

Tunable Self-Assembly Properties of Amphiphilic  
Phosphole Alkynylgold(I) Complexes Through Variation  
of the Extent of Aromatic  $\pi$ -Surface at the Alkynyl  
Moieties

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**Supporting Information**

## **Experimental Section**

**Materials and Reagents.** All commercially available reagents were of analytical grade and were used as received. All solvents were purified and distilled using standard procedures before use. 1-Methoxy-5-phenyl-5*H*-dibenzophosphole 5-oxide,<sup>1</sup> [Au(tht)Cl] (tht = tetrahydrothiophene),<sup>2</sup> 3-ethynylperylene<sup>3</sup> and [(R-C≡C)Au]<sub>∞</sub><sup>4</sup> were synthesized according to literature procedures. **Caution:** *The alkynylgold(I) polymers are potentially explosive and should be handled with great caution.*

**Physical Measurements and Instrumentation.** <sup>1</sup>H NMR spectra were recorded on a Bruker AV 400 NMR spectrometer with chemical shifts reported relative to tetramethylsilane, Me<sub>4</sub>Si. <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded either on a Bruker AV 400 or a Bruker DRX-500 NMR spectrometer with chemical shifts reported relative to 85 % phosphoric acid. Electron impact (EI) and positive FAB mass spectra were recorded using a Thermo Scientific DFS High Resolution Magnetic Sector Mass Spectrometer. Elemental analyses for the metal complexes were performed on the Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences in Beijing. UV-Vis spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer. Steady-state excitation and emission spectra at room temperature and at 77 K were recorded on a Spex Fluorolog-3 model FL3-211 fluorescence spectrofluorometer equipped with an R2658P PMT detector. Photophysical measurements in low temperature glass were carried out with the sample solution loaded in a quartz tube inside a quartz-walled Dewar flask. Liquid nitrogen was placed into the Dewar flask for low temperature (77 K) photophysical measurements. Excited-state lifetime measurements were performed using a conventional laser system. The excitation source used was the 355-nm output (third harmonic, 8 ns) of a Spectra-Physics Quanta-Ray Q-switched GCR-150 pulsed Nd:YAG laser (10 Hz). Luminescence quantum yields were measured by the optical dilute method reported by Demas and Crosby.<sup>5</sup> A degassed aqueous solution of quinine sulfate in 1.0 N sulfuric acid (excitation wavelength = 365 nm,  $\Phi = 0.546$ ) was used as the reference and corrected for the refractive index of the solution.<sup>6</sup> All solutions for emission lifetime and luminescence quantum yield studies were degassed on a high-vacuum line in a two-compartment cell consisting of a 10-mL Pyrex bulb and a 1-cm path length quartz cuvette and sealed from the atmosphere by a Bibby Rotaflo HP6 Teflon stopper. The solutions were rigorously degassed with at least four successive freeze-pump-thaw cycles.

**Electron Microscopy.** TEM experiments were performed on a Philips CM100 transmission electron microscope. They were conducted at the Electron Microscope Unit of The University of Hong Kong. The samples were prepared by dropping a few drops of solutions onto a carbon-coated copper grid. Slow evaporation of solvents in air for 10 min was allowed before placing the samples into the instrument.

**Atomic Force Microscopy.** The AFM images were obtained using a Digital Instruments Nanoscope III AFM with a scan rate of  $1.0 \mu\text{m s}^{-1}$ . The sample was prepared by dropping a few drops of solution onto a silicon wafer which was then dried under vacuum before the measurement.

**Curve-Fitting with the Nucleation-Elongation Equilibrium Model.** The nucleation-elongation model for solvent-dependent self-assembly was reported recently by Meijer and coworkers.<sup>7</sup> In this equilibrium model, the Gibbs free energy gain upon monomer addition  $\Delta G^{0'}$  is linearly correlated with the good solvent volume fraction  $f$ :

$$\Delta G^{0'} = \Delta G^0 + m \cdot f$$

where  $\Delta G^0$  is the Gibbs free energy gain upon monomer addition in a pure poor solvent and  $m$  is the parameter showing the dependence of  $\Delta G^{0'}$  on  $f$ .

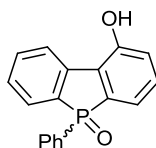
The normalized degree of aggregation was deduced from the changes in UV-vis absorption band maxima (**2**, *ca.* 335 nm; **3**, *ca.* 334 nm; **4**, *ca.* 383 nm; **5**, *ca.* 471 nm),

$$\text{normalized degree of aggregation } (f) = \frac{\text{Abs } (f) - \text{Abs } (f=0)}{\text{Abs } (f=1) - \text{Abs } (f=0)}$$

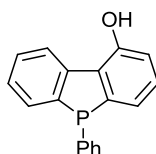
where  $f$  is the DMSO volume fraction.

The simulations and the curve-fittings with the equilibrium model were performed using Matlab R2013a under an isodesmic system.<sup>7</sup>

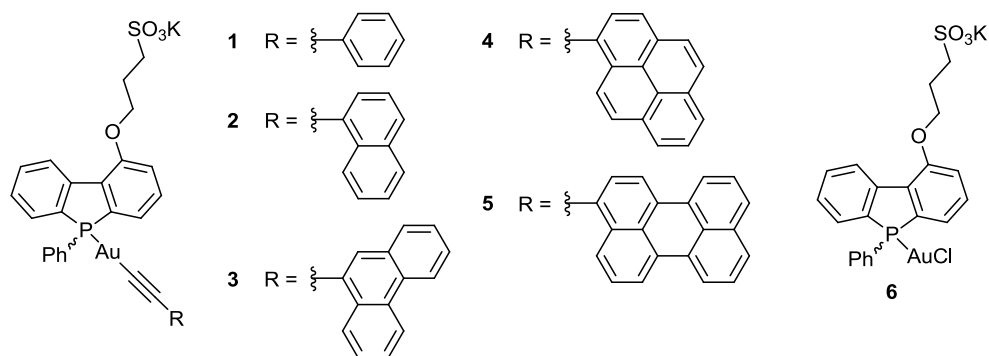
## Synthesis and Characterization.



**1-Hydroxy-5-phenyl-5H-dibenzophosphole 5-oxide.** To a stirred solution of 1-methoxy-5-phenyl-5H-dibenzophosphole 5-oxide (1.1 g, 3.59 mmol) in dry dichloromethane (50 ml) at  $-78\text{ }^{\circ}\text{C}$  was added dropwise boron tribromide solution (1.0 M in dichloromethane, 18 ml, 18 mmol). The resulting mixture was gradually raised to room temperature and stirred for another 24 hr under nitrogen. The reaction was quenched by pouring the reaction mixture to ice-water slowly. The mixture was extracted with ethyl acetate and the combined organic layer was dried over anhydrous magnesium sulfate, filtered and evaporated to dryness under reduced pressure. The crude product was then purified by flash column chromatography on silica gel using ethyl acetate as eluent to give the product as a white solid. Yield: 0.26 g (25 %).  $^1\text{H}$  NMR (400 MHz,  $[\text{D}_6]$ -DMSO, 298 K):  $\delta$  7.11–7.18 (m, 2H, phenyl), 7.30 (td,  $J = 7.5, 4.4$  Hz, 1H), 7.40 (td,  $J = 7.5, 3.4$  Hz, 1H), 7.43–7.59 (m, 5H, phenyl), 7.61–7.73 (m, 2H, phenyl), 8.42 (dd,  $J = 7.8, 2.4$  Hz, 1H, phenyl), 10.77 (s, 1H, -OH).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $[\text{D}_6]$ -DMSO, 298 K):  $\delta$  31.89. Positive EI-MS:  $m/z$  292 ( $[\text{M}]^+$ ).



**1-Hydroxy-5-phenyl-5H-dibenzophosphole.** To a stirred solution of 1-hydroxy-5-phenyl-5H-dibenzophosphole 5-oxide (0.16 g, 0.55 mmol) in degassed dioxane (15 ml) was added phenylsilane (0.2 ml, 1.62 mmol). The mixture was refluxed overnight under nitrogen. After removal of solvent and the excess phenylsilane under reduced pressure, water was added to the residual oil. The mixture was extracted with ethyl acetate and the combined organic layer was dried over anhydrous magnesium sulfate, filtered and evaporated to dryness under reduced pressure. The crude product was then purified by flash column chromatography on silica gel using hexane–ethyl acetate (4:1 v/v) as eluent to give the product as a colourless oil. Yield: 0.15 g (99 %).  $^1\text{H}$  NMR (400 MHz,  $[\text{D}_6]$ -DMSO, 353 K):  $\delta$  6.96–7.03 (m, 1H, phenyl), 7.18–7.24 (m, 2H, phenyl), 7.26–7.34 (m, 6H, phenyl), 7.44–7.50 (m, 1H, phenyl), 7.69–7.76 (m, 1H, phenyl), 8.55 (d,  $J = 7.9$  Hz, 1H, phenyl), 10.05 (s, 1H, -OH).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $[\text{D}_6]$ -DMSO, 353 K):  $\delta$  -8.86. Positive EI-MS:  $m/z$  276 ( $[\text{M}]^+$ ).



**Complex 1.** To a stirred solution of 1-hydroxy-5-phenyl-5*H*-dibenzophosphole (78 mg, 0.28 mmol) in degassed DMSO (5 ml) was added 1,3-propanesultone (34 mg, 0.28 mmol) and then KO<sup>t</sup>Bu (32 mg, 0.28 mmol). The mixture was stirred at 55 °C overnight. After removal of solvent under reduced pressure, acetone was added to precipitate out the white solid which was then washed with acetone and diethyl ether under inert atmosphere. After the white solid was dried under vacuum, it was dissolved in degassed DCM–MeOH (1:3 v/v, 60 ml). To the stirred solution was added [(C<sub>6</sub>H<sub>5</sub>-C≡C)Au]<sub>∞</sub> (84 mg, 0.28 mmol). The mixture was stirred at room temperature under nitrogen for 3 hr. The solution was filtered and evaporated to dryness under reduced pressure. Subsequent recrystallization from a minimum amount of DCM–MeOH (1:3 v/v) yielded the complex a yellow solid. Yield: 68 mg (33 %). <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]-DMSO, 298 K): δ 2.16–2.29 (m, 2H, -CH<sub>2</sub>-), 2.67 (t, *J* = 7.2 Hz, 2H, -CH<sub>2</sub>SO<sub>3</sub>), 4.36 (t, *J* = 5.9 Hz, 2H, -OCH<sub>2</sub>-), 7.02–7.63 (m, 14H, phenyl), 7.72 (t, *J* = 7.5 Hz, 1H, phenyl), 7.82–8.02 (m, 1H, phenyl), 8.54 (d, *J* = 7.8 Hz, 1H, phenyl). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, [D<sub>6</sub>]-DMSO, 298 K): δ 36.45. Negative FAB-MS: *m/z* 694 ([M–K]<sup>–</sup>). Elemental analysis calcd (%) for C<sub>29</sub>H<sub>23</sub>AuKO<sub>4</sub>PS•1.5H<sub>2</sub>O: C, 45.73; H, 3.44; found: C, 45.61; H, 3.29.

**Complex 2.** The procedure was similar to that used to prepare **1**, except that [(C<sub>10</sub>H<sub>7</sub>-C≡C)Au]<sub>∞</sub> (91 mg, 0.26 mmol) was used in place of [(C<sub>6</sub>H<sub>5</sub>-C≡C)Au]<sub>∞</sub>. The product was isolated as a yellow solid. Yield: 67 mg (33 %). <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]-DMSO, 298 K): δ 2.18–2.28 (m, 2H, -CH<sub>2</sub>-), 2.68 (t, *J* = 7.0 Hz, 2H, -CH<sub>2</sub>SO<sub>3</sub>), 4.37 (t, *J* = 6.1 Hz, 2H, -OCH<sub>2</sub>-), 7.31–7.65 (m, 13H, phenyl and naphthyl), 7.74 (t, *J* = 7.7 Hz, 1H, phenyl), 7.80 (d, *J* = 8.0 Hz, 1H, naphthyl), 7.90 (d, *J* = 7.6 Hz, 1H, naphthyl), 7.98 (t, *J* = 8.0 Hz, 1H, phenyl), 8.37 (d, *J* = 7.6 Hz, 1H, naphthyl), 8.57 (d, *J* = 8.0 Hz, 1H, phenyl). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, [D<sub>6</sub>]-DMSO, 298 K): δ 37.77. Negative FAB-MS: *m/z* 744 ([M–K]<sup>–</sup>). Elemental analysis calcd (%) for C<sub>33</sub>H<sub>25</sub>AuKO<sub>4</sub>PS•CH<sub>2</sub>Cl<sub>2</sub>: C, 46.96; H, 3.13; found: C, 47.17; H, 3.28.

**Complex 3.** The procedure was similar to that used to prepare **1**, except that [(C<sub>14</sub>H<sub>9</sub>-C≡C)Au]<sub>∞</sub> (0.11 g, 0.28 mmol) was used in place of [(C<sub>6</sub>H<sub>5</sub>-C≡C)Au]<sub>∞</sub>. The product was isolated as a yellow solid. Yield: 70 mg (30 %). <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]-DMSO, 298 K): δ 2.16–2.31 (m, 2H, -CH<sub>2</sub>-), 2.70 (t, *J* = 7.3 Hz, 2H, -CH<sub>2</sub>SO<sub>3</sub>), 4.36 (t, *J* = 5.9 Hz, 2H, -OCH<sub>2</sub>-), 7.24–7.79 (m, 14H, phenyl and phenanthrenyl), 7.85–8.02 (m, 3H, phenyl and phenanthrenyl), 8.45–8.62 (m, 2H, phenyl and phenanthrenyl), 8.77 (d, *J*

= 8.0 Hz, 1H, phenanthrenyl), 8.81 (d,  $J = 8.0$  Hz, 1H, phenanthrenyl).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $[\text{D}_6]$ -DMSO, 298 K):  $\delta$  36.34. Negative FAB-MS:  $m/z$  794 ( $[\text{M}-\text{K}]^-$ ). Elemental analysis calcd (%) for  $\text{C}_{37}\text{H}_{27}\text{AuKO}_4\text{PS}\cdot 2.5\text{H}_2\text{O}$ : C, 50.61; H, 3.41; found: C, 50.51; H, 3.67.

**Complex 4.** The procedure was similar to that used to prepare **1**, except that  $[(\text{C}_{16}\text{H}_9-\text{C}\equiv\text{C})\text{Au}]_\infty$  (0.11 g, 0.26 mmol) was used in place of  $[(\text{C}_6\text{H}_5-\text{C}\equiv\text{C})\text{Au}]_\infty$ . The product was isolated as a yellow solid. Yield: 85 mg (38 %).  $^1\text{H}$  NMR (400 MHz,  $[\text{D}_6]$ -DMSO, 298 K):  $\delta$  2.19–2.29 (m, 2H,  $-\text{CH}_2-$ ), 2.68 (t,  $J = 7.3$  Hz, 2H,  $-\text{CH}_2\text{SO}_3$ ), 4.38 (t,  $J = 6.7$  Hz, 2H,  $-\text{OCH}_2-$ ), 7.29–7.67 (m, 10H, phenyl and pyrenyl), 7.74 (t,  $J = 7.4$  Hz, 1H, phenyl), 7.91–8.00 (m, 1H, phenyl), 8.01–8.10 (m, 2H, pyrenyl), 8.13–8.33 (m, 5H, pyrenyl), 8.57 (d,  $J = 7.6$  Hz, 1H, phenyl), 8.62 (d,  $J = 9.1$  Hz, 1H, pyrenyl).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $[\text{D}_6]$ -DMSO, 298 K):  $\delta$  35.96. Negative FAB-MS:  $m/z$  818 ( $[\text{M}-\text{K}]^-$ ). Elemental analysis calcd (%) for  $\text{C}_{39}\text{H}_{27}\text{AuKO}_4\text{PS}\cdot\text{CH}_2\text{Cl}_2$ : C, 50.91; H, 3.10; found: C, 51.21; H, 3.16.

**Complex 5.** The procedure was similar to that used to prepare **1**, except that  $[(\text{C}_{20}\text{H}_{11}-\text{C}\equiv\text{C})\text{Au}]_\infty$  (46 mg, 0.097 mmol) was used in place of  $[(\text{C}_6\text{H}_5-\text{C}\equiv\text{C})\text{Au}]_\infty$ . The product was isolated as a red solid. Yield: 29 mg (33 %).  $^1\text{H}$  NMR (400 MHz,  $[\text{D}_6]$ -DMSO, 298 K):  $\delta$  2.19–2.28 (m, 2H,  $-\text{CH}_2-$ ), 2.68 (t,  $J = 7.3$  Hz, 2H,  $-\text{CH}_2\text{SO}_3$ ), 4.37 (t,  $J = 6.4$  Hz, 2H,  $-\text{OCH}_2-$ ), 7.33–7.65 (m, 13H, perylenyl and phenyl), 7.66–7.85 (m, 3H, perylenyl and phenyl), 7.89–8.02 (m, 1H, phenyl), 8.19–8.48 (m, 4H, perylenyl), 8.56 (d,  $J = 7.8$  Hz, 1H, phenyl).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $[\text{D}_6]$ -DMSO, 298 K):  $\delta$  37.66. Negative FAB-MS:  $m/z$  869 ( $[\text{M}-\text{K}]^-$ ). Elemental analysis calcd (%) for  $\text{C}_{43}\text{H}_{29}\text{AuKO}_4\text{PS}\cdot 1.5\text{CH}_2\text{Cl}_2$ : C, 51.58; H, 3.11; found: C, 51.81; H, 3.40.

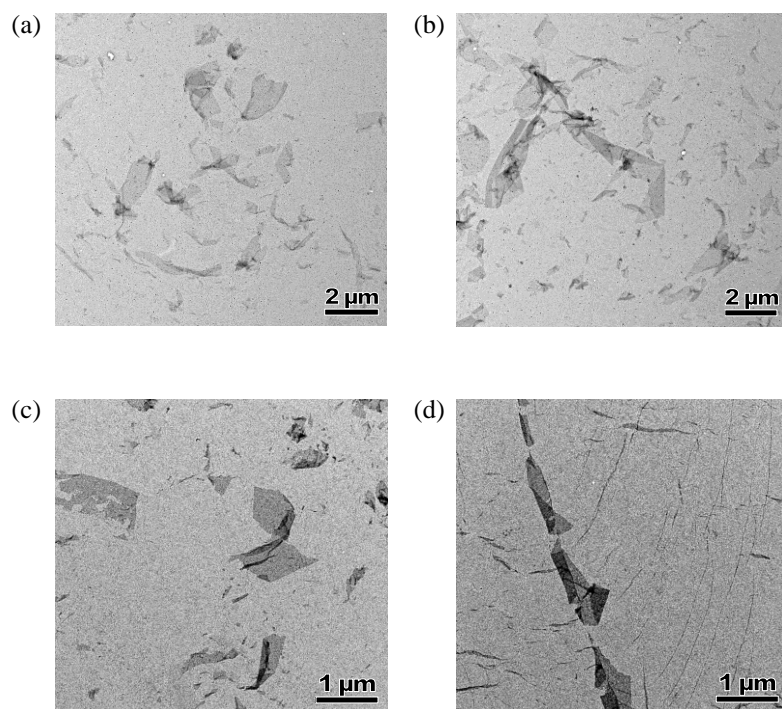
**Complex 6.** The procedure was similar to that used to prepare **1**, except that  $[\text{Au}(\text{tht})\text{Cl}]$  (82 mg, 0.26 mmol) was used in place of  $[(\text{C}_6\text{H}_5-\text{C}\equiv\text{C})\text{Au}]_\infty$ . The product was isolated as a white solid. Yield: 60 mg (36 %).  $^1\text{H}$  NMR (400 MHz,  $[\text{D}_6]$ -DMSO, 298 K):  $\delta$  2.17–2.27 (m, 2H,  $-\text{CH}_2-$ ), 2.68 (t,  $J = 7.3$  Hz, 2H,  $-\text{CH}_2\text{SO}_3$ ), 4.36 (t,  $J = 6.1$  Hz, 2H,  $-\text{OCH}_2-$ ), 7.39 (d,  $J = 7.0$  Hz, 1H, phenyl), 7.47–7.60 (m, 8H, phenyl), 7.74 (t,  $J = 7.7$  Hz, 1H, phenyl), 7.96 (m, 1H, phenyl), 8.54 (d,  $J = 7.7$  Hz, 1H, phenyl).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $[\text{D}_6]$ -DMSO, 298 K):  $\delta$  23.76. Negative FAB-MS:  $m/z$  629 ( $[\text{M}-\text{K}]^-$ ). Elemental analysis calcd (%) for  $\text{C}_{21}\text{H}_{18}\text{AuClKO}_4\text{PS}\cdot 2\text{H}_2\text{O}$ : C, 35.78; H, 3.15; found: C, 35.78; H, 2.96.

**Table S1** Photophysical data of complexes **1–6**

Complex	Absorption <sup>a</sup>	Emission		
	$\lambda_{\max}$ / nm ( $\epsilon_{\max}$ / dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup> )	Medium ( <i>T</i> / K)	$\lambda_{\max}$ / nm ( $\tau_0$ / $\mu$ s)	$\Phi_{\text{lum}}$ <sup>b</sup>
<b>1</b>	300 (10690), 330 (5470)	MeOH (298)	420 (< 0.1), 470sh, 504sh (26)	0.006
		glass (77) <sup>c</sup>	470, 500, 536 (4464)	
<b>2</b>	301 (15130), 312 (18700), 330 (21610)	MeOH (298)	421 (< 0.1), 540, 571, 622sh (24)	0.016
		glass (77) <sup>c</sup>	540, 578, 629 (397)	
<b>3</b>	301 (17770), 314 (26425), 329 (35545)	MeOH (298)	417 (< 0.1), 536, 572, 624sh (26)	0.019
		glass (77) <sup>c</sup>	533, 575, 627 (400)	
<b>4</b>	339 (24790), 356 (44835), 375 (63520)	MeOH (298)	410 (< 0.1), 447, 475sh (< 0.1)	0.015
		glass (77) <sup>c</sup>	424, 455sh (< 0.1)	
<b>5</b>	301 (9445), 327 (7770), 411 (10350), 434 (22755), 463 (31615)	MeOH (298)	479, 505, 542sh (< 0.1)	0.115
		glass (77) <sup>c</sup>	485, 518, 550 (< 0.1)	
<b>6</b>	301 (3875), 334 (3465)	MeOH (298)	421 (< 0.1), 474, 501, 534sh (36)	0.036
		glass (77) <sup>c</sup>	473, 504, 538 (4912)	

<sup>a</sup>Measured in methanol solution at 298 K. <sup>b</sup>Luminescence quantum yield, measured at room temperature using quinine sulfate in 1.0 N H<sub>2</sub>SO<sub>4</sub> as a standard. <sup>c</sup>Measured in ethanol–methanol (4:1 v/v).

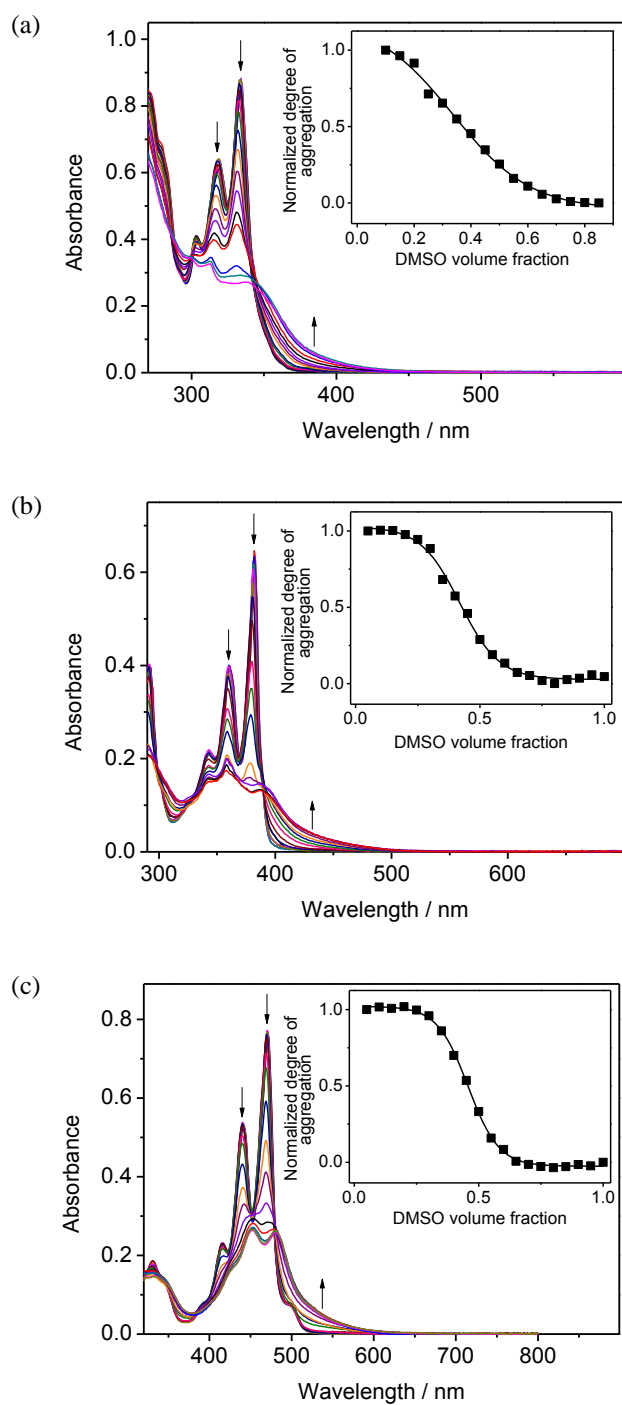
**TEM Images.**



**Fig. S1** TEM images of the aggregates prepared from **1** (a, b) and **3** (c, d) in 25 % DMSO–water mixture ( $1 \times 10^{-4}$  M).



## UV-Vis Absorption Spectra.



**Fig. S2** UV-Vis absorption spectral traces of (a) **3** ( $2.4 \times 10^{-5}$  M), (b) **4** ( $1.0 \times 10^{-5}$  M) and (c) **5** ( $1.8 \times 10^{-5}$  M) upon increasing the water content in DMSO at 298 K. The insets show the plot of normalized degree of aggregation as a function of DMSO volume fraction with curve fitting to the equilibrium model.

**References:**

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