



## Supporting Information

for

### Self-assembly behaviors of perylene- and naphthalene-crown macrocycle conjugates in aqueous medium

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## Experimental and analytical data

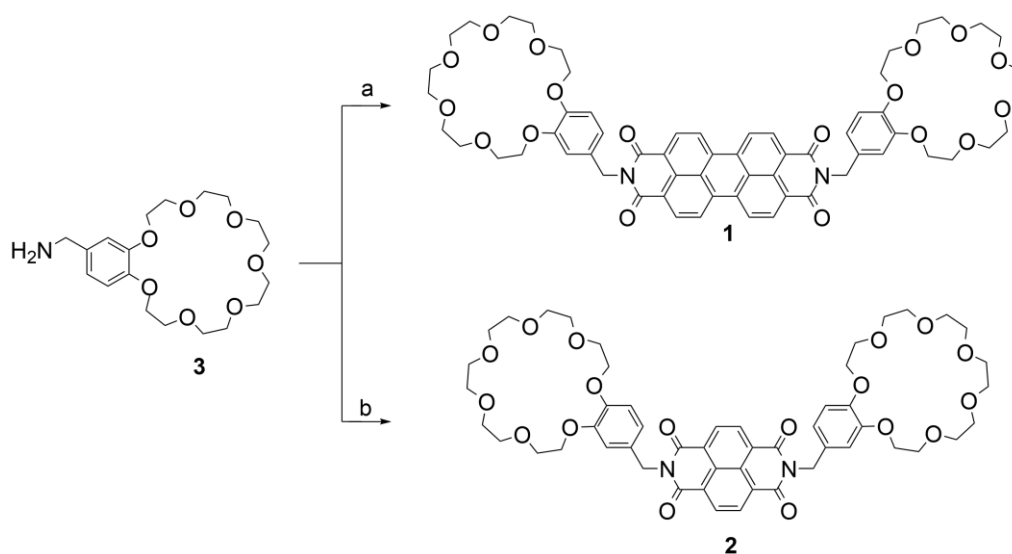
## General Methods and Materials

All reagents were commercially available and used without further purification. Milli-Q water was used in all measurements. Nuclear magnetic resonance (NMR) spectra were recorded with a Bruker Avance III-400 spectrophotometer, using the deuterated solvent as the lock and residual solvent or TMS as the internal reference. For the structural characterization of synthetic compounds, high-resolution mass spectrometry (HR-MS) was performed using an electrospray ionization (ESI) interface on an Agilent LC/MSD TOF system. Dynamic light scattering (DLS) characterization was performed on Zetasizer Nano ZS, Malvern Instruments, Worcestershire, U. K.

**UV and fluorescence spectrometry.** The sample was dissolved in different solvents at a concentration of 5  $\mu$ M. The UV-vis spectra were recorded on a ThermoEvolution 260 Bio UV/Vis/NIR spectrometer with a temperature controllable system in the scan range of 300 to 750 nm using a 1.0 cm quartz micro cuvette. Fluorescence experiments were performed in a 1.0 cm quartz cuvette and recorded on an F-380 spectrofluorimeter (GANGDONG SCI. & TECH.) with 5 nm slit.

**Transmission electron microscopy (TEM) images.** Droplets ( $\approx$ 5  $\mu$ L) of sample solution were placed on carbon-film-coated copper grids (ELECTRON MICROSCOPY CHINA) at ambient temperature. The grids were allowed to air-dry for at least 40 min and were subsequently transferred into the microscope without use of a contrasting or cryo-fixation step. TEM images were obtained with a FEI Talos F200X transmission electron microscope with an accelerating voltage of 300 kV.

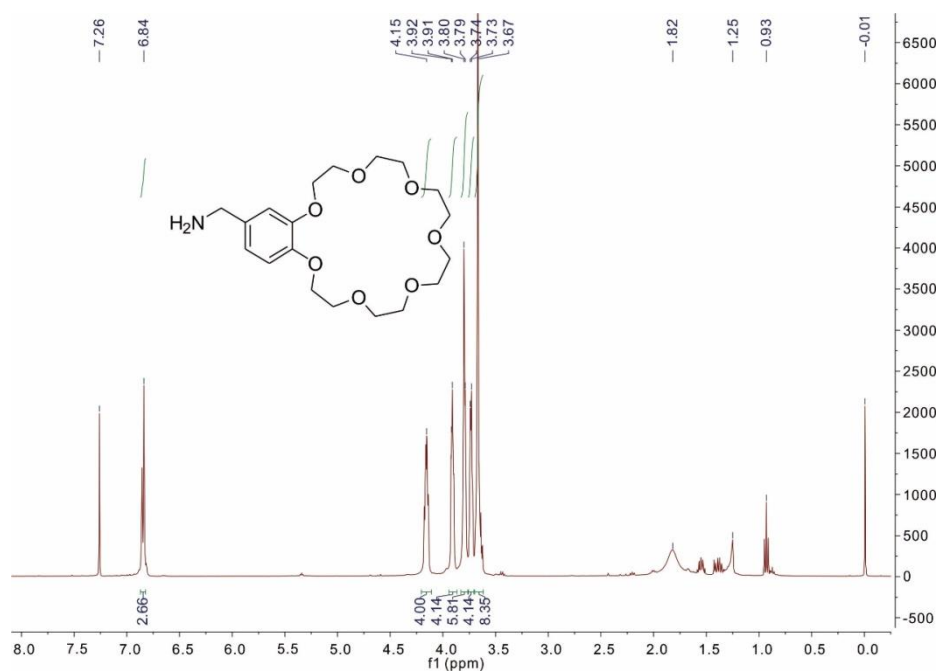
## Synthesis and characterization of compounds



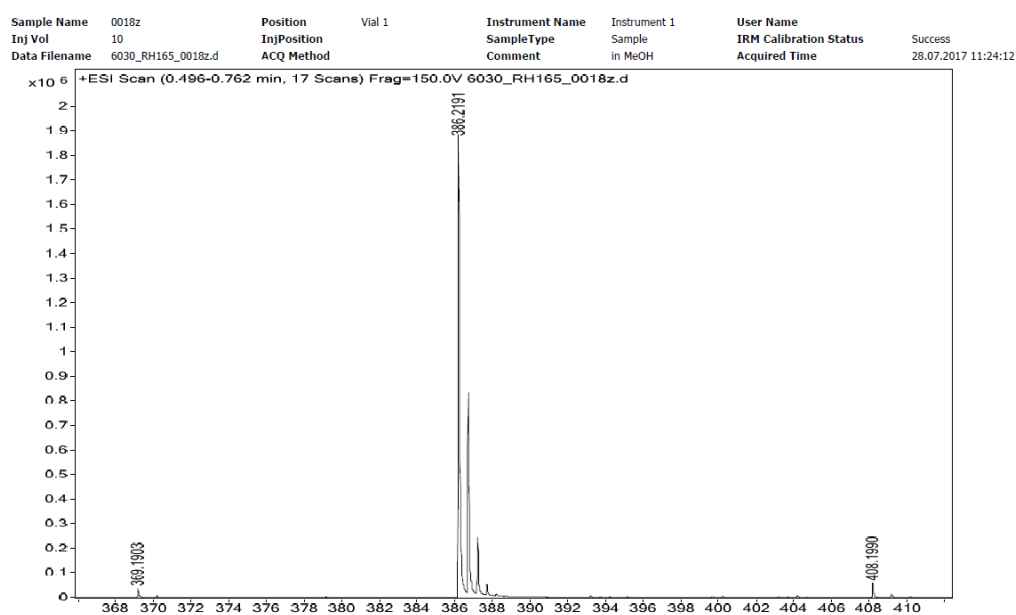
**Scheme S1:** The synthetic route of compounds **1** and **2**. a) 3,4,9,10-Perylenetetracarboxylic dianhydride (PDI), DMAP, 140 °C; b) 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NDI), DMAP, 140 °C.

### *Preparation of Compound 3*

The synthesis of compound **3** was based on previously reported reference.<sup>1</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 6.84 (s, 3H), 4.15 (s, 4H), 3.91 (d,  $J$  = 3.5 Hz, 4H), 3.79 (d,  $J$  = 4.9 Hz, 6H), 3.73 (d,  $J$  = 4.1 Hz, 4H), 3.67 (s, 8H). HR-MS (ESI)  $m/z$  ( $M+H^+$ ) *calcd.* for C<sub>19</sub>H<sub>32</sub>NO<sub>7</sub><sup>+</sup>: 386.2179, *Found*: 386.2191.



**Figure S1:**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 298 K) of **3**.

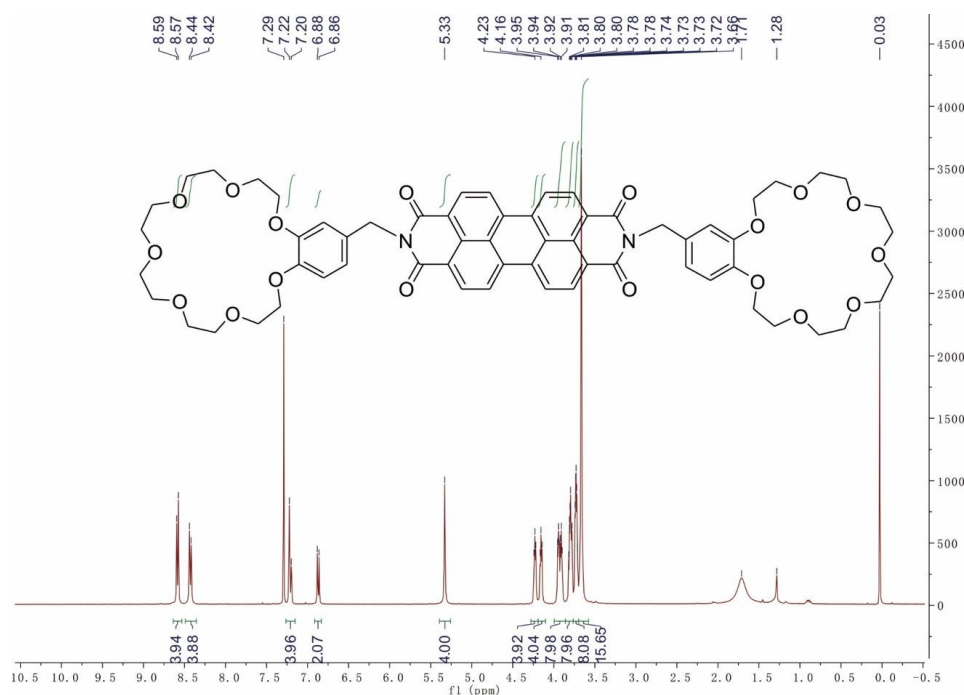


**Figure S2:** HR-MS characterization of **3**.

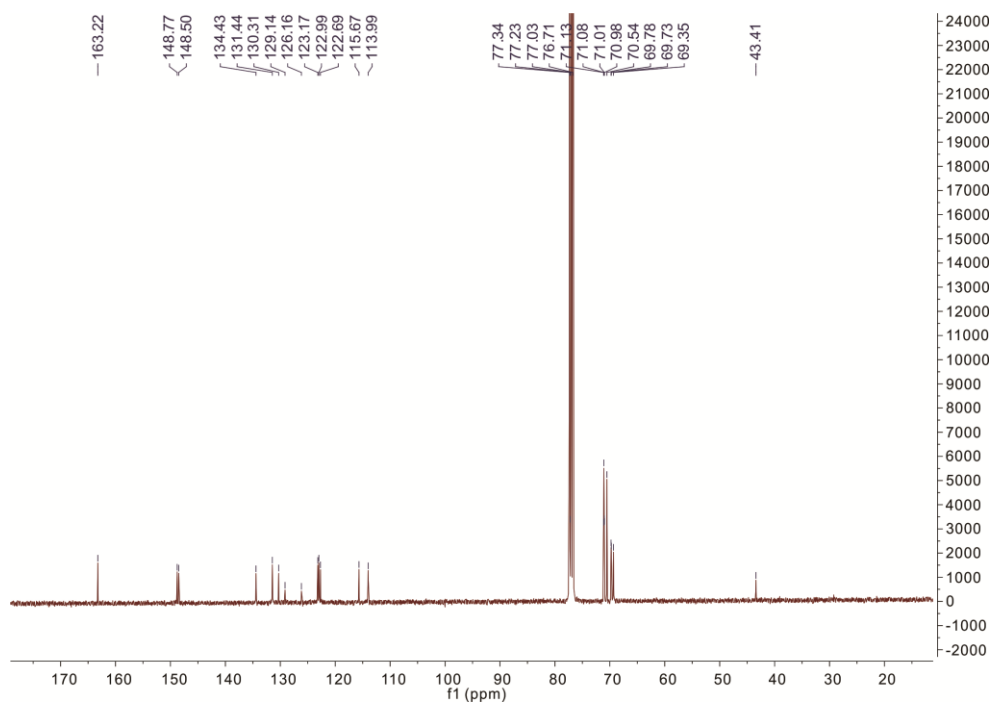
### *Preparation of Compound 1*

To the solution of compound **3** (1.03 g, 2.68 mmol) dissolved in glycol (20 mL) in a 50 mL flask, 3,4,9,10-perylenetetracarboxylic dianhydride (0.5 g, 1.28 mmol) and DMAP (7.7 mg,  $6.3 \times 10^{-2}$  mmol) was added. The mixture was heated to 140 °C and stirred for 24 h. After the reaction mass was cooled to room temperature, it was poured into  $\text{CH}_2\text{Cl}_2$  (200 mL). The organic phase was

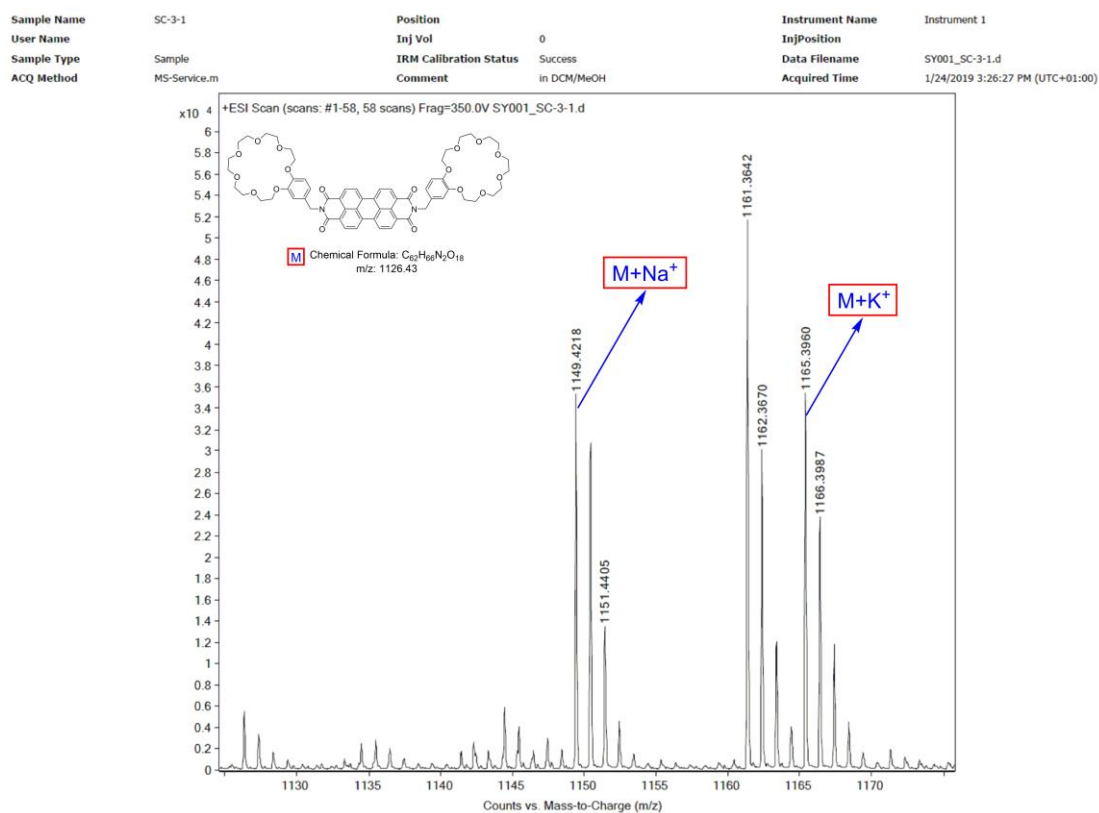
washed with HCl aqueous (0.05 M, 100 mL  $\times$  2), and brine (100 mL), respectively. Then, the organic layer was dried by Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to obtain the crude product. The crude product was purified by silica gel column chromatography with MeOH/CH<sub>2</sub>Cl<sub>2</sub> = 1/100 to 1/30 (v/v) as eluent to yield the pure product as a brown solid (yield: 1.21 g, 84%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.58 (d,  $J$  = 8.0, 4H), 8.43 (d,  $J$  = 8.1, 4H), 7.21 (d,  $J$  = 9.2, 4H), 6.87 (d,  $J$  = 8.1, 2H), 5.33 (s, 4H), 4.28 – 4.19 (m, 4H), 4.19 – 4.10 (m, 4H), 3.99 – 3.86 (m, 8H), 3.80 (t,  $J$  = 6.5, 3.1, 8H), 3.73 (t,  $J$  = 6.4, 3.3, 8H), 3.66 (s, 16H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 163.22, 148.77, 148.50, 134.43, 131.44, 130.31, 129.14, 126.16, 123.17, 122.99, 122.69, 115.67, 113.99, 71.13, 71.08, 71.01, 70.98, 70.54, 69.78, 69.73, 69.35, 43.41. HR-MS (ESI)  $m/z$  (M+Na<sup>+</sup>) *calcd.* for C<sub>62</sub>H<sub>66</sub>N<sub>2</sub>O<sub>18</sub>Na<sup>+</sup>: 1149.4208, *Found*: 1149.4218;  $m/z$  (M+K<sup>+</sup>) *calcd.* for C<sub>62</sub>H<sub>66</sub>N<sub>2</sub>O<sub>18</sub>K<sup>+</sup>: 1165.3948, *Found*: 1165.3960.



**Figure S3:** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 298 K) of **1**.



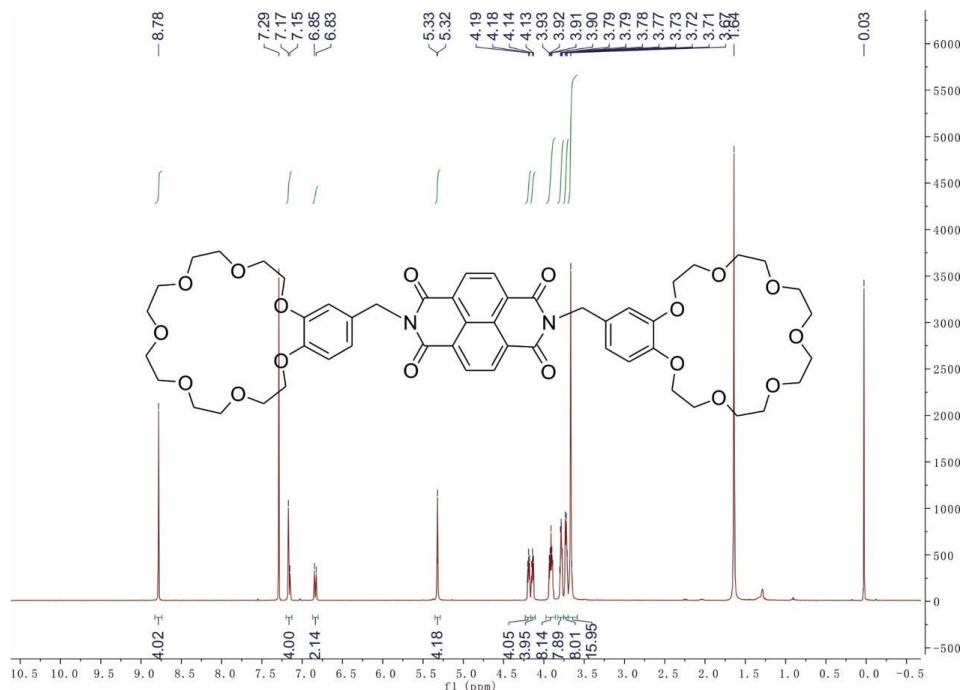
**Figure S4:**  $^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{CDCl}_3$ , 298 K) of **1**.



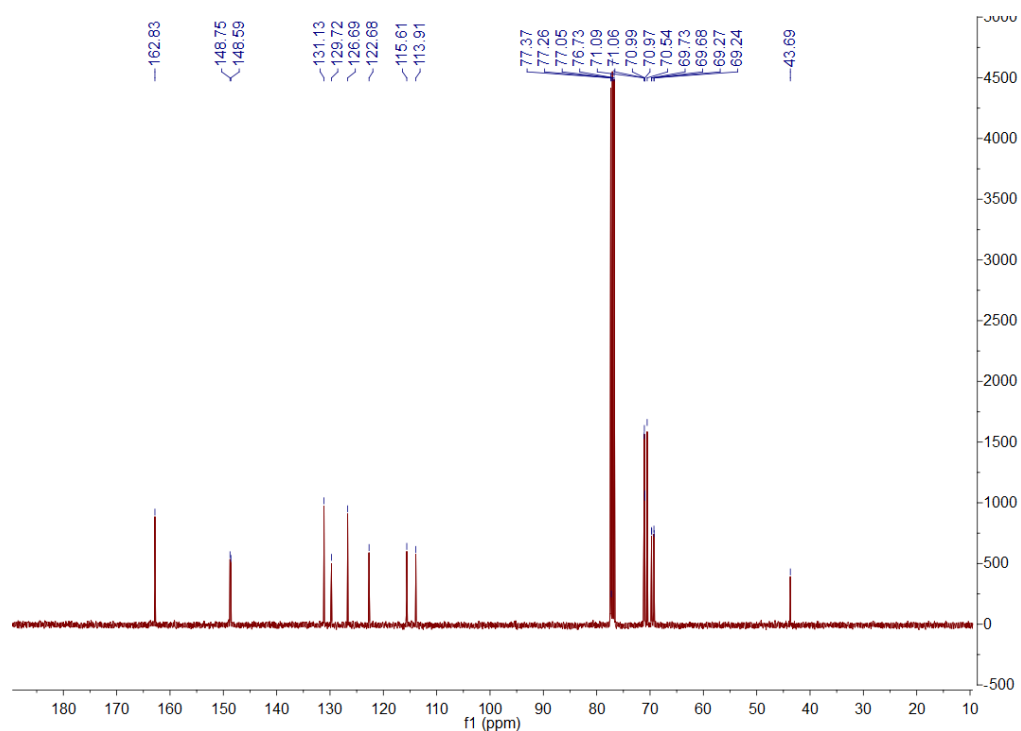
**Figure S5:** HR-MS characterization of **1**.

### Preparation of Compound 2

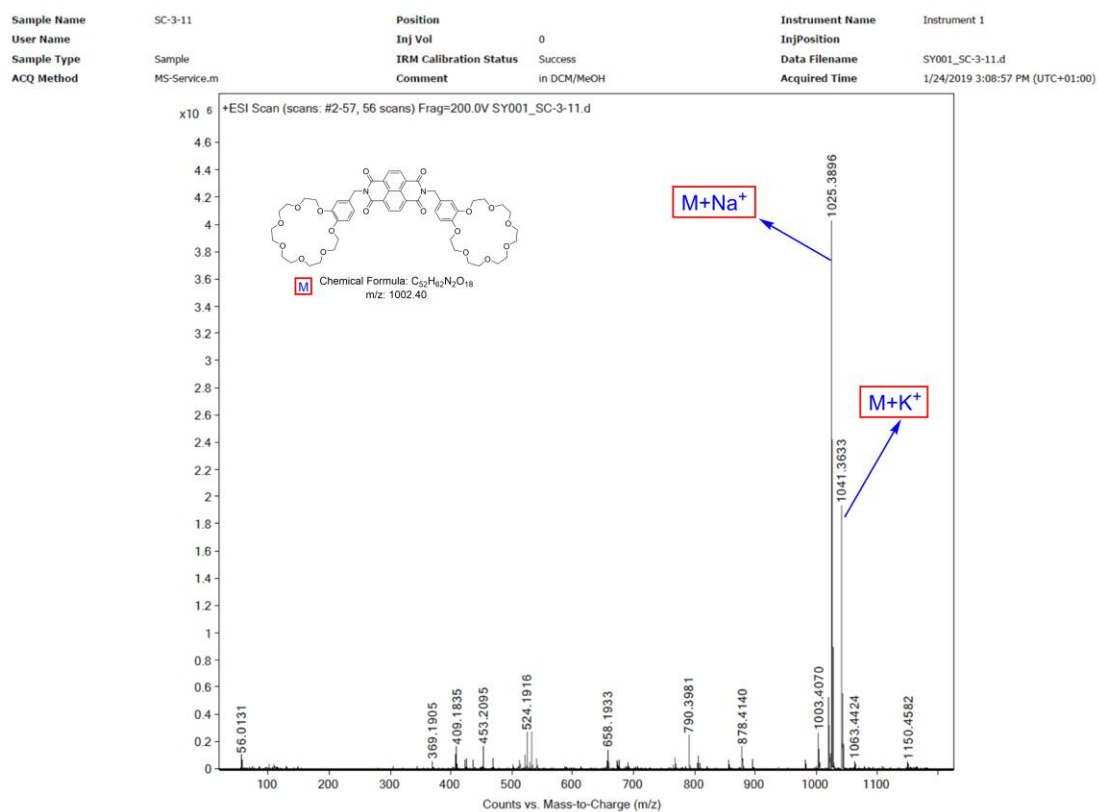
To the solution of compound **3** (0.75 g, 1.95 mmol) dissolved in 20 mL glycol in a 50 mL flask, 1,4,5,8-naphthalenetetracarboxylic dianhydride (0.25 g, 0.93 mmol) and DMAP (5.7 mg,  $4.6 \times 10^{-2}$  mmol.) were added. The mixture was heated to 140 °C and stirred overnight. After the reaction mass was cooled to room temperature, it was poured into CH<sub>2</sub>Cl<sub>2</sub> (100 mL). The organic phase was washed by HCl aqueous (0.05 M, 50 mL  $\times$  2) and brine (50 mL), respectively. Then, the organic layer was dried by Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduce pressure to obtain the crude product. The crude product was purified by silica gel column chromatography with MeOH/CH<sub>2</sub>Cl<sub>2</sub> = 1/100 to 1/30 (v/v) as eluent to yield pure product as yellow solid (yield: 0.71 g 76%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.78 (s, 4H), 7.16 (d,  $J$  = 7.3, 4H), 6.84 (d,  $J$  = 8.5, 2H), 5.32 (d,  $J$  = 2.5, 4H), 4.23 – 4.16 (m, 4H), 4.16 – 4.11 (m, 4H), 3.97 – 3.86 (m, 8H), 3.83 – 3.75 (m, 8H), 3.75 – 3.70 (m, 8H), 3.70 – 3.59 (m, 16H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 162.83, 148.75, 148.59, 131.13, 129.72, 126.69, 122.68, 115.61, 113.91, 71.09, 71.06, 70.99, 70.97, 70.54, 69.73, 69.68, 69.27, 69.24, 43.69. HR-MS (ESI)  $m/z$  (M+Na<sup>+</sup>) *calcd.* for C<sub>52</sub>H<sub>62</sub>N<sub>2</sub>O<sub>18</sub>Na<sup>+</sup>: 1025.3895, *Found:* 1025.3896 ;  $m/z$  (M+K<sup>+</sup>) *calcd.* for C<sub>52</sub>H<sub>62</sub>N<sub>2</sub>O<sub>18</sub>Na<sup>+</sup>: 1041.3635, *Found:* 1041.3633.



**Figure S6:** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, 298 K) of **2**.

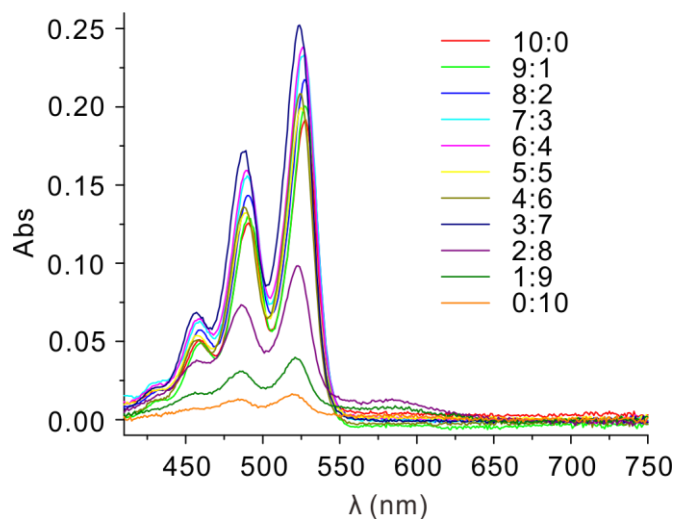


**Figure S7:**  $^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{CDCl}_3$ , 298 K) of **2**.

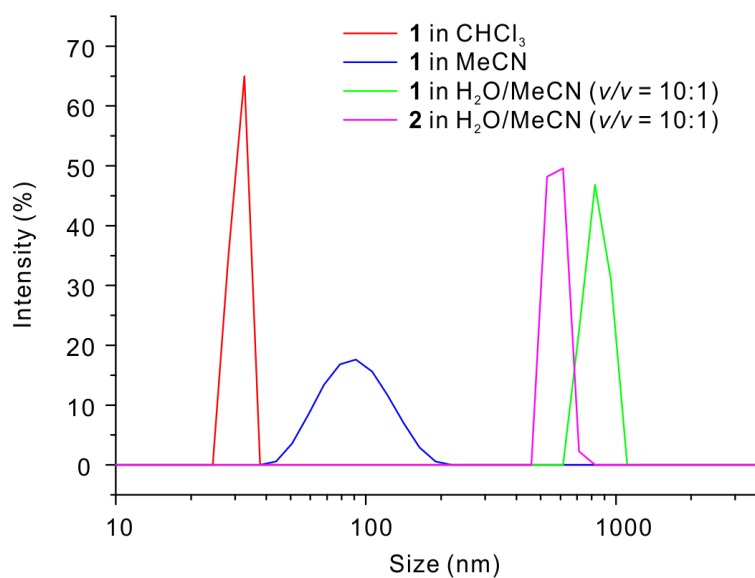


**Figure S8:** HR-MS characterization of **2**.





**Figure S9:** UV-vis spectra of **1** in (mixed) solvents of  $\text{CHCl}_3$  and MeCN with different volume ratio ranging from 10:0 to 0:10.



**Figure S10:** Size distribution of aggregates formed by **1** and **2** in different solvents (100  $\mu\text{M}$ , 25  $^\circ\text{C}$ ) based on DLS measurements.

## Reference

1. Qi, Z.; de Molina, P. M.; Jiang, W.; Wang, Q.; Nowosinski, K.; Schulz, A.; Gradzielski, M.; Schalley, C. A. *Chem. Sci.*, **2012**, 3, 2073-2082.