Supporting Information

Visible-light-responsive gels with long-lasting functions via combining metallopolymers and coordination solvents with reduced volatilization

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Synthesis

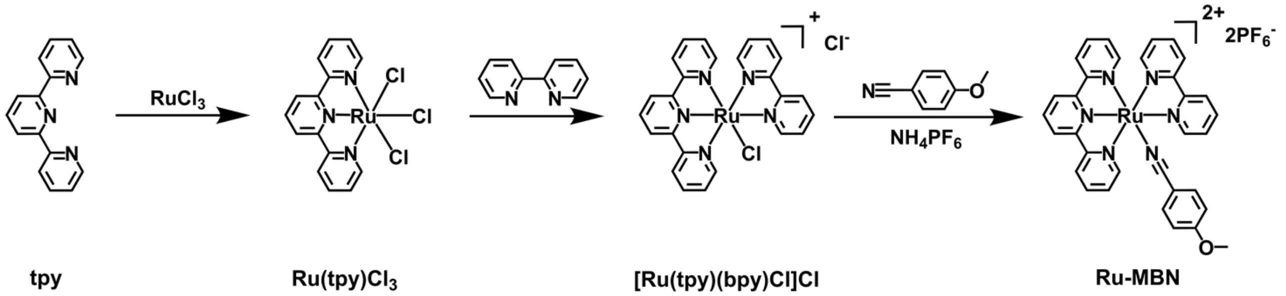

Fig. S1. Schematic representation of synthesis of Ru-MBN.

Synthesis of Ru(tpy)Cl$_3$: It was synthesized according to the literature[1]. $RuCl_3 \cdot 3H_2O$ (262 mg, 1.0 mmol) and 2,2':6',2''-terpyridine (233 mg, 1.0 mmol) were dissolved in ethanol (150 mL). The mixture was heated under reflux at 85 °C for 3 h. After completion, the reaction solution was cooled to room temperature and filtered. The solid was sequentially washed with ethanol and diethyl ether, then dried under vacuum to afford Ru(tpy)Cl$_3$ as a brown solid. Yield: 78%.

Synthesis of [Ru(tpy)(bpy)Cl]Cl: Ru(tpy)Cl$_3$ (468 mg, 1.06 mmol), 2,2'-bipyridine (168 mg, 1.07 mmol) and lithium chloride (337 mg, 7.9 mmol) were mixed in 3:1 ethanol/H_2O (20 mL). The mixture was bubbled with nitrogen for 10 min before it was heated under refluxed overnight. While mixture was bubbled, 295.4 μL triethylamine was added into. After cooling to room temperature, mixture was filtered and product was purified by column chromatography with silica gel using methanol/DCM (1/12) as the eluent. ^1H NMR (400 MHz, Methanol-d4) δ (ppm): 10.20 (d, J = 6.3 Hz, 1H), 8.77 (dt, J = 8.2, 1.1 Hz, 1H), 8.66 (d, J = 8.1 Hz, 2H), 8.53 (dt, J = 8.1, 1.1 Hz, 2H), 8.49 (dt, J = 8.1, 1.1 Hz, 1H), 8.32 (td, J = 7.9, 1.6 Hz, 1H), 8.17 (t, J = 8.1 Hz, 1H), 8.00 (ddd, J = 7.6, 5.6, 1.3 Hz, 1H), 7.94 (td, J = 7.8, 1.5 Hz, 2H), 7.74 (ddd, J = 8.1, 7.5, 1.4 Hz, 1H), 7.70 (ddd, J = 5.5, 1.6, 0.8 Hz, 2H), 7.38 (d, J = 6.5 Hz, 1H), 7.33 (ddd, J = 7.6, 5.6, 1.3 Hz, 2H), 7.04 (ddd, J = 7.3, 5.8, 1.4 Hz, 1H).

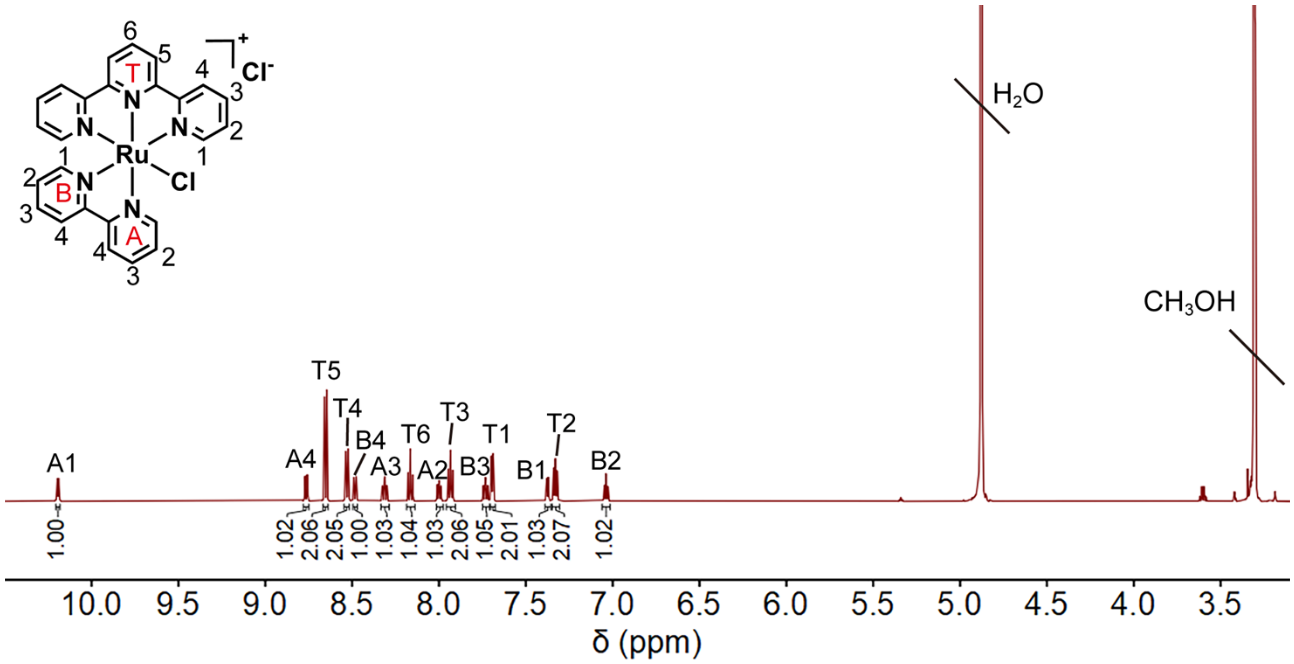

Fig. S2. ^{1}H NMR spectrum of [Ru(tpy)(bpy)Cl]Cl (600 MHz, Methanol-d4, 25 ^{o}C).

Synthesis of [Ru(tpy)(bpy)MBN](PF_6)$_2$ (Ru-MBN): [Ru(tpy)(bpy)Cl]Cl (192 mg, 0.3 mmol), 4-cyanophenol (48 mg, 0.36 mmol) and silver hexafluorophosphate (270 mg, 1.05 mmol) were mixed in 3:1 acetone/ H_2O (16 mL). The mixture was heated under refluxed in dark overnight with nitrogen. Then mixture was filtered while hot and evaporated under reduced pressure. The product was purified by column chromatography with aluminum oxide gel using methanol/ dichloromethane (from 1/50 to 1/20) as the eluent. ^{1}H NMR (400 MHz, Methanol-d4) δ (ppm): 10.07 (dd, *J* = 5.2, 1.3 Hz, 1H), 9.00 (dd, *J* = 8.3, 1.3 Hz, 1H), 8.82 (d, *J* = 8.2 Hz, 2H), 8.65 (ddd, *J* = 8.1, 1.4, 0.8 Hz, 2H), 8.50 (dd, *J* = 8.3, 1.3 Hz, 1H), 8.46 (d, *J* = 8.1 Hz, 1H), 8.44-8.39 (m, 2H), 8.22 (d, *J* = 8.9 Hz, 1H), 8.04 (td, *J* = 7.9, 1.5 Hz, 2H), 7.81 (dd, *J* = 5.3, 1.3 Hz, 1H), 7.69 (ddd, *J* = 5.5, 1.6, 0.7 Hz, 2H), 7.57-7.52 (m, 3H), 7.32 (ddd, *J* = 7.7, 5.5, 1.3 Hz, 2H), 7.00 (d, *J* = 9.0 Hz, 2H), 3.83 (s, 3H).

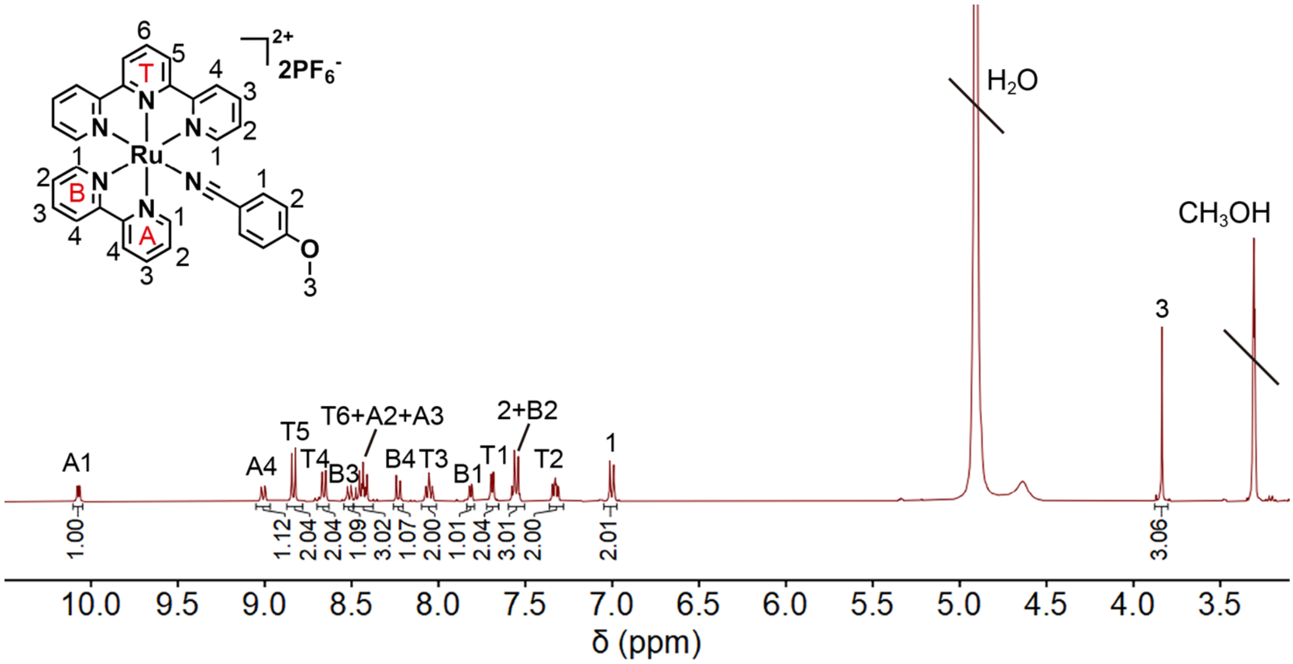

Fig. S3. ^{1}H NMR spectrum of Ru-MBN (400 MHz, Methanol-d4, 25 ^{o}C).

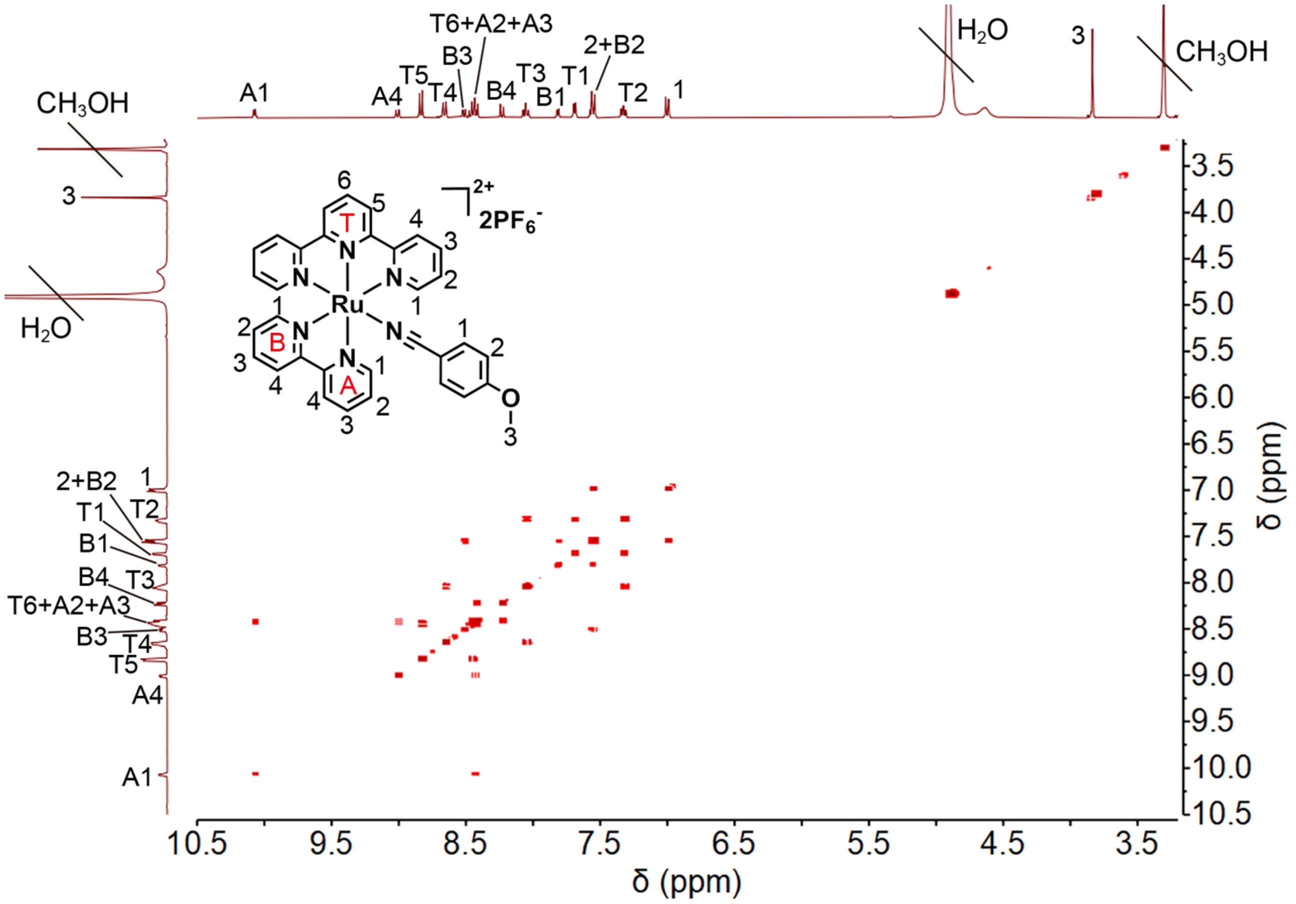

Fig. S4. ^{1}H -^{1}H COSY spectrum of Ru-MBN (400 MHz, Methanol-d4, 25 ^{o}C).

Synthesis of 3-(2,2’:6’,2’’-terpyridin-4’-yloxy) propylamine (NH_2-tpy): It was synthesized according to the literature.[2] Potassium hydroxide (392 mg, 7.0 mmol) was added into 20 mL dimethylsulfoxide and heated to 65 °C under stirring. After 30 min, 4’-chloro-2,2’:6’,2’’-terpyridine (1000 mg, 3.7 mmol) was added into suspension. After stirring for 24 hours at 65 °C, the solution was cooled to room temperature and poured into 200 mL deionized water. The crude product was further extracted with dichloromethane and dried with magnesium sulfate. After filtration and removal of the solvent in vacuum, the crude product was recrystallized from ethyl acetate to give the light yellow solid. ^1H NMR (400 MHz, chloroform-d) δ (ppm): 8.68 (ddd, $J = 4.8, 1.8, 0.9$ Hz, 2H), 8.60 (dt, $J = 8.0, 1.1$ Hz, 2H), 8.02 (s, 2H), 7.84 (td, $J = 7.7, 1.8$ Hz, 2H), 7.32 (ddd, $J = 7.5, 4.8, 1.3$ Hz, 2H), 4.25 (t, $J = 5.1$ Hz, 2H), 3.16 (t, $J = 5.1$ Hz, 2H).

Synthesis of *N*-(3-([2,2’:6’,2’’-terpyridin]-4’-yloxy)propyl)acrylamide (tpy-AAm): NH_2-tpy (343 mg, 1.156 mmol) was mixed in 40 mL dry dichloromethane. The mixture was stirred for 30 min after 0.45 mL triethylamine was added into solution at 0 °C under nitrogen. Then, acryloyl chloride (607 mg, 6.71 mmol) was slowly added before the mixture was stirred at 0 °C for 2 h and at room temperature for 21 h. After that, 20 mL deionized water was poured into solution and mixture was extracted by dichloromethane. Collected dichloromethane solution was washed by saturated salt water. Crude product was purified by silica column chromatography after evaporating under reduced pressure. ^1H NMR (400 MHz, Chloroform-d) δ (ppm): 8.68 (ddd, $J = 4.9, 1.9, 0.9$ Hz, 2H), 8.60 (dt, $J = 8.0, 1.1$ Hz, 2H), 8.00 (s, 2H), 7.84 (td, $J = 7.7, 1.8$ Hz, 2H), 7.32 (ddd, $J = 7.5, 4.8, 1.2$ Hz, 2H), 6.16 (m, 2H), 5.65 (dd, $J = 10.8$ Hz, 1H), 4.25 (t, $J = 5.1$ Hz, 2H), 3.16 (t, $J = 5.1$ Hz, 2H).

Synthesis of Ru(tpy-AAm)Cl_3: AAm-tpy (359.4 mg, 1 mmol) and $RuCl_3$ (262 mg, 1 mmol) were dissolved in 60 mL ethanol. The mixture was heated under 85 °C at reflux for 4 h and then cooled to room temperature. Brown powders were filtered and washed with ethanol and diethyl ether sequentially.

Synthesis of [Ru(tpy-AAm)(bpy)Cl]Cl: Ru(tpy-AAm)Cl_3 (110 mg, 0.2 mmol), 2,2′- bipyridine (31 mg, 0.2 mmol) and lithium chloride (63 mg, 1.5 mmol) were mixed in 3:1 ethanol/H_2O mixture (20 mL) and the solution was bubbled with nitrogen for 10 min. Triethylamine (55.45 μL) was added while bubbling. The mixture was heated at reflux for 21 h in the dark. After cooling to room temperature, the mixture was filtered. The product was purified by column chromatography (eluent: methanol/dichloromethane =1:12). ^1H NMR (400 MHz, Methanol-d4) δ (ppm): 8.51 (dd, *J* = 27.5, 8.1 Hz, 3H), 8.37 (s, 2H), 8.00-7.87 (m, 3H), 7.77-7.65 (m, 3H), 7.46 (d, *J* = 5.7 Hz, 1H), 7.30 (ddd, *J* = 7.2, 5.5, 1.3 Hz, 2H), 7.06 (t, *J* = 6.6 Hz, 1H), 6.39-6.25 (m, 2H), 4.59 (t, *J* = 5.6 Hz, 2H), 3.86 (t, *J* = 5.5 Hz, 2H), 3.34 (s, 1H), 3.21 (q, *J* = 7.3 Hz, 2H), 1.31 (t, *J* = 7.3 Hz, 2H).

Synthesis of [Ru(tpy-AAm)(bpy)(H_2O)](PF_6)$_2$ (AAmRu): [Ru(tpy-AAm)(bpy)Cl]Cl (202 mg, 0.3 mmol) and $AgPF_6$ (102 mg, 0.6 mmol) were dissolved in 3:1 acetone/H_2O (16 mL). The solution was bubbled under nitrogen for 10 min and then stirred at reflux in the dark overnight. After that, the mixture was filtered while hot and reduced to 4 mL by evaporation under reduced pressure. The crude product was precipitated by adding saturated ammonium hexafluorophosphate solution. The precipitate was filtered, washed with ice water and dried to give final product AAmRu ^1H NMR (400 MHz, Methanol-d4) δ (ppm): 9.55 (dd, *J* = 17.0, 5.5 Hz, 1H), 8.79 (d, *J* = 8.2 Hz, 1H), 8.66-8.59 (m, 2H), 8.50-8.41 (m, 3H), 8.37 (td, *J* = 7.8, 1.5 Hz, 1H), 8.11-7.99 (m, 3H), 7.83-7.71 (m, 3H), 7.49-7.39 (m, 3H), 7.09 (ddd, *J* = 7.4, 5.7, 1.4 Hz, 1H), 6.40-6.25 (m, 2H), 5.72 (dd, *J* = 8.8, 3.2 Hz, 1H), 4.64 (q, *J* = 7.8, 6.7 Hz, 2H), 3.88 (t, *J* = 5.6 Hz, 2H).

Synthesis of 4-(2-hydroxyethoxy)benzonitrile: Potassium carbonate (1.38 g, 10 mmol), 4-hydroxybenzonitrile (1.19 g, 10 mmol) and potassium Iodide (99.6 mg, 0.6 mmol) were mixed in 20 mL DMF, and stirred at 110 °C for 30 min. And then, 3-chloro-1-propanol (1.017 g, 11 mol) was dissolved in 10 mL DMF and added into the mixture. After stirring in 110 °C for 24 h, mixture was filtered, washed with dichloromethane and reduced by evaporation under reduced pressure. The product was purified by column chromatography with silica gel (eluent: petroleum ether/ethyl acetate = 1/1). ^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 7.79-7.70 (m, 2H), 7.12-7.05 (m, 2H), 4.64-4.54 (m, 1H), 4.12 (t, *J* = 6.4 Hz, 2H), 3.54 (td, *J* = 6.2, 5.1 Hz, 2H), 1.86 (p, *J* = 6.3 Hz, 2H).

Synthesis of MA-cyanophenol (MACN): Triethylamine (1.19 mL) and 4-(2-hydroxyethoxy)benzonitrile (998 mg, 5.64 mmol) were mixed in 40 mL dry dichloromethane. Acryloyl chloride (782 mg,8.64 mmol) was slowly added under argon at 0 °C after the mixture was stirred for 10 min. The reaction solution was stirred for 2 h at 0 °C and stirred for another 2 h at room temperature. After that, 20 mL water was added and extracted by dichloromethane. The solution was then washed by 5 mL NaCl solution and reduced by evaporation under reduced pressure. The final product was purified by column chromatography with silica gel (eluent: petroleum ether/ethyl acetate = 10/1). ^{1}H NMR (400 MHz, Chloroform-d) δ (ppm): 7.59 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.42 (dd, *J* = 17.3, 1.4 Hz, 1H), 6.13 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.85 (dd, *J* = 10.4, 1.4 Hz, 1H), 4.37 (t, *J* = 6.2 Hz, 2H), 4.11 (t, *J* = 6.1 Hz, 2H), 2.20 (p, *J* = 6.2 Hz, 2H).

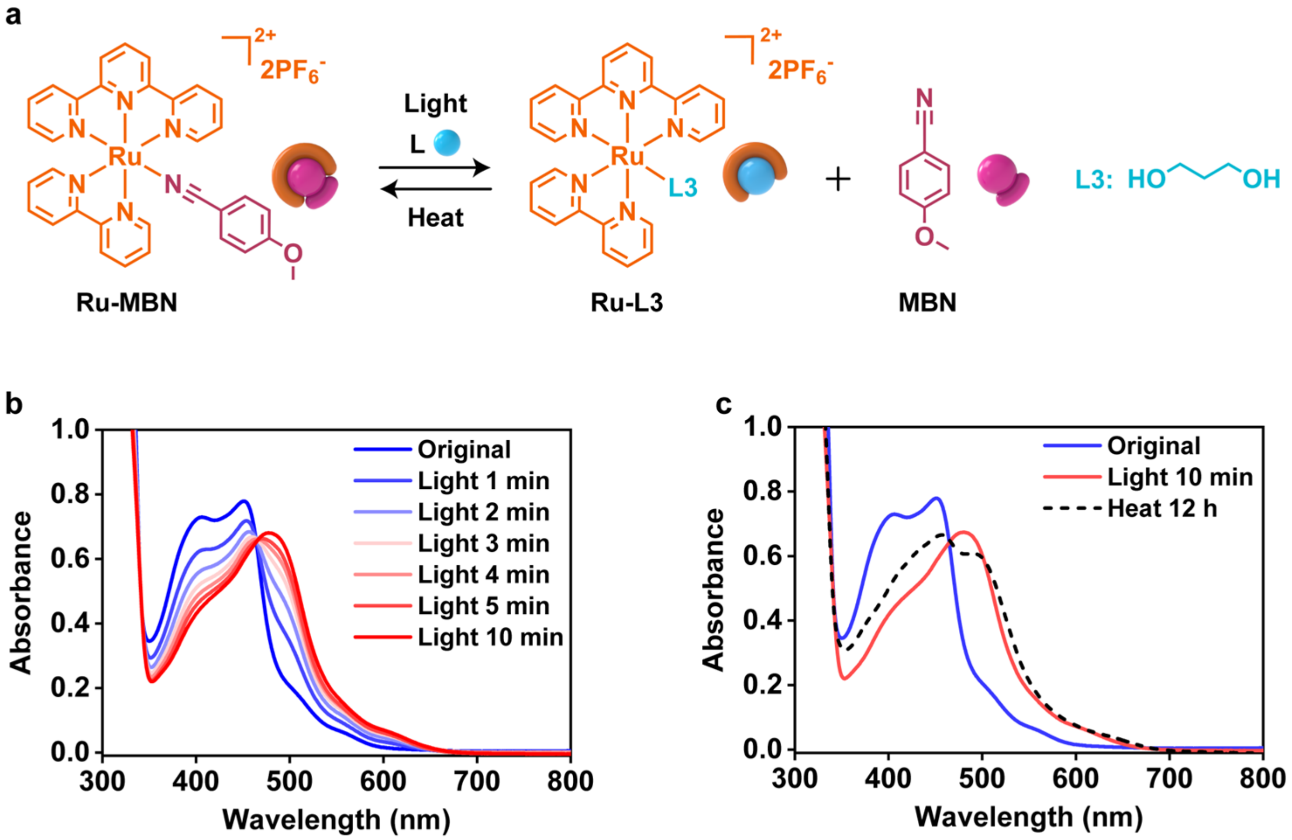

Fig. S5. (a) UV-vis absorption spectra of the mixture of Ru-MBN (1 mM) and MBN (19 mM) after sequential light irradiation (455 nm, 17 mW/cm^2) in 1,3-Propanedio (L3). (b) UV-vis absorption spectra of the mixture of Ru-MBN (1 mM) and MBN (19 mM) in L3 underwent a light-heat cycle.

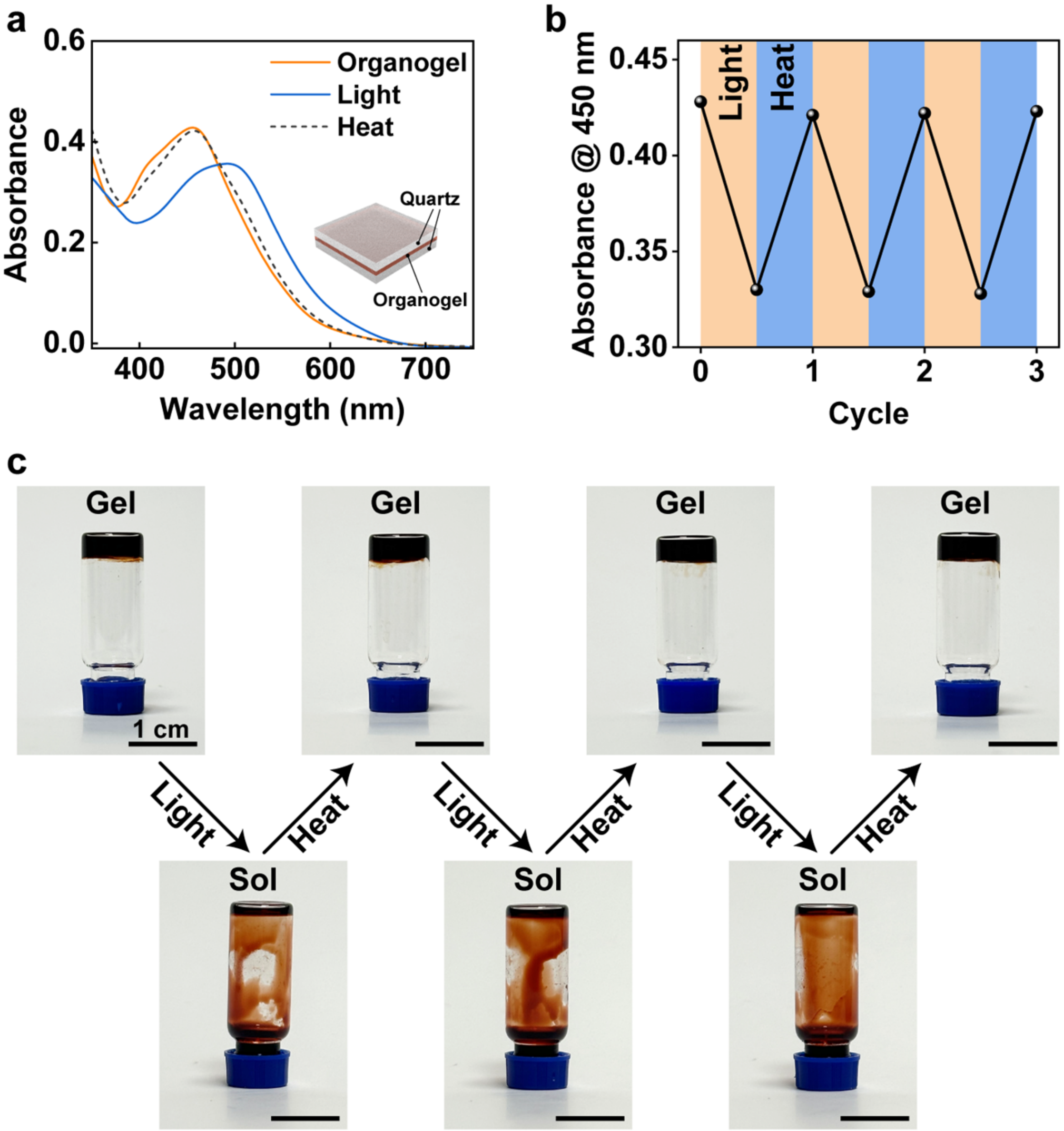

Fig. S6. (a) UV-vis absorption spectra of Ru_1CN_{10} organogel in L3 underwent a light (455 nm, 30 mW/cm^2, 10 min) and heat (100 °C, 10 min) cycle. The inset is a sample model diagram for testing the ultraviolet-visible spectroscopy of the organogel. It consists of an organogel sandwiched between two quartz slides. (b) Absorbance changes at 450 nm for Ru_1CN_{10} organogel during 3 cycles. (c) Images showing reversible gel-to-sol transitions of the Ru_1CN_{10} organogel under light irradiation and heat during 3 cycles.

References

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2 Schubert, U. S.; Eschbaumer, C.; Hien, O.; Andres, P. R. 4'-functionalized 2,2':6',2"-terpyridines as building blocks for supramolecular chemistry and nanoscience. *Tetrahedron Lett.* 2001, **42**, 4705-4707.