

## **Supplementary Information for**

# **Dinuclear Coumarin-Containing Alkynylplatinum(II) Terpyridine Complexes with Supramolecular Assembly-Assisted Photodimerization**

Shishi Fang, Michael Ho-Yeung Chan, and Vivian Wing-Wah Yam\*

Institute of Molecular Functional Materials, State Key Laboratory of Synthetic Chemistry and  
Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong (P. R.  
China)

E-mail: [wwyam@hku.hk](mailto:wwyam@hku.hk); Fax: (852) 28571586; Tel: (852) 28592153

## Experimental Section

**Materials and Reagents.** Potassium tetrachloroplatinate(II) ( $K_2[PtCl_4]$ ) was purchased from Chem. Pur., 98%. Dimethyl sulfoxide (Sigma-Aldrich Co. Ltd., spectrophotometric grade) for spectroscopic studies were used as received without further purification. DMSO- $d_6$  used for NMR experiments were purchased from Cambridge Isotope Laboratories, Inc. All other reagents, unless otherwise specified, were of analytical grade and were used as received. Coumarin-containing terpyridine ligands<sup>1,2</sup> and substituted alkynyl ligand<sup>3</sup> were prepared according to previously reported literature with slight modifications.

### Synthesis of Dinuclear Coumarin-Containing Alkynylplatinum(II) Terpyridine Complexes

**1–6.** The dinuclear coumarin-containing alkynylplatinum(II) terpyridine complexes were synthesized according to modifications of procedures for the synthesis of dinuclear alkynylplatinum(II) terpyridine derivatives previously reported by Yam and coworkers in the literature.<sup>4</sup>

**([C<sub>2</sub>-CM-tpy-Pt]<sub>2</sub>-2TEG-*p*PE3](OTf)<sub>2</sub> (1).** To a solution of 1,4-(HC≡C-C<sub>6</sub>H<sub>4</sub>-1,4-C≡C)<sub>2</sub>-2,5-(OTEG)<sub>2</sub>-C<sub>6</sub>H<sub>2</sub> (26 mg, 0.04 mmol) and [Pt{tpy-C<sub>6</sub>H<sub>4</sub>-(OC<sub>2</sub>H<sub>4</sub>O-(4-Me-CM)-7)-4}Cl]OTf (80 mg, 0.09 mmol) in degassed dimethylformamide (30 ml) containing triethylamine (2 ml) was added a catalytic amount of CuI. The solution was stirred at room temperature in the dark under a nitrogen atmosphere overnight. After removing the solvent, the crude product was purified by the diffusion of diethyl ether vapor into a dichloromethane-chloroform mixture to give a red solid. Yield: 63 mg (66 %). <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ , 298 K):  $\delta$ /ppm = 2.37 (s, 6H, -CH<sub>3</sub>), 3.23 (s, 6H, -OCH<sub>3</sub>), 3.43 (t,  $J$  = 4.5 Hz, 4H, -OCH<sub>2</sub>-), 3.53–3.57 (m, 8H, -OCH<sub>2</sub>-), 3.70 (t,  $J$  = 4.5 Hz, 4H, -OCH<sub>2</sub>-), 3.79 (s, 4H, -OCH<sub>2</sub>-), 4.11 (s, 4H, -OCH<sub>2</sub>-), 4.46 (s, 8H, -OCH<sub>2</sub>-), 6.19 (s,

2H, -COCH-), 6.97–7.00 (m, 4H, -C<sub>6</sub>H<sub>3</sub>-), 7.09 (s, 2H, -C<sub>6</sub>H<sub>2</sub>-), 7.17 (d, *J* = 8.5 Hz, 4H, -C<sub>6</sub>H<sub>4</sub>-), 7.42 (d, *J* = 7.5 Hz, 4H, -C<sub>6</sub>H<sub>4</sub>-), 7.49 (d, *J* = 7.5 Hz, 4H, -C<sub>6</sub>H<sub>4</sub>-), 7.64 (d, *J* = 8.5 Hz, 2H, -C<sub>6</sub>H<sub>3</sub>-), 7.90 (t, *J* = 7.5 Hz, 4H, tpy), 8.10 (d, *J* = 8.5 Hz, 4H, -C<sub>6</sub>H<sub>4</sub>-), 8.48 (t, *J* = 7.5 Hz, 4H, tpy), 8.78 (d, *J* = 7.5 Hz, 4H, tpy), 8.86 (s, 4H, tpy), 9.10 (d, *J* = 5.5 Hz, 4H, tpy). Positive HR-ESI-MS: calcd for [C<sub>106</sub>H<sub>90</sub>N<sub>6</sub>O<sub>16</sub>Pt<sub>2</sub>]<sup>2+</sup> *m/z* = 1046.2850; found: 1046.2879 [M]<sup>2+</sup>; elemental analysis calcd (%) for C<sub>108</sub>H<sub>90</sub>F<sub>6</sub>N<sub>6</sub>O<sub>22</sub>Pt<sub>2</sub>S<sub>2</sub>•CHCl<sub>3</sub>: C 52.13, H 3.65, N 3.35; found: C 51.87, H 3.83, N 3.05.

([C<sub>4</sub>-CM-tpy-Pt]<sub>2</sub>-2TEG-*p*PE3)(OTf)<sub>2</sub> (**2**). The titled complex was synthesized according to the procedure similar to that described for the preparation of **1**, except that [Pt{tpy-C<sub>6</sub>H<sub>4</sub>-(OC<sub>4</sub>H<sub>8</sub>O-(4-Me-CM)-7)-4}Cl]OTf (82 mg, 0.09 mmol) was used in place of [Pt{tpy-C<sub>6</sub>H<sub>4</sub>-(OC<sub>2</sub>H<sub>4</sub>O-(4-Me-CM)-7)-4}Cl]OTf. The product was isolated as a red solid. Yield: 56 mg (57 %). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, 298 K): δ/ppm = 1.93 (s, 8H, -CH<sub>2</sub>-), 2.36 (s, 6H, -CH<sub>3</sub>), 3.23 (s, 6H, -OCH<sub>3</sub>), 3.42 (s, 4H, -OCH<sub>2</sub>-), 3.52–3.56 (m, 8H, -OCH<sub>2</sub>-), 3.70 (s, 4H, -OCH<sub>2</sub>-), 3.78 (s, 4H, -OCH<sub>2</sub>-), 4.12–4.15 (m, 12H, -OCH<sub>2</sub>-), 6.17 (s, 2H, -COCH-), 6.92 (s, 4H, -C<sub>6</sub>H<sub>3</sub>-), 7.10 (s, 6H, -C<sub>6</sub>H<sub>2</sub>- and -C<sub>6</sub>H<sub>4</sub>-), 7.42 (d, *J* = 8.0 Hz, 4H, -C<sub>6</sub>H<sub>4</sub>-), 7.49 (d, *J* = 8.0 Hz, 4H, -C<sub>6</sub>H<sub>4</sub>-), 7.62 (d, *J* = 9.0 Hz, 2H, -C<sub>6</sub>H<sub>3</sub>-), 7.88 (t, *J* = 7.5 Hz, 4H, tpy), 8.07 (d, *J* = 8.0 Hz, 4H, -C<sub>6</sub>H<sub>4</sub>-), 8.48 (t, *J* = 7.5 Hz, 4H, tpy), 8.77 (d, *J* = 7.5 Hz, 4H, tpy), 8.83 (s, 4H, tpy), 9.08 (d, *J* = 5.5 Hz, 4H, tpy). Positive HR-ESI-MS: calcd for [C<sub>110</sub>H<sub>98</sub>N<sub>6</sub>O<sub>16</sub>Pt<sub>2</sub>]<sup>2+</sup> *m/z* = 1074.3164; found: 1074.3180 [M]<sup>2+</sup>; elemental analysis calcd (%) for C<sub>112</sub>H<sub>98</sub>F<sub>6</sub>N<sub>6</sub>O<sub>22</sub>Pt<sub>2</sub>S<sub>2</sub>•CH<sub>2</sub>Cl<sub>2</sub>: C 53.58, H 3.98, N 3.32; found: C 53.49, H 3.82, N 3.16.

([C<sub>6</sub>-CM-tpy-Pt]<sub>2</sub>-2TEG-*p*PE3)(OTf)<sub>2</sub> (**3**). The titled complex was synthesized according to the procedure similar to that described for the preparation of **1**, except that [Pt{tpy-C<sub>6</sub>H<sub>4</sub>-(OC<sub>6</sub>H<sub>12</sub>O-(4-Me-CM)-7)-4}Cl]OTf (84 mg, 0.09 mmol) was used in place of [Pt{tpy-C<sub>6</sub>H<sub>4</sub>-

(OC<sub>2</sub>H<sub>4</sub>O-(4-Me-CM)-7)-4}Cl]OTf. The product was isolated as a red solid. Yield: 51 mg (51 %). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, 298 K): δ/ppm = 1.52 (s, 8H, -CH<sub>2</sub>-), 1.79 (s, 8H, -CH<sub>2</sub>-), 2.36 (s, 6H, -CH<sub>3</sub>), 3.23 (s, 6H, -OCH<sub>3</sub>), 3.42 (t, *J* = 5.0 Hz, 4H, -OCH<sub>2</sub>-), 3.52–3.57 (m, 8H, -OCH<sub>2</sub>-), 3.71 (t, *J* = 5.0 Hz, 4H, -OCH<sub>2</sub>-), 3.80 (s, 4H, -OCH<sub>2</sub>-), 4.08 (t, *J* = 5.0 Hz, 8H, -OCH<sub>2</sub>-), 4.15 (s, 4H, -OCH<sub>2</sub>-), 6.17 (s, 2H, -COCH-), 6.92–6.94 (m, 4H, -C<sub>6</sub>H<sub>3</sub>-), 7.10 (d, *J* = 7.5 Hz, 4H, -C<sub>6</sub>H<sub>4</sub>-), 7.14 (s, 2H, -C<sub>6</sub>H<sub>2</sub>-), 7.44 (d, *J* = 8.0 Hz, 4H, -C<sub>6</sub>H<sub>4</sub>-), 7.51 (d, *J* = 8.0 Hz, 4H, -C<sub>6</sub>H<sub>4</sub>-), 7.63 (d, *J* = 9.0 Hz, 2H, -C<sub>6</sub>H<sub>3</sub>-), 7.90 (t, *J* = 7.5 Hz, 4H, tpy), 8.07 (d, *J* = 7.5 Hz, 4H, -C<sub>6</sub>H<sub>4</sub>-), 8.50 (t, *J* = 7.5 Hz, 4H, tpy), 8.79 (d, *J* = 7.5 Hz, 4H, tpy), 8.86 (s, 4H, tpy), 9.10 (d, *J* = 5.5 Hz, 4H, tpy). Positive HR-ESI-MS: calcd for [C<sub>114</sub>H<sub>106</sub>N<sub>6</sub>O<sub>16</sub>Pt<sub>2</sub>]<sup>2+</sup> *m/z* = 1102.3477; found: 1102.3495 [M]<sup>2+</sup>; elemental analysis calcd (%) for C<sub>116</sub>H<sub>106</sub>F<sub>6</sub>N<sub>6</sub>O<sub>22</sub>Pt<sub>2</sub>S<sub>2</sub>: C 55.63, H 4.27, N 3.36; found: C 55.84, H 3.97, N 3.08.

([{C<sub>2</sub>-CM-tpy-Pt}<sub>2</sub>-*p*PE3](OTf)<sub>2</sub> (**4**). The titled complex was synthesized according to the procedure similar to that described for the preparation of **1**, except that 1,4-(HC≡C-C<sub>6</sub>H<sub>4</sub>-1,4-C≡C)<sub>2</sub>-C<sub>6</sub>H<sub>4</sub> (16 mg, 0.05 mmol) was used in place of 1,4-(HC≡C-C<sub>6</sub>H<sub>4</sub>-1,4-C≡C)<sub>2</sub>-2,5-(OTEG)<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>. The product was isolated as a red solid. Yield: 62 mg (60 %). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, 298 K): δ/ppm = 2.35 (s, 6H, -CH<sub>3</sub>), 4.39–4.42 (m, 8H, -OCH<sub>2</sub>-), 6.17 (s, 2H, -COCH-), 6.92–6.95 (m, 4H, -C<sub>6</sub>H<sub>3</sub>-), 7.04 (s, 4H, -C<sub>6</sub>H<sub>4</sub>-), 7.42–7.49 (m, 12H, -C<sub>6</sub>H<sub>4</sub>-), 7.58 (d, *J* = 8.5 Hz, 2H, -C<sub>6</sub>H<sub>3</sub>-), 7.82–7.95 (m, 8H, -C<sub>6</sub>H<sub>4</sub>- and tpy), 8.34 (s, 4H, tpy), 8.61 (s, 8H, tpy), 8.98 (s, 4H, tpy). Positive HR-ESI-MS: calcd for [C<sub>92</sub>H<sub>62</sub>N<sub>6</sub>O<sub>8</sub>Pt<sub>2</sub>]<sup>2+</sup> *m/z* = 884.1958; found: 884.1918 [M]<sup>2+</sup>; elemental analysis calcd (%) for C<sub>94</sub>H<sub>62</sub>F<sub>6</sub>N<sub>6</sub>O<sub>14</sub>Pt<sub>2</sub>S<sub>2</sub>•CHCl<sub>3</sub>: C 53.00, H 3.00, N 3.90; found: C 52.76, H 2.76, N 3.99.

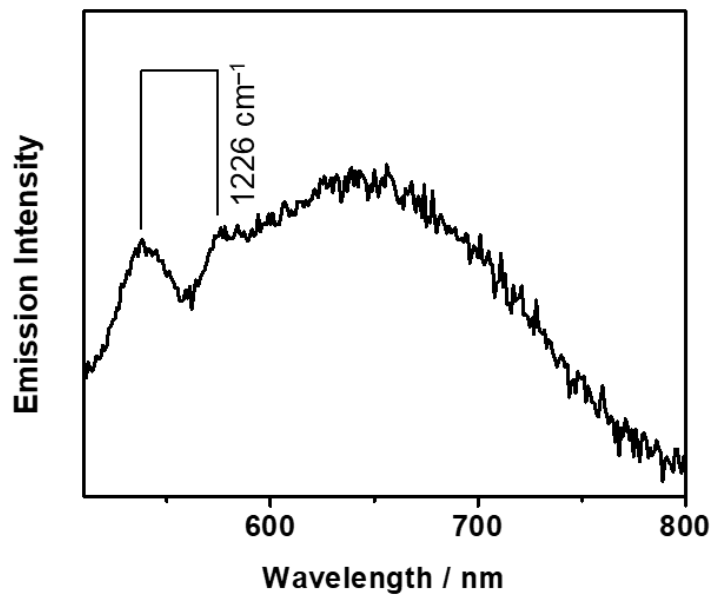
([{C<sub>2</sub>-CM-tpy-Pt}<sub>2</sub>-2C<sub>4</sub>-*p*PE3](OTf)<sub>2</sub> (**5**). The titled complex was synthesized according to the procedure similar to that described for the preparation of **1**, except that 1,4-(HC≡C-C<sub>6</sub>H<sub>4</sub>-1,4-

$\text{C}\equiv\text{C})_2\text{-}2,5\text{-(OC}_4\text{H}_9)_2\text{-C}_6\text{H}_2$  (24 mg, 0.05 mmol) was used in place of  $1,4\text{-(HC}\equiv\text{C-C}_6\text{H}_4\text{-}1,4\text{-C}\equiv\text{C})_2\text{-}2,5\text{-(OTEG)}_2\text{-C}_6\text{H}_2$ . The product was isolated as a red solid. Yield: 65 mg (59 %).  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ , 298 K):  $\delta/\text{ppm} = 0.99$  (t,  $J = 7.5$  Hz, 6H,  $-\text{CH}_3$ ), 1.49–1.53 (m, 4H,  $-\text{CH}_2-$ ), 1.70 (s, 4H,  $-\text{CH}_2-$ ), 2.36 (s, 6H,  $-\text{CH}_3$ ), 3.94 (s, 4H,  $-\text{OCH}_2-$ ), 4.43 (s, 8H,  $-\text{OCH}_2-$ ), 6.18 (s, 2H,  $-\text{COCH-}$ ), 6.95–7.01 (m, 6H,  $-\text{C}_6\text{H}_2-$  and  $-\text{C}_6\text{H}_3-$ ), 7.13 (s, 4H,  $-\text{C}_6\text{H}_4-$ ), 7.38 (d,  $J = 8.0$  Hz, 4H,  $-\text{C}_6\text{H}_4-$ ), 7.46 (d,  $J = 8.0$  Hz, 4H,  $-\text{C}_6\text{H}_4-$ ), 7.61 (d,  $J = 7.5$  Hz, 2H,  $-\text{C}_6\text{H}_3-$ ), 7.86 (s, 4H, tpy), 8.04 (s, 4H,  $-\text{C}_6\text{H}_4-$ ), 8.44 (s, 4H, tpy), 8.71–8.78 (m, 8H, tpy), 9.04 (s, 4H, tpy). Positive HR-ESI-MS: calcd for  $[\text{C}_{100}\text{H}_{78}\text{N}_6\text{O}_{10}\text{Pt}_2]^{2+}$   $m/z = 956.2533$ ; found: 956.2577  $[\text{M}]^{2+}$ ; elemental analysis calcd (%) for  $\text{C}_{102}\text{H}_{78}\text{F}_6\text{N}_6\text{O}_{16}\text{Pt}_2\text{S}_2\cdot\text{CH}_2\text{Cl}_2$ : C 53.06, H 3.42, N 3.60; found: C 53.29, H 3.41, N 3.83.

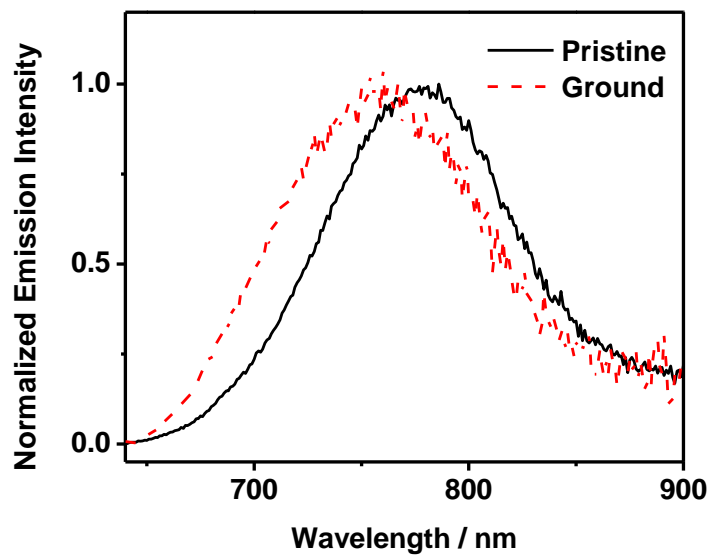
**( $[\{\text{C}_2\text{-CM-tpy-Pt}\}_2\text{-}p\text{PE}](\text{OTf})_2$ ) (6).** The titled complex was synthesized according to the procedure similar to that described for the preparation of **1**, except that  $\text{HC}\equiv\text{C-C}_6\text{H}_4\text{-}1,4\text{-C}\equiv\text{CH}$  (8.0 mg, 0.06 mmol) was used in place of  $1,4\text{-(HC}\equiv\text{C-C}_6\text{H}_4\text{-}1,4\text{-C}\equiv\text{C})_2\text{-}2,5\text{-(OTEG)}_2\text{-C}_6\text{H}_2$ . The product was isolated as a red solid. Yield: 69 mg (62 %).  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ , 298 K):  $\delta/\text{ppm} = 2.32$  (s, 6H,  $-\text{CH}_3$ ), 4.46 (s, 8H,  $-\text{OCH}_2-$ ), 6.13 (s, 2H,  $-\text{COCH-}$ ), 6.90–6.93 (m, 4H,  $-\text{C}_6\text{H}_3-$ ), 7.11 (s, 4H,  $-\text{C}_6\text{H}_4-$ ), 7.36 (s, 4H,  $-\text{C}_6\text{H}_4-$ ), 7.56 (d,  $J = 8.0$  Hz, 2H,  $-\text{C}_6\text{H}_3-$ ), 7.85 (s, 4H, tpy), 8.00 (s, 4H,  $-\text{C}_6\text{H}_4-$ ), 8.38 (s, 4H, tpy), 8.68–8.75 (m, 8H, tpy), 9.02 (s, 4H, tpy). Positive HR-ESI-MS: calcd for  $[\text{C}_{76}\text{H}_{54}\text{N}_6\text{O}_8\text{Pt}_2]^{2+}$   $m/z = 784.1644$ ; found: 784.1604  $[\text{M}]^{2+}$ ; elemental analysis calcd (%) for  $\text{C}_{78}\text{H}_{54}\text{F}_6\text{N}_6\text{O}_{14}\text{Pt}_2\text{S}_2\cdot\text{CH}_2\text{Cl}_2$ : C 48.60, H 2.89, N 4.30; found: C 48.36, H 3.06, N 4.57.

**Photophysical Measurements and Instrumentation.**  $^1\text{H NMR}$  spectra were recorded on a Bruker Ascend 500 (500 MHz) Fourier-transform NMR spectrometer with chemical shifts reported relative to tetramethylsilane,  $(\text{CH}_3)_4\text{Si}$ . Positive-ion high-resolution electrospray

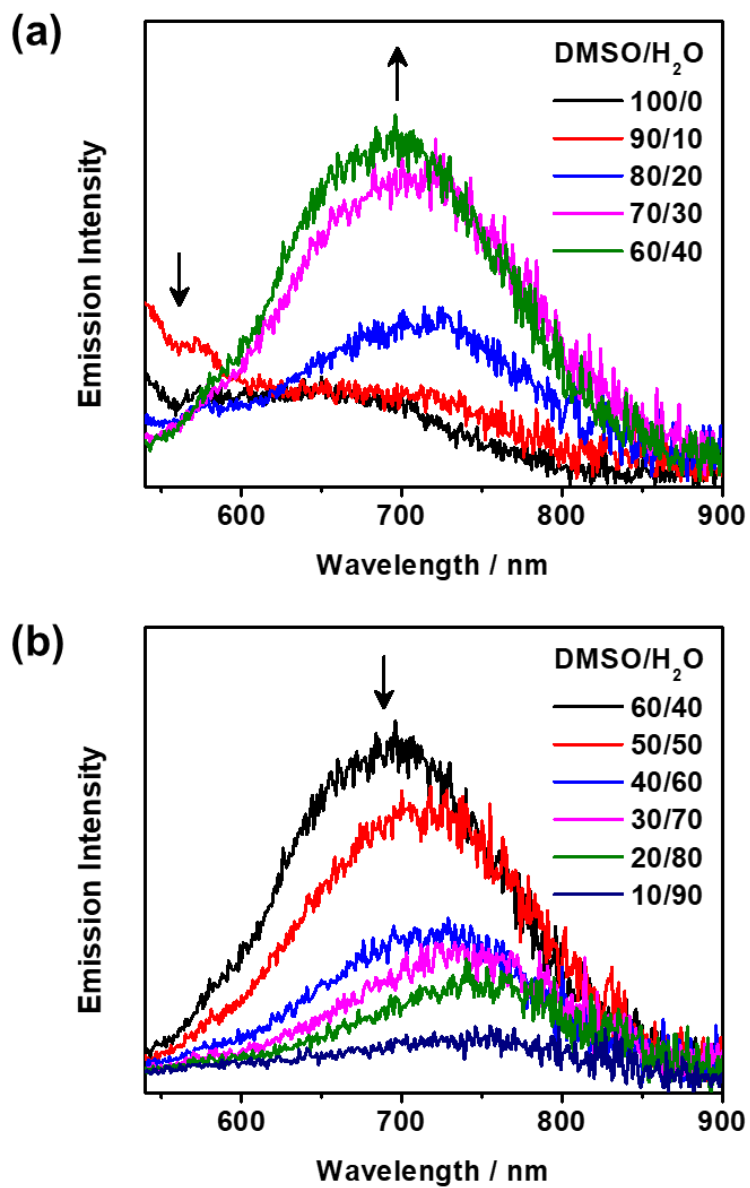
ionization (HR-ESI) mass spectra were recorded on a Bruker maXis II High Resolution Liquid Chromatography Quadrupole-Time of Flight (LC-QTOF) spectrometer. Elemental analyses were performed with a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences, Beijing, P. R. China. UV–Vis absorption spectra for variable-concentration and -temperature measurements were recorded using a Varian Cary 50 UV–vis spectrophotometer. The temperature was maintained by a Varian Cary single-cell Peltier thermostat. UV–Vis absorption spectral changes during photoirradiation were recorded on a Cary 8454 spectrophotometer. Photoirradiations were carried out with a 300 W Oriel Corporation Model 60011 Xe (ozone-free) lamp with an Applied Photophysics F 3.4 monochromator to select the monochromatic light. Transmission electron microscopy (TEM) experiments were performed on a Philips CM100 TEM equipped with a TENGRA 2.3 K × 2.3 K camera for digital imaging. All measurements were conducted at room temperature unless specified otherwise.



**Figure S1.** Emission spectrum of **6** in degassed DMSO solution at 298 K.

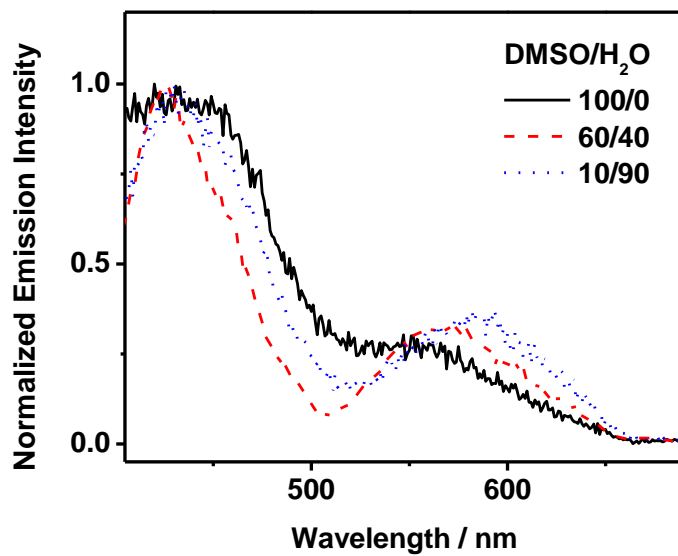


**Figure S2.** Normalized emission spectra of **2** in the solid state of different forms at 298 K.

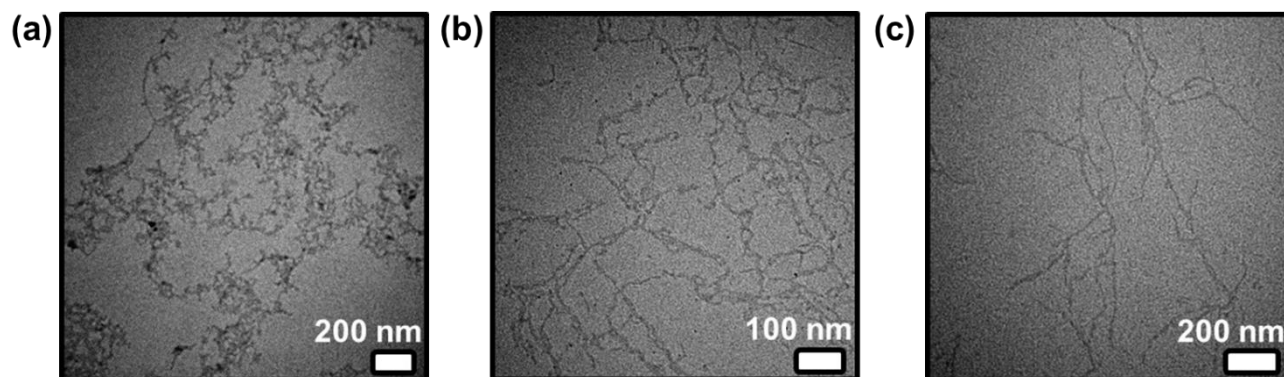


**Figure S3.** Emission spectral changes of **1** in DMSO solutions upon increasing water content from (a) 0 to 40 % and (b) 40 to 90 % at the concentration regime of  $10^{-5}$  M.

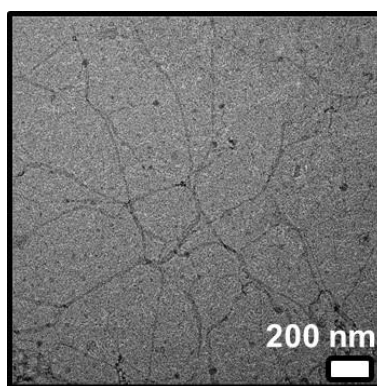




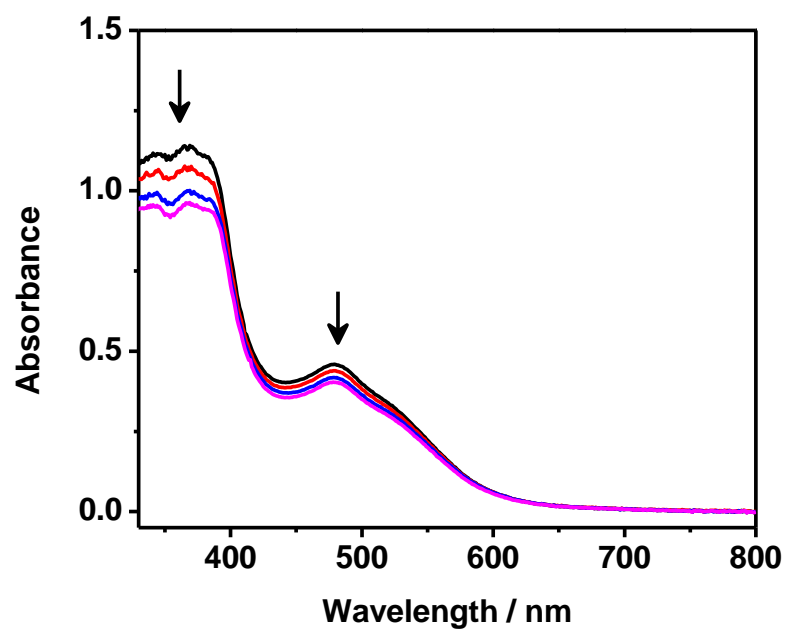
**Figure S4.** Normalized excitation spectra of **1** in DMSO solutions upon increasing water content from 0 to 40 and to 90 % monitored at 700 nm.



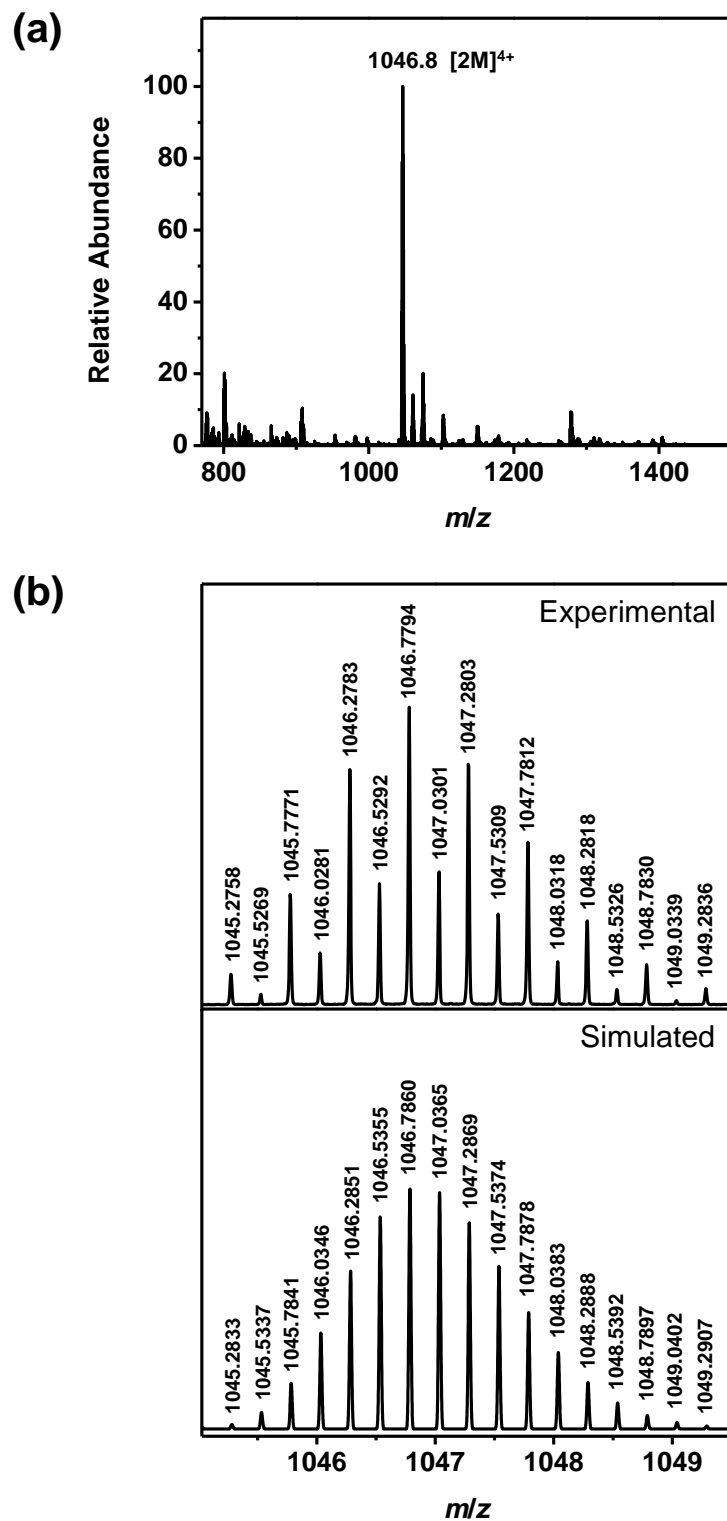
**Figure S5.** TEM images prepared from (a) **1**, (b) **2** and (c) **3** in water–DMSO (90:10) mixture.



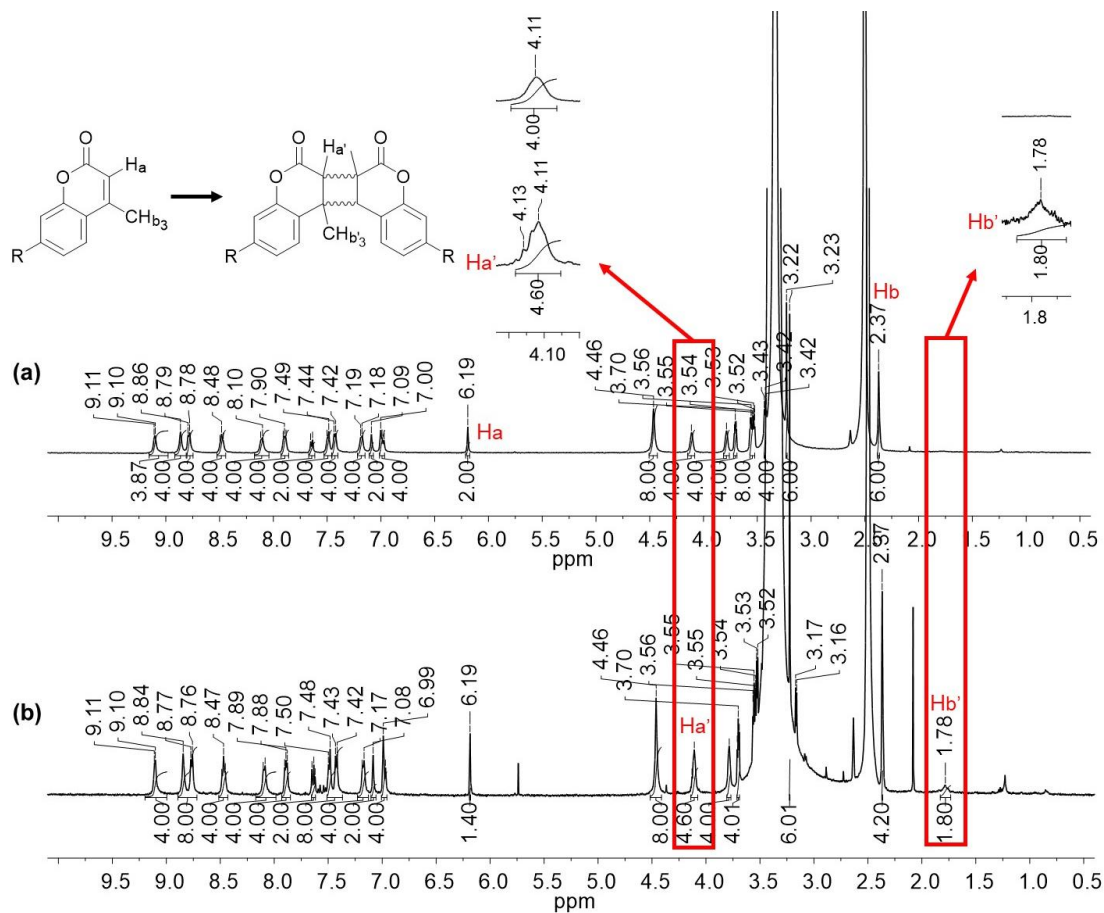
**Figure S6.** A TEM image prepared from **2** in water–DMSO (30:70) mixture.



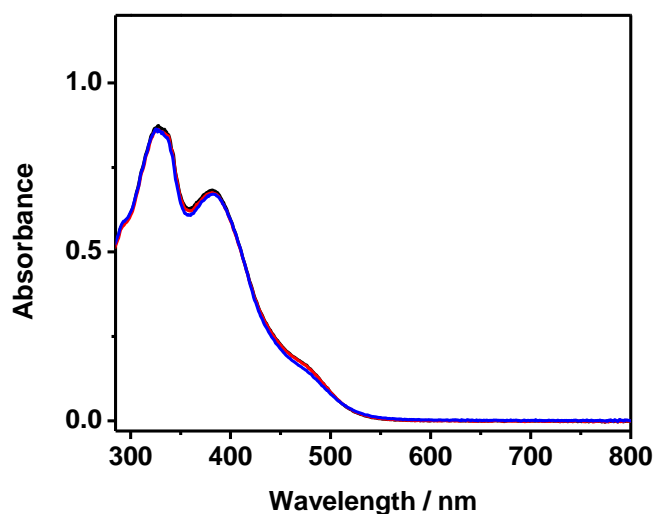
**Figure S7.** UV-Vis absorption spectral changes of **4** in degassed water-DMSO (90:10) mixtures upon photoirradiation at 365 nm at 298 K.



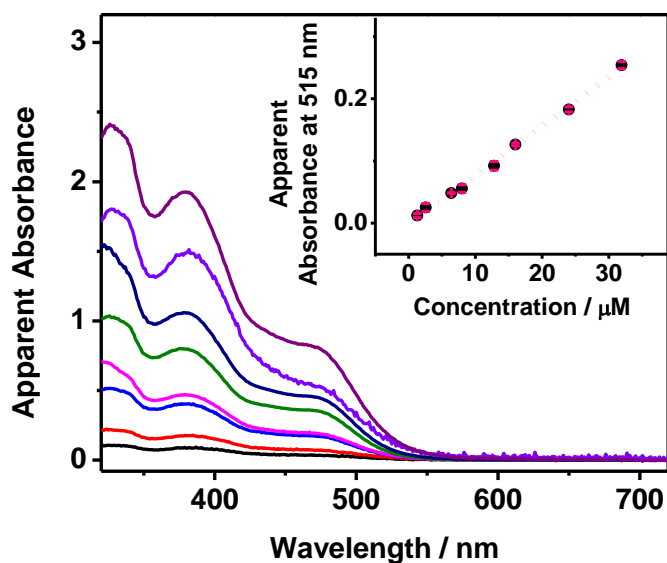
**Figure S8.** (a) High-resolution ESI-mass spectrum of **1** after photoirradiation. (b) Expanded ion cluster [2M]<sup>4+</sup> of photodimer of **1** and the corresponding simulated isotopic pattern.



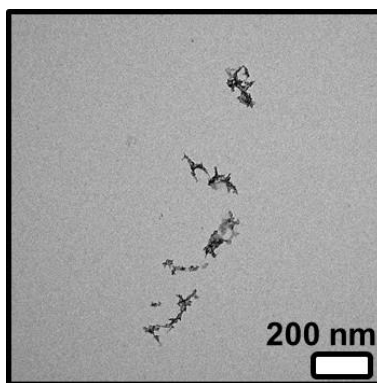
**Figure S9.**  $^1\text{H}$  NMR spectra recorded in  $\text{DMSO-}d_6$  for **1** (a) before and (b) after photoirradiation at 365 nm in degassed 90 %  $\text{D}_2\text{O-DMSO-}d_6$  mixtures at 298 K. The insets show the expanded  $^1\text{H}$  NMR spectra at the aliphatic region.



**Figure S10.** UV–Vis absorption spectral changes of **1** in degassed DMSO solution upon photoirradiation at 365 nm at 298 K.



**Figure S11.** Concentration-dependent UV–vis absorption spectra of **3** in DMSO solution in the concentration range of  $1.28 \times 10^{-6}$  to  $3.19 \times 10^{-5}$  M. Inset: Plot of apparent absorbance against concentration with error bars, monitored at 515 nm. The apparent absorbance values were obtained by correcting to 1-cm path length equivalence.



**Figure S12.** A TEM image prepared from **2** in water–DMSO (90:10) mixture after photoirradiation.

**Table S1.** Electronic absorption data of complexes **1–6** in DMSO solutions

Complex	Absorption	
	$\lambda_{\text{max}} / \text{nm}$ ( $\epsilon / \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ )	
$[\{\text{C}_2\text{-CM-tpy-Pt}\}_2\text{-2TEG-}p\text{PE3}]\text{-(OTf)}_2$ ( <b>1</b> )	378sh (54000), 469 (22300)	
$[\{\text{C}_4\text{-CM-tpy-Pt}\}_2\text{-2TEG-}p\text{PE3}]\text{-(OTf)}_2$ ( <b>2</b> )	378sh (68500), 469 (31800)	
$[\{\text{C}_6\text{-CM-tpy-Pt}\}_2\text{-2TEG-}p\text{PE3}]\text{-(OTf)}_2$ ( <b>3</b> )	379sh (67500), 469 (27800)	
$[\{\text{C}_2\text{-CM-tpy-Pt}\}_2\text{-}p\text{PE3}]\text{-(OTf)}_2$ ( <b>4</b> )	343sh (91300), 368sh (81400), 471 (33000)	
$[\{\text{C}_2\text{-CM-tpy-Pt}\}_2\text{-2C}_4\text{-}p\text{PE3}]\text{-(OTf)}_2$ ( <b>5</b> )	377sh (63800), 468 (29900)	
$[\{\text{C}_2\text{-CM-tpy-Pt}\}_2\text{-}p\text{PE}]\text{-(OTf)}_2$ ( <b>6</b> )	337sh (60000), 424sh (17100), 485 (16900)	

**Table S2.** Emission data of complexes **1–6**

Complex	Emission		
	Medium ( $T / \text{K}$ )	$\lambda_{\text{em}} / \text{nm}$ ( $\tau_0 / \mu\text{s}$ )	$\phi_{\text{lum}}^a$
$[\{\text{C}_2\text{-CM-tpy-Pt}\}_2\text{-2TEG-}p\text{PE3}]\text{-(OTf)}_2$ ( <b>1</b> )	DMSO (298)	– <sup>d</sup>	– <sup>d</sup>
	Solid (298)	782 (0.12)	
	Solid (77)	783 (0.26)	
	Glass <sup>c</sup> (77)	663 (0.30), <sup>b</sup> 753 (0.22)	

<b>(2)</b>	[{C <sub>4</sub> -CM-tpy-Pt} <sub>2</sub> -2TEG- <i>p</i> PE3]-(OTf) <sub>2</sub>	DMSO (298)	– <sup>d</sup>	– <sup>d</sup>
		Solid (298)	777 (0.11)	
		Solid (77)	780 (0.35)	
		Glass <sup>c</sup> (77)	676 (0.27), <sup>b</sup> 743 (0.26)	
<b>(3)</b>	[{C <sub>6</sub> -CM-tpy-Pt} <sub>2</sub> -2TEG- <i>p</i> PE3]-(OTf) <sub>2</sub>	DMSO (298)	– <sup>d</sup>	– <sup>d</sup>
		Solid (298)	770 (0.11)	
		Solid (77)	765 (0.32)	
		Glass <sup>c</sup> (77)	675 (0.25), <sup>b</sup> 742 (0.22)	
<b>(4)</b>	[{C <sub>2</sub> -CM-tpy-Pt} <sub>2</sub> - <i>p</i> PE3](OTf) <sub>2</sub>	DMSO (298)	539 (0.40), <sup>b</sup> 656 (0.34)	< 10 <sup>-3</sup>
		Solid (298)	751 (0.10)	
		Solid (77)	757 (0.29)	
		Glass <sup>c</sup> (77)	749 (0.26)	
<b>(5)</b>	[{C <sub>2</sub> -CM-tpy-Pt} <sub>2</sub> -2C <sub>4</sub> - <i>p</i> PE3]-(OTf) <sub>2</sub>	DMSO (298)	– <sup>d</sup>	– <sup>d</sup>
		Solid (298)	778 (<0.1)	
		Solid (77)	781 (0.20)	
		Glass <sup>c</sup> (77)	688 (0.25), <sup>b</sup> 764 (0.23)	
<b>(6)</b>	[{C <sub>2</sub> -CM-tpy-Pt} <sub>2</sub> - <i>p</i> PE](OTf) <sub>2</sub>	DMSO (298)	538 (0.39), <sup>b</sup> 650 (0.25)	2.2×10 <sup>-3</sup>
		Solid (298)	716 (<0.1)	
		Solid (77)	704 (0.75)	
		Glass <sup>c</sup> (77)	684 (0.61), <sup>b</sup> 739 (0.30)	

<sup>a</sup> Measured at room temperature using a degassed aqueous solution of [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> as the reference.

<sup>b</sup> Vibronic-structured emission with vibrational progressional spacings of about 1000–1300 cm<sup>-1</sup>.

<sup>c</sup> Measured in EtOH–MeOH (4:1 v/v).

<sup>d</sup> Non-emissive.

## References

---

- 1 Duan, Y.-C.; Ma, Y.-C.; Zhang, E.; Shi, X.-J.; Wang, M.-M.; Ye, X.-W.; Liu, H.-M. Design and synthesis of novel 1,2,3-triazole-dithiocarbamate hybrids as potential anticancer agents. *Eur. J. Med. Chem.* **2013**, *62*, 11–19.
- 2 Yam, V. W.-W.; Tang, R. P.-L.; Wong, K. M.-C.; Cheung, K.-K. Synthesis, luminescence, electrochemistry, and ion-binding studies of platinum(II) terpyridyl acetylide complexes. *Organometallics*, **2001**, *20*, 4476–4482.
- 3 Bunz, U. H. F. Poly(aryleneethynylene)s: Syntheses, Properties, Structures, and Applications. *Chem. Rev.* **2000**, *100*, 1605–1644.
- 4 Leung, S. Y.-L.; Wong, K. M.-C.; Yam, V. W.-W. Self-assembly of alkynylplatinum(II) terpyridine amphiphiles into nanostructures via steric control and metal–metal interactions. *Proc. Natl. Acad. Sci. USA* **2016**, *113*, 2845–2850.