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Choi, Sok-Yong
Mochida, Tomoyuki

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Luminescent Rhenium-containing Ionic Liquid Exhibiting Photoinduced Vapochromism

Sok-Yong Cho[1] and Tomoyuki Mochida*[1,2]
[1]Department of Chemistry, Graduate School of Science, Kobe University, 1-1 Rokkodai, Nada, Kobe, Hyogo 657-8501, Japan
[2]Research Center for Membrane and Film Technology, Kobe University, 1-1 Rokkodai, Nada, Kobe, Hyogo 657-8501, Japan

E-mail: tmochida@platinum.kobe-u.ac.jp

A luminescent ionic liquid containing a cationic rhenium tricarbonyl complex was synthesized. UV photoirradiation of this liquid in the presence of an organic solvent vapor caused a color change and luminescence quenching via photochemical ligand exchange, thereby enabling the photocontrol of vapochromism.

Keywords: Ionic liquid | Re complex | Vapochromism

The synthesis and applications of room-temperature ionic liquids, which are salts with melting points below 100 °C, have been extensively studied.[1] Although the majority of ionic liquids contain organic cations, functional metal-containing ionic liquids have also been developed recently.[2,3] We have synthesized ionic liquids containing cationic metal complexes, which exhibit various functions such as vapochromism, thermochromism, magnetism, and chemical reactivity.[4] Vapochromism is useful for colorimetric detection of volatile organic compounds,[5,6] but vapochromic liquids are scarce.[4a]

The chemistry of rhenium complexes has expanded in recent years because of their applicability in varied fields such as radiotherapy, diagnosis, photochemical reactions, optical materials, and photocatalysis.[7–10] We have previously reported a Re-containing ionic liquid, *fac*-[Re(CO)$_3$(L′)]Tf$_2$N (L′ = tridentate ligand, Tf$_2$N = (CF$_3$SO$_2$)$_2$N$^-$).[11] An imidazolium ionic liquid containing a luminescent Re cluster has been reported recently.[12] We aim to develop functional ionic liquids that utilize the characteristic photoreactivity of Re complexes.

In this paper, we report the synthesis and properties of a Re-containing luminescent ionic liquid, [**1-CO**]Tf$_2$N (Figure 1, left), which exhibits the novel phenomenon of photoinduced vapochromism. The ligand with the hexyl group and the Tf$_2$N anion were used to lower the melting point. Re tricarbonyl complexes have attracted significant attention in the field of biology because of their photochemical CO-release properties.[8,9] In particular, Re carbonyl complexes bearing an aromatic chelating ligand, such as 2,2′-bipyridine, undergo photochemical ligand exchange via photochemical CO release followed by solvent coordination.[10] We hypothesized that this mechanism could be used to develop a liquid with unique stimuli-responsive properties. This led to the development of [**1-CO**]Tf$_2$N, which exhibits a color change and luminescence quenching upon UV photoirradiation in the presence of an organic solvent vapor.

[**1-CO**]Tf$_2$N is a pale orange liquid (Figure 2a, left), which exhibits a glass transition at 243 K upon cooling. The CO stretching vibration peaks of the liquid were observed at 2029, 1940, and 1910 cm^{-1} in the IR spectrum, positions that are characteristic of *fac*-Re-tricarbonyl complexes.[10] A metal-to-ligand charge-transfer (MLCT) absorption peak was observed at λ_{max} = 377 nm in the UV spectrum. The liquid exhibited orange luminescence when irradiated with UV light (Figure 2a, right).

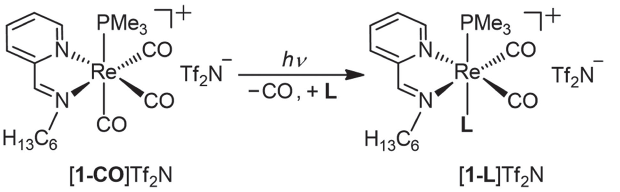

Figure 1. Photochemical ligand exchange reaction of the ionic liquid synthesized in this study.

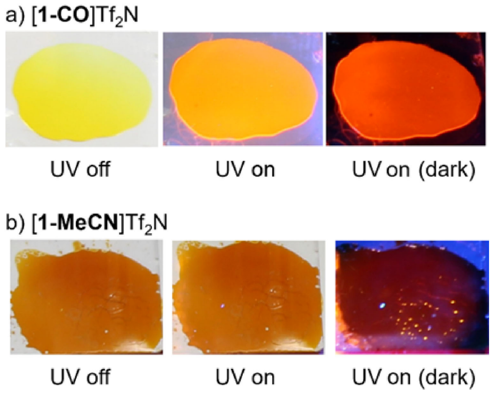

Figure 2. Photographic images of (a) [**1-CO**]Tf$_2$N and (b) [**1-MeCN**]Tf$_2$N. Left: UV off (taken in natural light), middle: UV on (365 nm LED, taken in natural light), and right: UV on (taken under dark conditions).

Photoemission was observed at 630 nm in the emission spectrum (Figure S1), which corresponds to phosphorescence from the ^{3}MLCT excited state.[10]

The photoreactivity of [**1-CO**]Tf$_2$N was examined by UV photoirradiation (365 nm, LED) of a solution of the ionic liquid in acetonitrile. CO release and solvent coordination occurred, producing [**1-MeCN**]Tf$_2$N quantitatively (Figure 1, L = MeCN). The excess solvent was removed by vacuum drying. The product was a brown ionic liquid that did not exhibit luminescence (Figure 2b). The loss of luminescence upon photochemical ligand exchange is a versatile property. Although Re tricarbonyl complexes are typically luminescent,[8] some complexes exhibit a loss of luminescence upon photochemical ligand exchange.[9b] The CO stretching vibration peaks of [**1-MeCN**]Tf$_2$N were observed at 1857 and 1933 cm^{-1} in the IR spectrum, and UV–vis absorption bands were observed at 290 and 460 nm, the latter tailing to longer wavelengths (Figure S2). These spectral changes indicate the release of the CO ligand *trans* to the phosphine ligand.[8,10] No ligand exchange occurred upon bubbling carbon monoxide into an acetonitrile solution of [**1-MeCN**]Tf$_2$N.

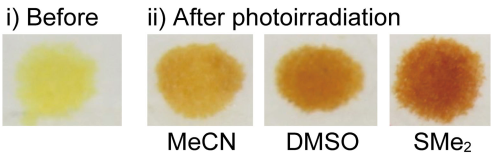

Figure 3. Photographic images of [**1-CO**]Tf_2N (i) before and (ii) after 10 min of photoirradiation in the presence of an organic solvent vapor (SMe_2, DMSO, or MeCN) under a nitrogen atmosphere (paper-supported samples).

The detection of solvent vapor based on the photoreactivity of [**1-CO**]Tf_2N was examined using small amounts of the ionic liquid mounted on thin papers, and exposing these to the solvent vapor of acetonitrile (MeCN), dimethyl sulfoxide (DMSO), or dimethyl sulfide (SMe_2) under a nitrogen atmosphere. No color change occurred upon exposure to the solvent vapors. However, upon UV (365 nm) photoirradiation of the samples, the color of the ionic liquid became orange, reddish orange, or reddish brown, respectively, within a few minutes (Figure 3). This photoinduced vapochromism is ascribed to photochemical ligand exchange. During the photoirradiation, luminescence was initially observed, but this gradually faded within approximately 20 s (SMe_2), 30 s (DMSO), or 5 min (MeCN). No further appreciable color change of the liquid was observed upon further photoirradiation.

The UV–vis spectra before and after 10 min of photoirradiation are shown in Figure 4a. The product was a mixture of the ligand-exchanged photoproduct and unreacted species, which was due to the photoreaction occurring from the surface. The edge of the absorption band was at ~460 nm before photoirradiation, whereas the MLCT absorption at longer wavelengths (450–600 nm) increased after photoirradiation in the order of MeCN < DMSO < SMe_2, which is consistent with the observed coloration. This absorption change primarily reflects the ratio of the photoproduct, rather than a difference in the coordinated molecules (see below), as shown by comparison of the spectra with those of neat [**1-CO**]Tf_2N and [**1-MeCN**]Tf_2N (Figure 4b). Analysis of the IR spectra obtained after 10 min of photoirradiation revealed CO stretching vibration peaks of the ligand-exchanged species at approximately 1860 cm^{-1} (Figure S3), together with the peaks of unreacted species. The ratio of the photoproduct to the unreacted species, as estimated from the IR spectra, decreased in the order SMe_2 > DMSO > MeCN. This tendency agrees with the observed differences in the luminescence fading time, which also reflect the reactivity.

Density functional theory (DFT) calculations revealed that coordination of a solvent molecule with a larger donor number (DN) stabilizes the ligand-exchanged product, making the MLCT absorption (HOMO–LUMO transition) slightly more red-shifted (Supporting Information). The dependence of the shift on the DN is very small (~20 nm), in contrast to that of the d-d transition in typical solvatochromic compounds.[4a] In the current study, no correlation was observed between the solvent DN (SMe_2 (9.0) < MeCN (14.1) < DMSO (29.8 kcal mol^{-1})[13]) or vapor pressures and the observed reactivity and coloration. These results indicate that other factors, such as the affinity of the vapor molecule for the ionic liquid phase, or the viscosity of the resultant liquid, may influence the reactivity. Further investigation is necessary to elucidate this point. In addition, the paper-supported liquid gradually turned brownish gray and nonluminescent upon photoirradiation, even under vapor-free conditions. This unfavorable photo-deterioration may be due to the formation of a CO-released species on the surface, although no significant change in the UV–vis or IR spectra was observed. The color and luminescence of the bulk liquid remained unchanged upon photoirradiation in the absence of solvent vapor.

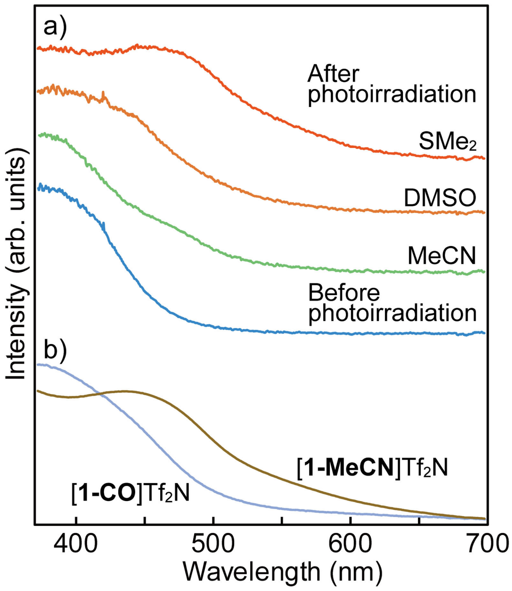

Figure 4. UV–vis spectra of (a) [**1-CO**]Tf_2N before and after photoirradiation in the presence of an organic solvent vapor (SMe_2, DMSO, or MeCN) under a nitrogen atmosphere (paper supported), and (b) [**1-CO**]Tf_2N and [**1-MeCN**]Tf_2N sandwiched between quartz plates.

In conclusion, we synthesized a rhenium-containing luminescent ionic liquid that exhibits photoinduced vapochromism. Currently, very few vapochromic ionic liquids exist,[4a] whereas there are numerous examples of luminescent ionic liquids.[3c,4b,12,14] Our liquid design enabled vapor-induced color change and luminescence quenching via photochemical ligand exchange, although these changes were irreversible. Further investigations are necessary to improve the coloration characteristics and elucidate the factors affecting the photocoloration. Furthermore, the liquid may be useful as a photo-CO-releasing agent. These studies are currently underway in our laboratories.

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Supporting Information is available on https://doi.org/10.1246/cl.210386.

References and Notes

1 M. Kar, K. Matuszek, D. R. MacFarlane, in *Kirk-Othmer Encyclopedia of Chemical Technology*; John Wiley & Sons, Inc (Ed.) **2021**. doi:10.1002/0471238961.ionisedd.a01.pub2.
2 a) N. R. Brooks, S. Schaltin, K. Van Hecke, L. Van Meervelt,

K. Binnemans, J. Fransaer, *Chem.—Eur. J.* **2011**, *17*, 5054. b) M. Iida, C. Baba, M. Inoue, H. Yoshida, E. Taguchi, H. Furusho, *Chem.—Eur. J.* **2008**, *14*, 5047.

3 a) P. Zhang, Y. Gong, Y. Lv, Y. Guo, Y. Wang, C. Wang, H. Li, *Chem. Commun.* **2012**, *48*, 2334. b) A. Branco, L. C. Branco, F. Pina, *Chem. Commun.* **2011**, *47*, 2300. c) Y. Yoshida, G. Saito, in *Ionic Liquids: Theory, Properties, New Approaches*, ed. A. Kokorin, IntechOpen, **2011**, pp. 723–738.

4 a) Y. Funasako, T. Mochida, K. Takahashi, T. Sakurai, H. Ohta, *Chem.—Eur. J.* **2012**, *18*, 11929. b) T. Tominaga, T. Mochida, *Chem.—Eur. J.* **2018**, *24*, 6239. c) Y. Funasako, T. Mochida, T. Inagaki, T. Sakurai, H. Ohta, K. Furukawa, T. Nakamura, *Chem. Commun.* **2011**, *47*, 4475. d) R. Sumitani, H. Yoshikawa, T. Mochida, *Chem. Commun.* **2020**, *56*, 6189.

5 N. A. Rakow, K. S. Suslick, *Nature* **2000**, *406*, 710.

6 A. Kobayashi, M. Kato, *Eur. J. Inorg. Chem.* **2014**, 4469.

7 a) E. B. Bauer, A. A. Haase, R. M. Reich, D. C. Crans, F. E. Kühn, *Coord. Chem. Rev.* **2019**, *393*, 79. b) R. Motterlini, L. Otterbein, *Nat. Rev. Drug Discovery* **2010**, *9*, 728. c) R. Schibli, A. P. Schubiger, *Eur. J. Nucl. Med. Mol. Imaging* **2002**, *29*, 1529. d) C. D. Windle, R. N. Perutz, *Coord. Chem. Rev.* **2012**, *256*, 2562. e) G.-W. Zhao, J.-H. Zhao, Y.-X. Hu, D.-Y. Zhang, X. Li, *Synth. Met.* **2016**, *212*, 131. f) S.-S. Sun, A. J. Lees, *Coord. Chem. Rev.* **2002**, *230*, 171.

8 A. E. Pierri, A. Pallaoro, G. Wu, P. C. Ford, *J. Am. Chem. Soc.* **2012**, *134*, 18197.

9 a) I. Chakraborty, J. Jimenez, W. M. C. Sameera, M. Kato, P. K. Mascharak, *Inorg. Chem.* **2017**, *56*, 2863. b) I. Chakraborty, S. J. Carrington, J. Hauser, S. R. J. Oliver, P. K. Mascharak, *Chem. Mater.* **2015**, *27*, 8387.

10 a) K. Koike, N. Okoshi, H. Hori, K. Takeuchi, O. Ishitani, H. Tsubaki, I. P. Clark, M. W. George, F. P. A. Johnson, J. J. Turner, *J. Am. Chem. Soc.* **2002**, *124*, 11448. b) K. Koike, J. Tanabe, S. Toyama, H. Tsubaki, K. Sakamoto, J. R. Westwell, F. P. A. Johnson, H. Hori, H. Saitoh, O. Ishitani, *Inorg. Chem.* **2000**, *39*, 2777.

11 S.-Y. Cho, T. Mochida, *Inorg. Chem.* **2020**, *59*, 847.

12 J. Yanagisawa, T. Hiraoka, F. Kobayashi, D. Saito, M. Yoshida, M. Kato, F. Takeiri, G. Kobayashi, M. Ohba, L. F. Lindoy, R. Ohtani, S. Hayami, *Chem. Commun.* **2020**, *56*, 7957.

13 V. G. Tsvetkov, B. I. Kozyrkin, L. Ya. Tsvetkova, I. B. Rabinovich, *Zh. Obshch. Khim.* **1978**, *48*, 2162.

14 a) T. Ogawa, M. Yoshida, H. Ohara, A. Kobayashi, M. Kato, *Chem. Commun.* **2015**, *51*, 13377. b) B. Monteiro, M. Outis, H. Cruz, J. P. Leal, C. A. T. Laia, C. C. L. Pereira, *Chem. Commun.* **2017**, *53*, 850.