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

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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)]$_n$.*n*FSA ([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.

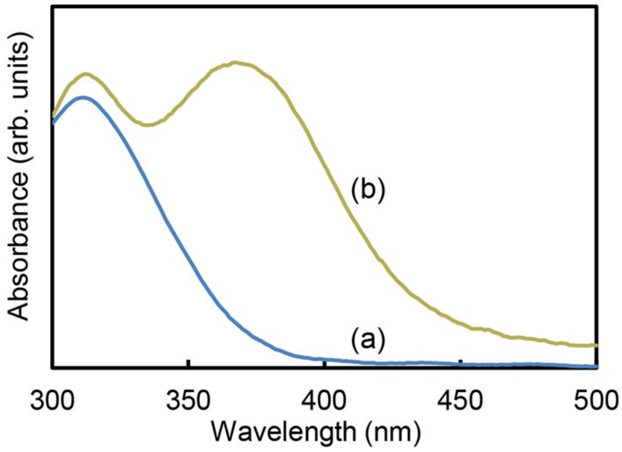

Fig. S1 UV–Vis absorption spectra of (a) [**1**]FSA and (b) [**2**]FSA.

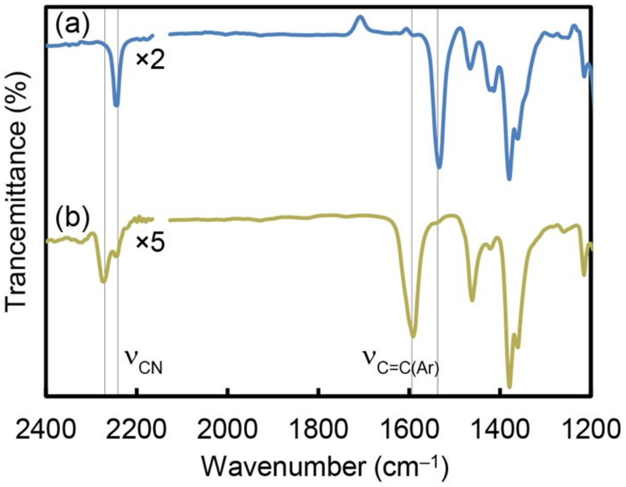

Fig. S2 IR absorption spectra of (a) [**1**]FSA and (b) [**2**]FSA.

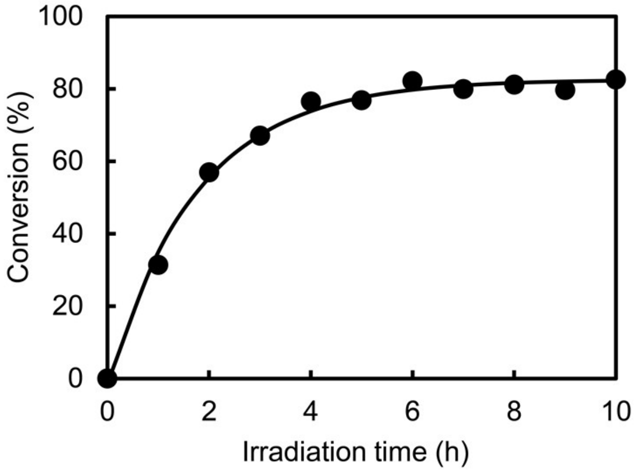

Fig. S3 Time evolution of the molar ratio of the tricyano-coordinated species generated during photoirradiation of [**1**]FSA.

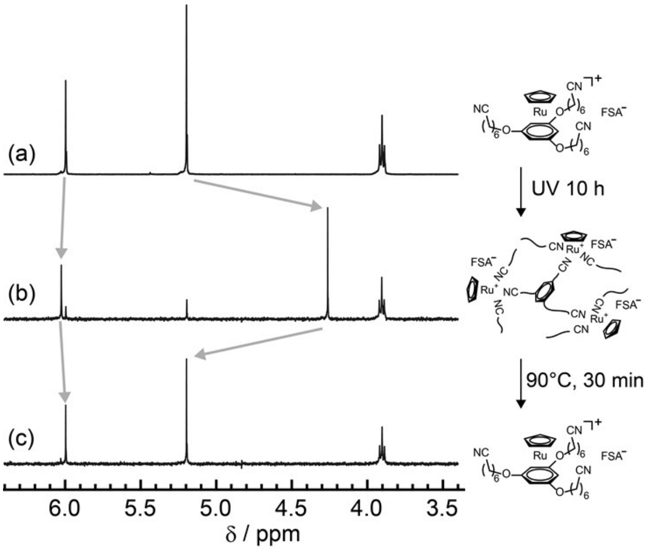

Fig. S4 ^{1}H NMR spectra (400 MHz, CD_3CN, room temperature) of [**1**]FSA (a) before and (b) after photoirradiation for 10 h, and (c) [**1**]FSA generated from the coordination polymer by heating at 90 °C for 30 min. The spectrum (b) comprises of the signals of $[Ru(C_5H_5)(CD_3CN)_3]$FSA (resulted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

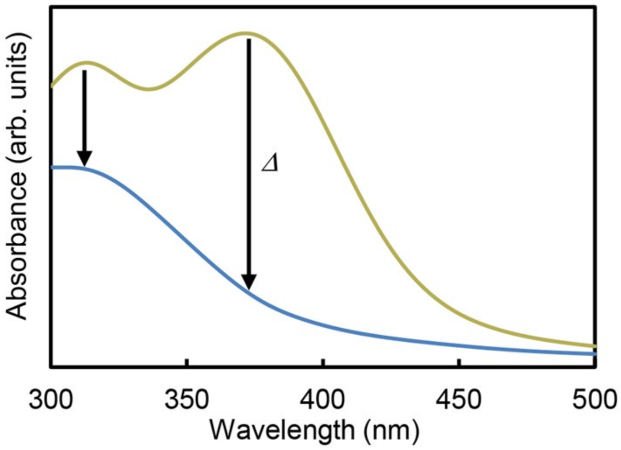

Fig. S5 Changes of UV–Vis absorption spectra of [**2**]FSA before and after heating at 90 °C for 30 min.