

# **An amphiphilic metallaclip with enhanced fluorescence emission in water: synthesis and controllable self-assembly into multi-dimensional micro-structures**

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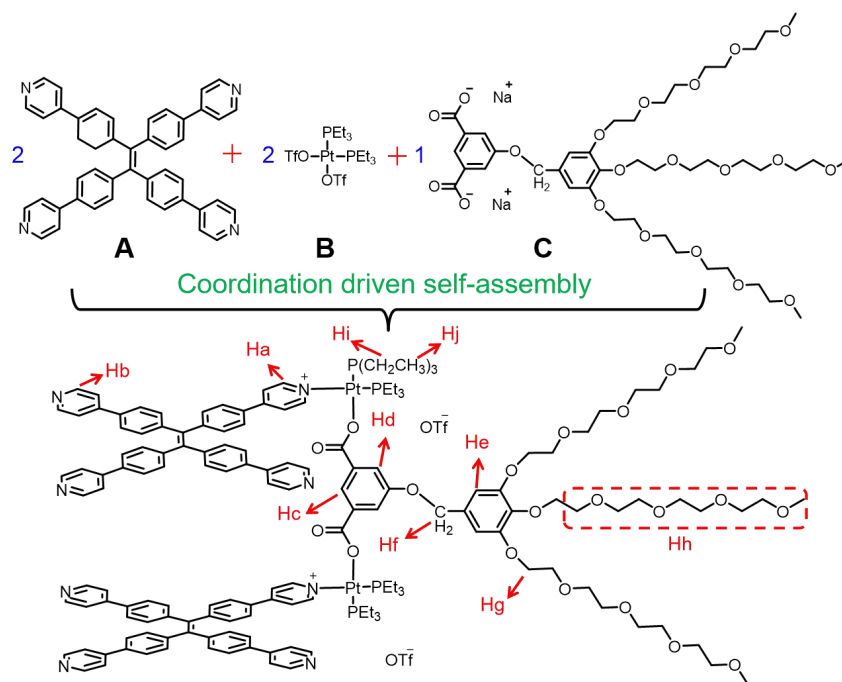
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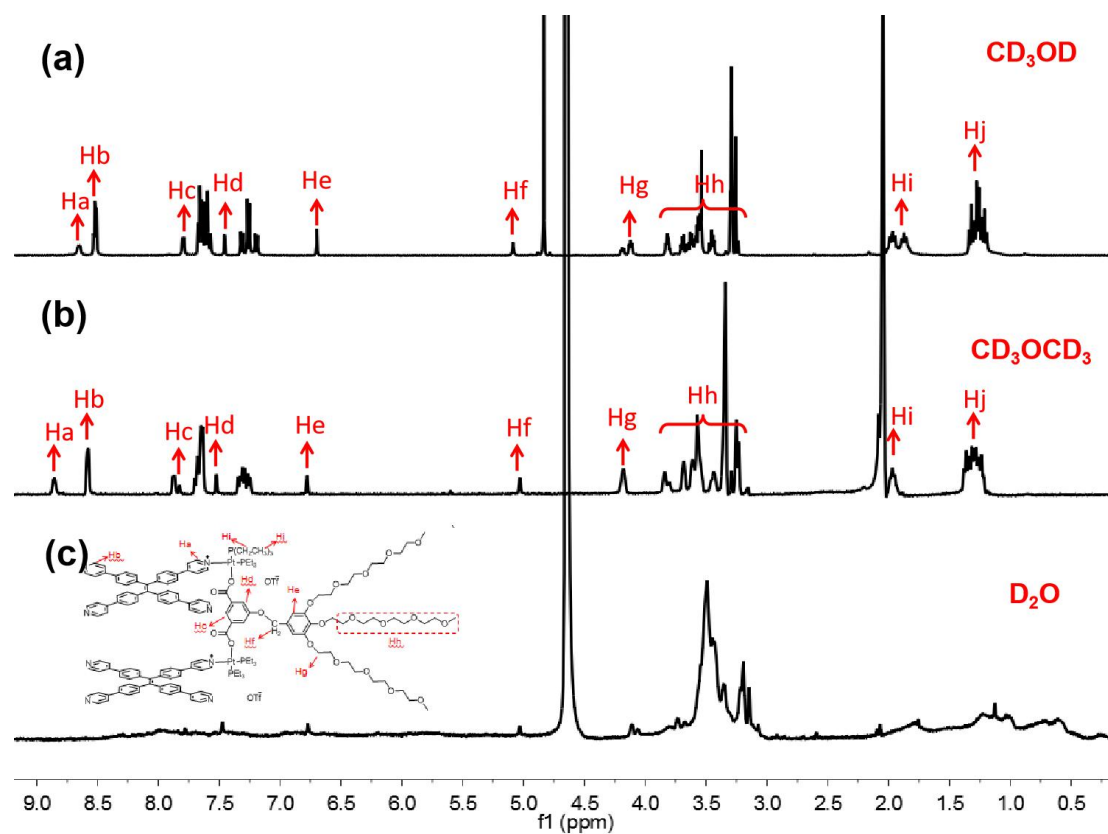
## 1. Materials/General Methods/Instrumentation

All reagents were commercially available and used as supplied without further purification. Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA). Compounds TPPE, Pt(II), and WSC were prepared according to modified literature procedures.<sup>S1,S2</sup> NMR experiments were recorded at room temperature. <sup>1</sup>H NMR and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded in the designated solvents on a Bruker Avance III HD 400 M spectrometer. <sup>31</sup>P{<sup>1</sup>H} NMR chemical shifts are referenced to an external unlocked sample of 85% H<sub>3</sub>PO<sub>4</sub> (δ 0.0 ppm). Mass spectra were recorded on a Micromass Quattro II triple quadrupole mass spectrometer using electrospray ionization with a MassLynx operating system. Ultraviolet-visible experiments were conducted on a Hitachi U-4100 absorption spectrophotometer. Fluorescence experiments were conducted on a Hitachi F-7000 fluorescence spectrophotometer. SEM images were applied to investigate the morphologies, which was carried out with a Hitachi S-4800 field emission scanning electron microscope.

## 2. Synthesis of Amphiphilic Metallaclip



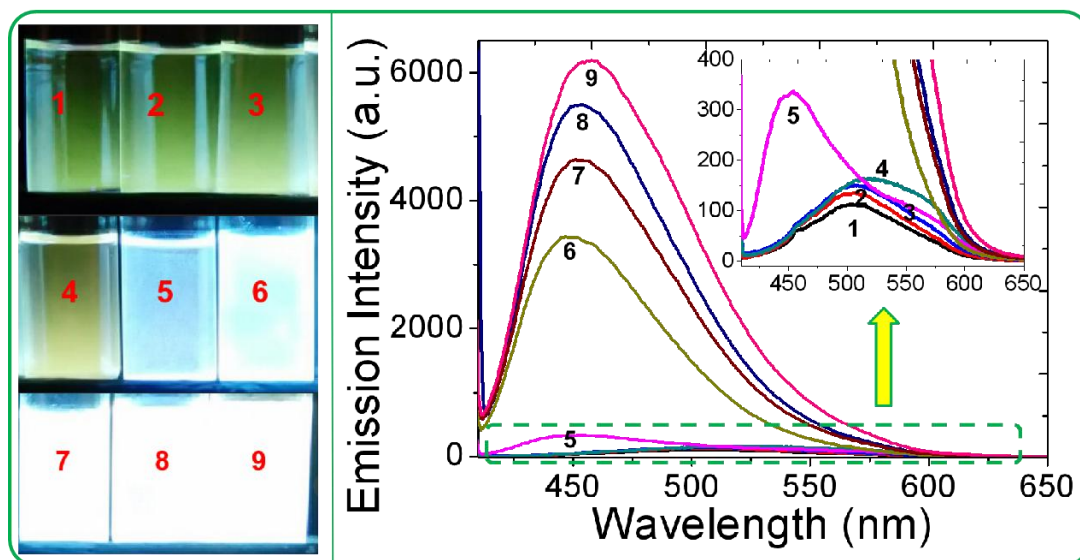
In a 4:2:1 molar ratio, tetra(4-pyridyl)ethylene (**A**) (2.56 mg, 4.00  $\mu\text{mol}$ ), *cis*-( $\text{PEt}_3$ )<sub>2</sub>Pt(OTf)<sub>2</sub> (**B**) (1.45 mg, 2.00  $\mu\text{mol}$ ), and water soluble carboxylate ligand (**C**) (0.80 mg, 1.00  $\mu\text{mol}$ ), were placed in a 2 mL vial, followed by addition of H<sub>2</sub>O (0.2 mL) and acetone (0.8 mL). After stirring overnight at 60°C, all solvent was removed by N<sub>2</sub> flow and the solid was dried under vacuum. Acetone (1.0 mL) was then added into the vial, and the solution was stirred for 5 h at room temperature. After storage in a refrigerator for 1 h, the mixture was filtered to remove insoluble materials. The resulting amphiphilic metallaclip (AMT) was precipitated with diethyl ether, isolated, and dried under reduced pressure (2.72 mg, yield: 85%) and then re-dissolved in acetone-*d*<sub>6</sub> for characterization. The <sup>1</sup>H NMR spectrum of AMT is shown in Figure S1. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, room temperature, 400 MHz)  $\delta$  (ppm): 8.67 (s, 4H), 8.52 (s, 12H), 7.79 (s, 4H), 7.68-7.61 (m, 31H), 7.47-7.27 (m, 16H), 6.75 (s, 2H), 5.09 (s, 2H), 4.16 (s, 6H), 3.83-3.47 (m, 42H), 3.27 (s, 9H), 1.97-1.90 (m, 24H), 1.29 (t, *J* = 6.0 Hz, 36H). The <sup>31</sup>P {<sup>1</sup>H} NMR spectrum of metallaclip (AMT) is shown in Figure 1b. <sup>31</sup>P {<sup>1</sup>H} NMR (acetone, room temperature, 121.4 MHz)  $\delta$  (ppm): 2.2 ppm (<sup>2</sup>*J*<sub>P-P</sub> = 20.6 Hz, <sup>195</sup>Pt satellites, <sup>1</sup>*J*<sub>Pt-P</sub> = 3374.9 Hz), -3.0 (<sup>2</sup>*J*<sub>P-P</sub> = 20.6 Hz, <sup>195</sup>Pt satellites, <sup>1</sup>*J*<sub>Pt-P</sub> = 3251.1 Hz). ESI-MS is shown in Figure 2: [M - 2 OTf]<sup>2+</sup> *m/z* = 1517.62; [M + H - 2 OTf + 2 CH<sub>3</sub>COCH<sub>3</sub>]<sup>2+</sup> *m/z* = 1649.18. EA: theoretical % (C = 57.7, H = 5.7, N = 3.4, S = 1.9), experimental % (C = 58.6, H = 5.9, N = 3.4, S = 2.0).



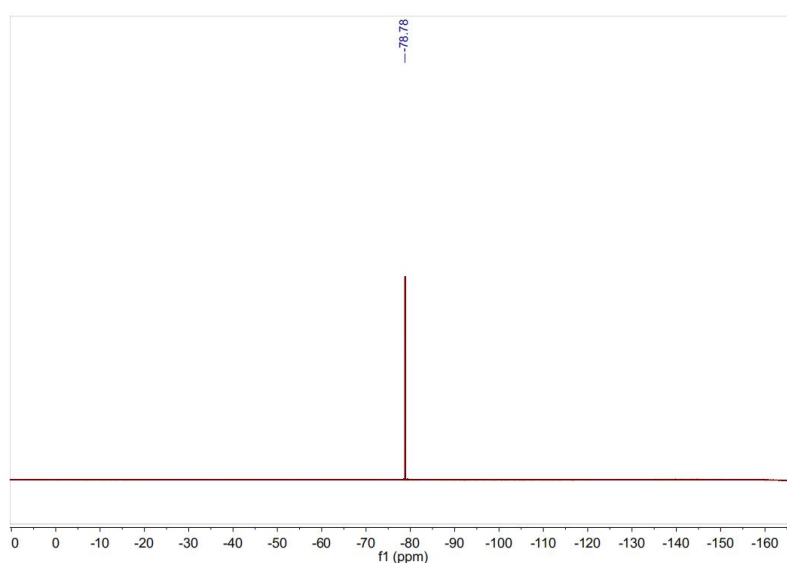
**Fig. S1.** <sup>1</sup>H NMR spectrum (room temperature, 400 MHz) of AMT in different solvents: a) CD<sub>3</sub>OD, b) acetone-*d*<sub>6</sub>, c) D<sub>2</sub>O.

### 3. Self-assembly of Amphiphilic Metallaclip

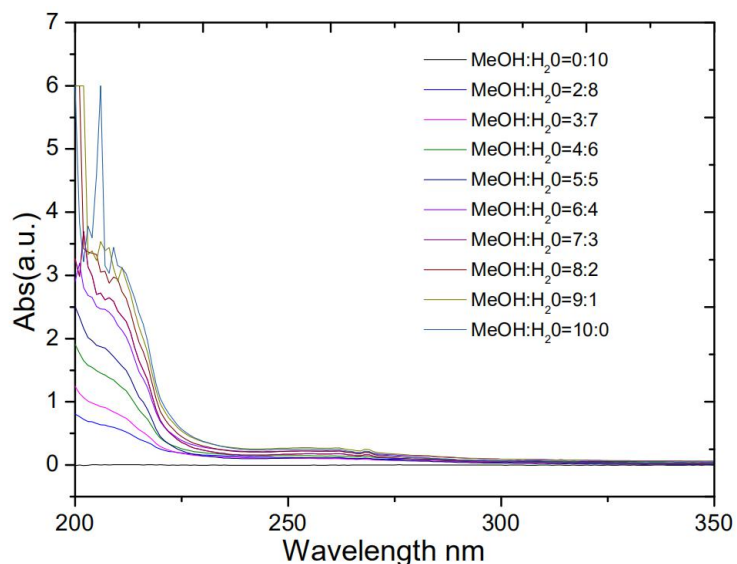
Self-Assembly of AMT in CH<sub>3</sub>OH/H<sub>2</sub>O. In a typical experiment: 100 mL of CH<sub>3</sub>OH solution of AMT (10 μM) [named solution I] and 100 mL of H<sub>2</sub>O solution of AMT (10 μM) [named solution II] were prepared in a vial firstly, and then mixed 1 ml solution I and 9 mL solution II to get 90% water content, others also used this method.



**Fig. S2.** Left: The photographs are of AMT in CH<sub>3</sub>OH-H<sub>2</sub>O mixture with different water content on excitation at 365 nm using an ultraviolet lamp at 298 K ( $c = 10.0 \mu\text{M}$ ). Right: Fluorescence emission spectra of AMT in CH<sub>3</sub>OH-H<sub>2</sub>O mixture with different water content ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ,  $c = 10.0 \mu\text{M}$ ). 1: 10%; 2: 20%; 3: 30%; 4: 40%; 5: 50%; 6: 60%; 7: 70%; 8: 80%; 9: 90%.



**Fig. S3.** <sup>19</sup>F NMR spectrum (room temperature, acetone) of AMT.



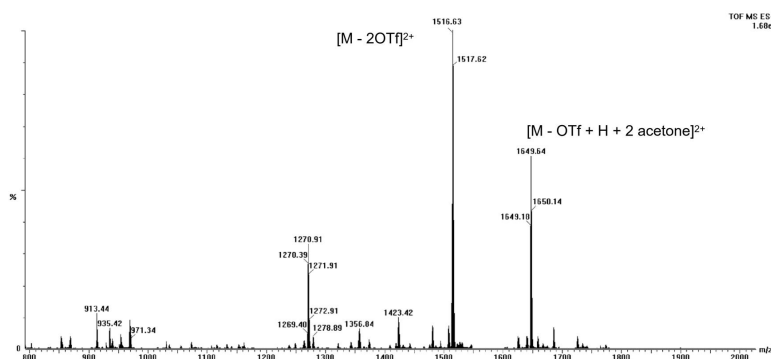
**Fig. S4.** UV-vis spectra of AMT in CH<sub>3</sub>OH-H<sub>2</sub>O mixture with different water content ( $c = 1.00 \mu\text{M}$ ).

The fluorescence quantum yields were determined using the following formula:<sup>S3</sup>

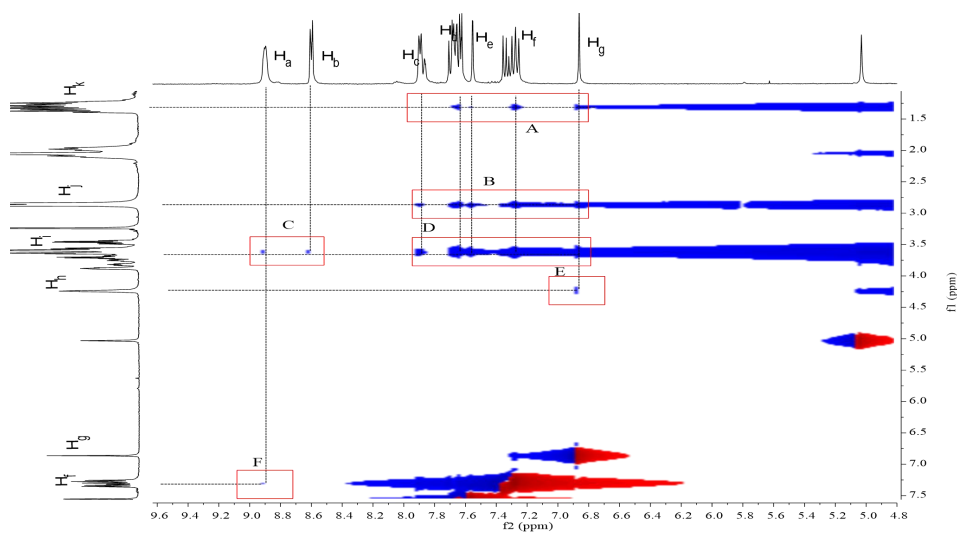
$$\varphi_i = \varphi_s \left( \frac{n^2/n_s^2}{I_i/I_s} \right) \left[ \frac{(1-10^{-As(\lambda_{exc})})}{(1-10^{-Ai(\lambda_{exc})})} \right]$$

where  $\varphi$  is fluorescence quantum yield,  $A$  is the absorbance at the excitation wavelength,  $I$  the area under the fluorescence spectra, and  $n$  is the refractive index of the solvent in which the sample was collected. The subscripts "i" and "S" refer to the sample of interest and the standard, respectively. Coumarin 153 in EtOH ( $\varphi = 0.546$ ) was used as a standard.

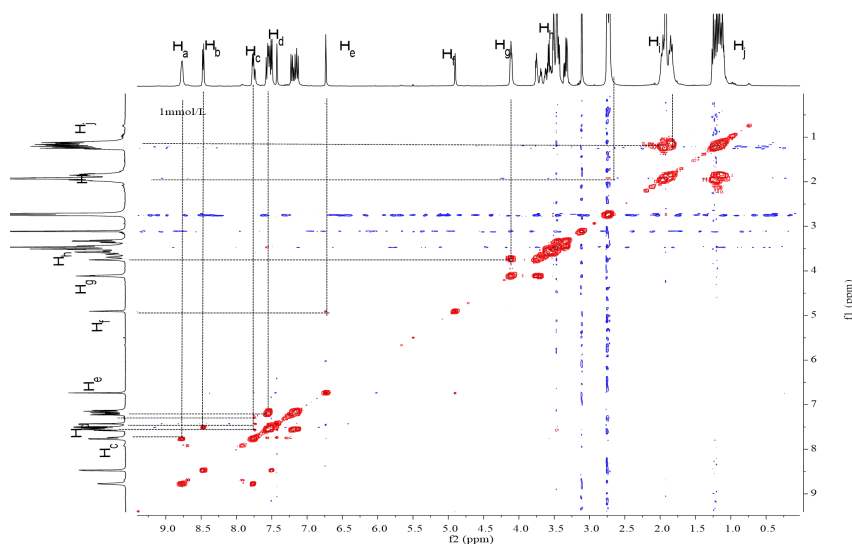
When the ratio of CH<sub>3</sub>OH:H<sub>2</sub>O is 9:1, the quantum yield was thus estimated to be 7.63%, when the ratio of CH<sub>3</sub>OH:H<sub>2</sub>O is 1:9, the quantum yield was thus estimated to be 36.8%.



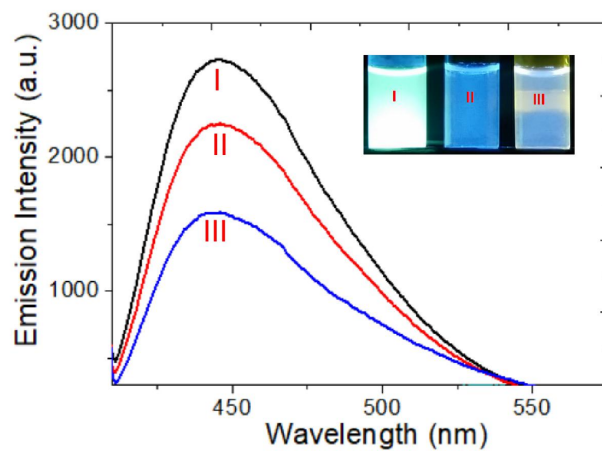
**Fig. S5.** ESI-TOF-MS spectra of AMT



**Fig. S6.** NOESY spectra of AMT.



**Fig. S7.**  $^1\text{H}$ - $^1\text{H}$  COSY spectra of AMT.



**Fig. S8.** Fluorescence emission spectra of AMT: I, in water; II, filled with  $\text{CO}_2$  for 5 min; III, filled with  $\text{CO}_2$  for 30 min ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ,  $c = 10.0 \mu\text{M}$ ).

#### 4. References

- S1. X. Yan, T. R. Cook, P. Wang, F. Huang and P. J. Stang, *Nature Chemistry*, 2015, **7**, 342
- S2. Y. Sun, F. Zhang, S. Jiang, Z. Wang, R. Ni, H. Wang, W. Zhou, X. Li and P. J. Stang, *J. Am. Chem. Soc.*, 2018, **140**, 17297
- S3 W.-C. Geng, Y.-C. Liu, Y.Y. Wang, Z. Xu, Z. Zhang, C.-B. Yang and D.S. Guo, *Chem. Commun.*, 2017, **53**, 392.