Near-Infrared Photon-Excited Energy Transfer in Platinum(II)-

Based Supramolecular Polymers Assisted by Upconverting

Nanoparticles

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1. Materials and methods

Compound 1, 3–4, and upconversion nanoparticles (UCNPs) were synthesized according to the previously reported procedures.^{S1–S4} Other reagents and solvents were employed as purchased.

¹H NMR and ¹³C NMR spectra were obtained from Bruker Avance 400 instruments. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry mass (MALDI-TOF-MS) measurements were recorded on a Bruker Autoflex Speed spectrometer with DCTB as the matrix. UV-Vis spectra were recorded on a UV-1800 Shimadzu spectrometer. Solution excitation and steady-state fluorescence emission spectra were recorded on a FluoroMax-4 spectrofluorometer (Horiba Scientific) and analyzed with an Origin (v8.0) integrated software FluoroEssence (v2.2). Upconversion luminescence spectra were measured on a Hitachi F-2700 spectrophotometer equipped with a 980 nm laser (Beijing Viasho Technology Co., Ltd). Circular dichroism (CD) measurements were performed on a Jasco J-1500 circular dichroism spectrometer, equipped with a PFD-425S/15 Peltier-type temperature controller. Transmission electron microscope (TEM) images were performed on a JEM-2100 electron microscope. Scanning electron microscopy (SEM) experiments were performed on a FEI Verios G4 instrument. For light irradiation experiments, a 460 nm LED lamp (12 W) was employed as light source, by keeping the distance between the LED and cuvette at 10 cm.

2. UCNPs and Supramolecular polymerization behaviors of 1-2



Figure S1. TEM images of UCNPs. TEM images of the UCNPs demonstrate the nearly monodisperse particle size with an average diameter of \sim 30 nm.



Figure S2. (a) CD spectra of the supramolecular polymer 1 ($1.0 \times 10^{-4} \text{ mol } \text{L}^{-1}$) in MCH at 293 K (black line) and 332 K (red line). The arrows indicate the variation of the CD signals upon increasing the temperature. (b) Net helicity φ_n as a function of temperature for 1 monitoring at the band of 486 nm. The red and pink lines denote the mathematical fitting according to the Meijer–Schenning–van-der-Schoot mathematical model.^{S5}



Figure S3. (a) CD spectra of the supramolecular polymer **2** $(1.0 \times 10^{-4} \text{ mol L}^{-1})$ in MCH at 293 K (red line) and 325 K (black line). The arrows indicate the variation of the CD signals upon increasing the temperature. (b) Net helicity φ_n as a function of temperature for **2** monitoring at the band of 365 nm. The red and pink lines denote the mathematical fitting according to the Meijer–Schenning–van-der-Schoot mathematical model.^{S5}

CD data.								
Monomer	$T_{\rm e}\left({\rm K}\right)$	$h_{\rm e}$ (kJ mol ⁻	Ka					
		1)						
1	312.5	-89.3	1.07×10^{-6}					
2	298.8	-81.3	3.04×10^{-5}					

Table S1. Thermodynamic parameters of 1-2 obtained by fitting the temperature-dependent

*T*_e: Critical elongation temperature. *h*_e: Enthalpy release upon elongation. *K*_a: Dimensionless equilibrium constant of the activation step at *T*_e. For **1**–**2**, $c = 1.0 \times 10^{-4}$ mol L⁻¹ in MCH.



Figure S4. Photographs of the gel of (a) 1 and (b) 2 in MCH. The test tube inversion experiments show the critical gelation concentration (CGC) of 2 is 20 mmol L^{-1} , whist that of 1 is 8 mmol L^{-1} .

3. NIR light-excited energy transfer supramolecular system



Figure S5. SEM images of (a) 1 (1.0×10^{-4} M), (b) 1/2 (30 mol% of 2, [1]= 1.0×10^{-4} M), (c) UCNPs/1 (weight ratio of UCNPs/1 = 5:1, [1]= 1.0×10^{-4} M) and (d) UCNPs/1/2 (30 mol% of 2, weight ratio of UCNPs/1 = 5:1, [1]= 1.0×10^{-4} M). By directly mixing 1 with UCNPs in MCH, the dried sample shows that UCNPs appear to sit on the surface of the fibers of 1, which clearly indicates the UCNPs are not embedded in the fibers, but immobilized and well dispersed in the fiber matrix.



Figure S6. CD spectra of the supramolecular polymer 1 $(1.0 \times 10^{-4} \text{ mol } \text{L}^{-1})$ in MCH upon addition of UCNPs. Upon adding of UCNPs into the supramolecular polymeric solution of 1, the CD signal of 1 maintains the initial state. Such results indicate the stacking mode of 1 cannot be disturbed by excess UCNPs.



Figure S7. Upconversion luminescence spectra of UCNPs in MCH upon 460 nm light irradiation. The excitation light source is a 980 nm laser. The signals of UCNPs hardly change during the 460 nm light irradiation process, indicating no chemical transformation takes place for UCNPs



Figure S8. The upconversion luminescence intensity variation of UCNPs/1 at 471 nm (a) upon 460 nm light irradiation, and (b) room temperature recovery. (c) upconversion luminescence spectra intensity at 471 nm upon multi-cycle irradiation and standing at room temperature. [1] = 2.00×10^{-4} mol L⁻¹, weight ratio of UCNPs/1 = 5 : 1.



Figure S9. UV–Vis absorption spectrum of **2** $(1.00 \times 10^{-4} \text{ mol } \text{L}^{-1})$ in MCH (red line), and upconversion luminescence spectrum of UCNPs under excitation at 980 nm laser (blue line). Owing to the small overlapping area of the upconversion luminescence band of UCNPs and absorption band of **2**, the energy transfer efficiency from UCNPs to **2** is very limited.

Calculation of the overlap integral (J)

The overlap integral (J) is calculated according to equation S1.

$$J(\lambda) = \lambda^4 \times f_{\rm D}(\lambda) \times \varepsilon_{\rm A}(\lambda) \qquad (\text{equation S1})$$

where λ is the wavelength (cm), and $\varepsilon_A(\lambda)$ is the molar extinction coefficient of fluorescence resonance energy transfer (FRET) acceptor at wavelength λ . $f_D(\lambda)$ is the fraction of fluorescence intensity of FRET donor.

The spectra overlap between the emission spectrum of donor 1 and the extinction spectrum of acceptor 2 are shown in Figure S10–S11. *J* value is calculated to be 3.85×10^{12} M⁻¹ cm⁻¹ nm⁴, indicative of the feasibility for the FRET process from 1 to 2.



Figure S10. The corrected emission spectrum $f_D(\lambda)$ of 1 and extinction coefficient spectrum $\varepsilon_A(\lambda)$ of 2.



Figure S11. Spectral overlap between the emission spectrum of 1 and absorption spectrum of 2.

Calculation of FRET efficiency ($\Phi_{\rm ET}$)

FRET efficiency ($\Phi_{\rm ET}$) is calculated according to equation S2.^{S6}

$$\Phi_{\rm ET} = 1 - I_{\rm DA}/I_{\rm D} \qquad (\text{equation S2})$$

where I_{DA} and I_D are the emission intensity of FRET donor with and without the presence of FRET acceptor, respectively.

 $\Phi_{\text{ET}(1/2)}$ is calculated to be 86.0% when 30 mol% of **2** is added into the MCH solution of **1**.

Calculation of energy transfer rate constant (ket)

Energy transfer rate constant (k_{ET}) is calculated according to equation S3.^{S7}

$$\Phi_{\rm ET} = k_{\rm ET} / (k_{\rm ET} + \tau_{\rm D}^{-1}) \qquad (\text{equation S3})$$

where τ_D is the singlet state fluorescence lifetime of donor **1** in MCH (2.11 ns). k_{ET} is calculated to be 2.91 × 10⁹ s⁻¹ when 30 mol% of **2** is added into MCH solution of **1**.

Table S2. Energy transfer parameters of 1/2, UCNPs/2 and UCNPs/1/2 at varying the molar ratio of 1 and 2. Weight ratio of UCNPs/1 maintains in 5:1, 5.00×10^{-5} mol L⁻¹ of 1 in MCH.

[2]/([1]+[2])	$\Phi_{ ext{ET(1/2)}}$ / %	$k_{\rm ET} \text{ of } \mathbf{1/2} \times 10^{9} \text{/ s}^{-1}$	$arPhi_{ ext{ET(UCNPs/1)}}$ / %	$\Phi_{ m ET(UCNPs/1/2)}$ / %
1 %	49.9	1.69	4.8	41.1
3 %	67.6	2.29	7.0	52.0
5 %	69.7	2.36	8.6	56.8
7 %	74.5	2.52	13.1	57.4
10 %	67.4	2.28	20.2	59.3
15 %	83.2	2.82	27.2	64.3
20 %	79.2	2.68	36.2	65.1
30 %	86.7	2.94	44.5	68.0
40 %	77.7	2.63	45.0	71.2



Figure S12. Fluorescence spectra of 2 (1.5×10^{-5} mol L⁻¹ in MCH, black line) and 1/2 (1.5×10^{-5} mol L⁻¹ for 2 and 5.0×10^{-5} mol L⁻¹ for 1, red line). $\lambda_{ex} = 400$ nm.



Figure S13. Upconversion luminescence spectra of UCNPs (black line, 1 mg/mL) and UCNPs/1/2 (red line, weight ratio of UCNPs/1 is 5:1, [2]/([1]+[2]) = 3:10) in CHCl₃ under excitation at 980 nm laser. Upon mixing UCNPs/1/2 in CHCl₃, the energy transfer only proceeds from UCNPs to 1. The sequential energy transfer from UCNPs *via* 1 to 2 cannot be observed in CHCl₃, because the FRET process is prohibited when 1 and 2 are in the monomeric states in such good solvent.



Figure S14. Upconversion luminescence spectra of UCNPs/1/2 in MCH upon 460 nm light irradiation. Upon irradiating the MCH solution of UCNPs/1/2 with 460 nm light, the original luminescence bands of UCNPs locates at 425–500 nm region gradually increase in their intensity, while the FRET emission band at around 596 nm gradually decreases.

4. Synthetic route to monomer 2



Compounds 3 (200 mg, 0.14 mmol), 4 (224 mg, 0.33 mmol), and CuI (~20 mg) were mixed in CH₂Cl₂/TEA (25 mL, 4: 1, v/v), and stirred at room temperature for 12 hours. After removal of the solvent, the residue was extracted with CH₂Cl₂/H₂O for three times. The combined organic extract was dried over anhydrous Na₂SO₄, and the solvent was removed with a rotary evaporator. The residue was purified by flash column chromatography (petroleum ether/ CH_2Cl_2 , 2 : 1, v/v as the eluent) to afford 2 as a red solid (280 mg, 81%). ¹H NMR (300 MHz, CDCl₃, room temperature) δ (ppm): 7.65 (s, 2H), 7.48 (d, J = 8.5 Hz, 4H), 7.28 (d, J = 8.4 Hz, 4H), 7.22 (s, 2H), 7.04 (s, 4H), 4.15-3.94 (m, 12H), 2.30–2.24 (m, 24H), 1.90–1.81 (m, 7H), 1.72–1.70 (m, 6H), 1.56–1.48 (m, 12H), 1.34-1.14 (m, 72H), 0.96-0.91 (m, 18H), 0.87 (d, J = 6.6 Hz, 36H). ¹³C NMR (75 MHz, CDCl₃, room temperature) δ (ppm): 165.50, 161.75, 153.36, 141.49, 135.20, 131.64, 130.80, 130.22, 125.28, 120.94, 119.89, 105.83, 71.89, 67.86, 39.48, 39.39, 37.63, 37.47, 36.48, 32.06, 29.95, 29.83, 29.77, 29.50, 28.12, 24.87, 22.85, 22.76, 22.74, 19.74, 19.71, 16.66, 16.49, 16.31, 14.27, 8.57. MALDI-TOF-MS m/z: [M + H]⁺, C₁₂₄H₂₀₃N₄O₈P₄Pt₂Se, calculated 2470.3012; found 2470.3284.



Figure S15. ¹H NMR spectrum (300 MHz, CDCl₃, room temperature) of monomer 2.



Figure S16. ¹³C NMR spectrum (75 MHz, CDCl₃, room temperature) of monomer 2.



Figure S17. MALDI-TOF mass spectrum of monomer 2.

5. References

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