from the coordination polymer by heating at 90 °C for 30 min. The spectrum (b) comprises of the signals of $[Ru(C_5H_5)(CD_3CN)_3]$FSA (resulted from dissociation of photo-generated [**2**]FSA in CD_3CN) and a small amount of [**1**]FSA (that remained in the coordination polymer).

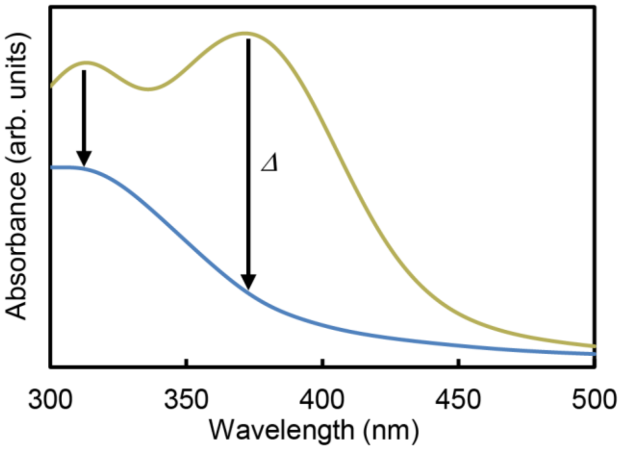


Fig. S5 Changes of UV–Vis absorption spectra of [**2**]FSA before and after heating at 90 °C for 30 min.