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

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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 (FSO₂)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.⁴ Coordination 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(C₅H₅)(benzene)]⁺ sandwich complex in acetonitrile is known to eliminate benzene

ligand to produce a half-sandwich complex [Ru(C₅H₅)(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-C₆H₃(OC₆H₁₂CN)₃ (L). Incorporation of two different coordination sites of the ligand, the arene and nitrile moieties, is the key feature of this molecular design.

Depending on the reaction conditions, the reactions of [Ru(C₅H₅)(MeCN)₃]X (X = FSA or PF₆) and the ligand L selectively afforded either the sandwich complex [1]X or coordination polymer [2]X with nitrile coordination (Fig. 2). The sandwich complex [1]FSA, a colorless viscous ionic liquid, was synthesized with a 60% yield by heating [Ru(C₅H₅)(MeCN)₃]PF₆ and L in acetonitrile at 90 °C, followed by anion exchange using KFSA. The ionic liquid can also be obtained by reacting [Ru(C₅H₅)(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(C₅H₅)(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(C₅H₅)(L)]_n·nFSA). While the coordination polymer was insoluble in most organic solvents, it was soluble in acetonitrile to produce [Ru(C₅H₅)(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

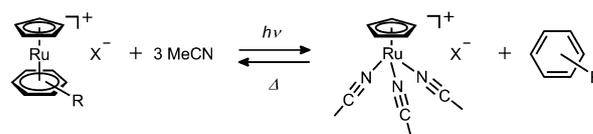


Fig. 1 Photochemical reaction of cyclopentadienyl arene–ruthenium complexes in acetonitrile solution.^{6b}

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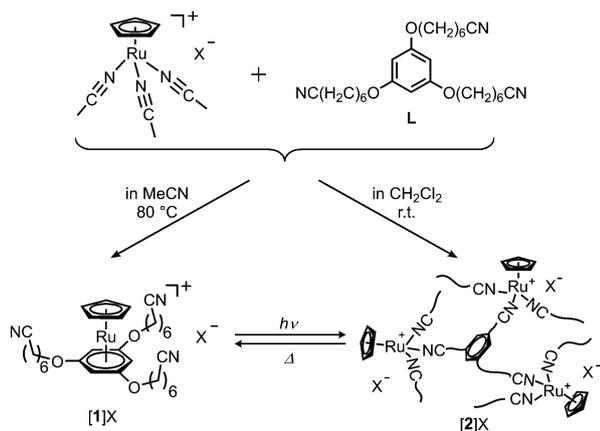


Fig. 2 Reactions of $[\text{Ru}(\text{C}_5\text{H}_5)(\text{MeCN})_3]\text{X}$ ($\text{X} = \text{FSA}, \text{PF}_6$) and **L**. Conversion between **[1]X** and **[2]X** occurs for $\text{X} = \text{FSA}$.

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 $[\text{Ru}(\text{C}_5\text{H}_5)(\text{MeCN})_3]\text{PF}_6$ (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 and b). UV-Vis, IR, and NMR spectra revealed that approximately 20% of **[1]FSA** remains unreacted (Fig. S3 and S4, ESI[†]); these molecules are

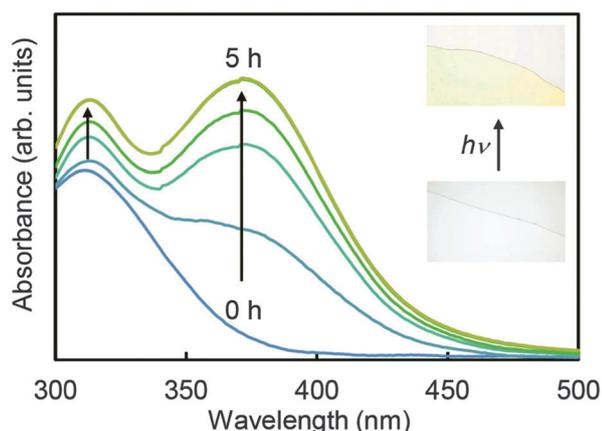


Fig. 3 Changes in UV-Vis absorption spectra of neat **[1]FSA** during photoirradiation taken at 1 h intervals. Note that the spectra obtained at 4 h and 5 h overlapped. The inset shows the images of **[1]FSA** before and after photoirradiation.

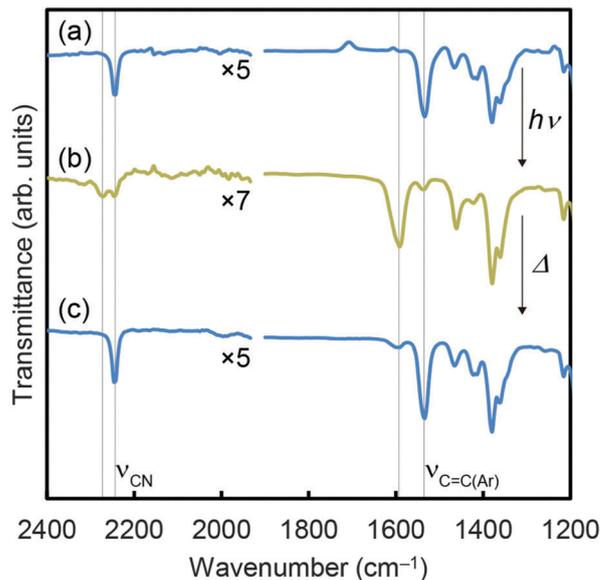


Fig. 4 IR spectra of **[1]FSA** (a) before and (b) after photoirradiation for 10 h, and (c) **[1]FSA** generated from the coordination polymer by heating at 90 °C for 30 min.

most likely incorporated in the network structure of the photo-generated 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** (Fig. 4c and Fig. S4 and S5, 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** ($\Delta H = 5.2 \text{ kJ mol}^{-1}$). Upon cooling the liquid, a glass transition was observed at -53 °C . These results clearly demonstrate that the transformation is reversible.

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 materials⁹ and molecular materials¹⁰ are known to exhibit reversible solid-liquid transformations driven 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

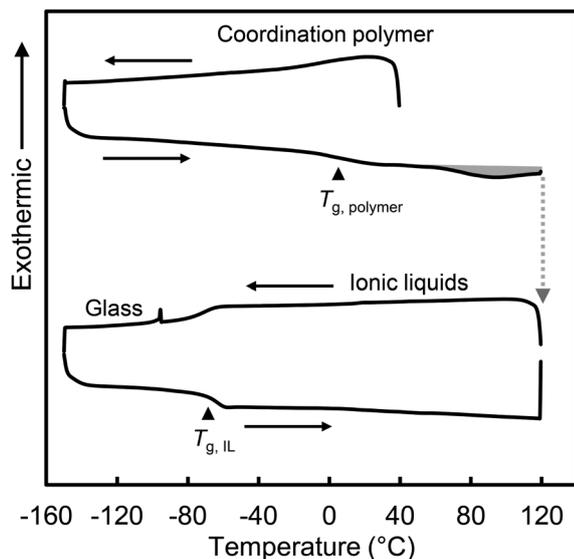


Fig. 5 DSC traces of [2]FSA, showing thermal conversion to [1]FSA. The broad endothermic peak shown in gray is ascribed to the conversion reaction.

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 ruthenium sandwich complexes by application of light and heat in solutions.¹² In this study, we have successfully extended the mechanism to intermolecular coordination transformation based on suitable ligand design.

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.

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Notes and references

- 1 A. Stark and K. R. Seddon, in *Kirk-Othmer Encyclopedia of Chemical Technology*, Wiley-Interscience, New York, 5th edn, 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, $[\text{Ru}(\text{C}_5\text{H}_5)\{1,3,5\text{-C}_6\text{H}_3(\text{OC}_3\text{H}_6\text{CN})_3\}]$. This salt was obtained as a solid ($T_m = 84\text{ }^\circ\text{C}$), but once melted, it maintained the liquid state at r.t. ($T_g = -28\text{ }^\circ\text{C}$). 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 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.