

# Figure-Eight Arylene Ethynylene Macrocycle: Facile Synthesis and Specific Binding behavior Toward Hg<sup>2+</sup>

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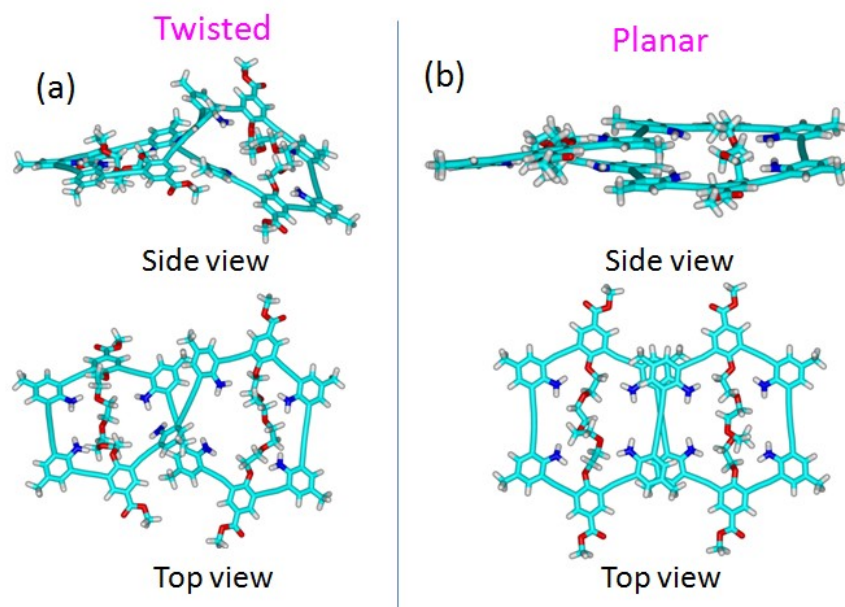
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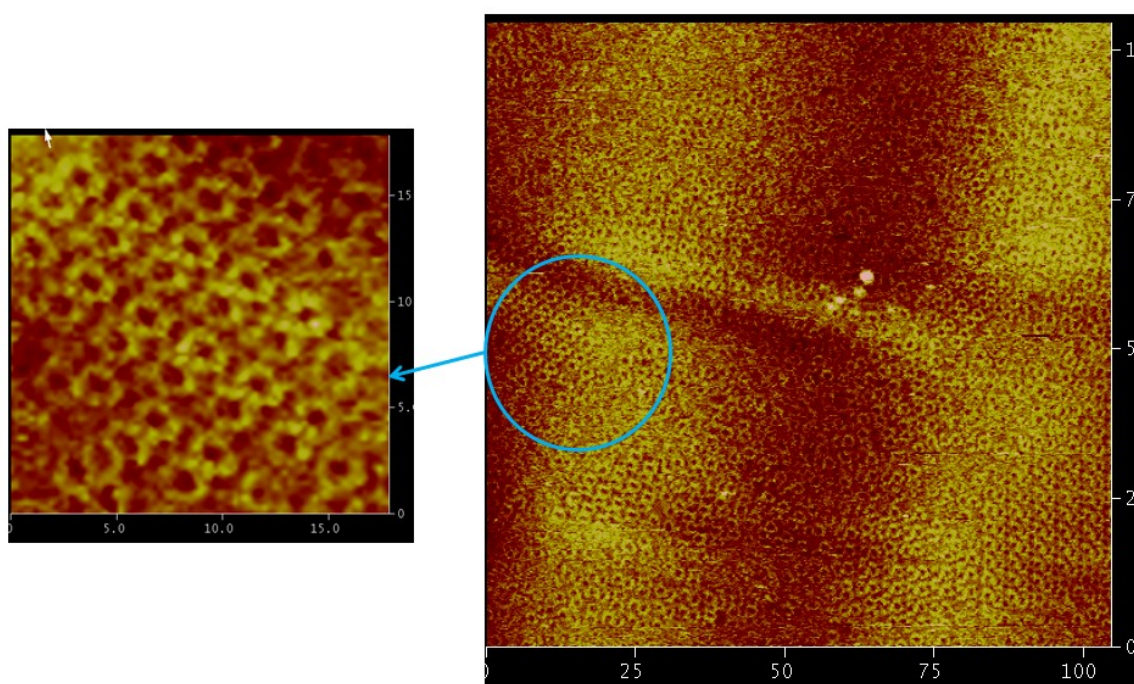
## Content

<b>1. Figures Referenced in the Manuscript.....</b>	<b>2</b>
<b>2. Tables Referenced in the Manuscript.....</b>	<b>7</b>
<b>3. Experimental details.....</b>	<b>8</b>
<b>3.1. General remarks.....</b>	<b>8</b>
<b>3.2. Synthetic procedure.....</b>	<b>10</b>
<b>3.3. <sup>1</sup>H NMR, <sup>13</sup>C NMR and Maldi-TOF mass spectra.....</b>	<b>17</b>
<b>4 · GPC plots of SPM-Q6 and SPM-Q12.....</b>	<b>27</b>
<b>5. Reference.....</b>	<b>29</b>

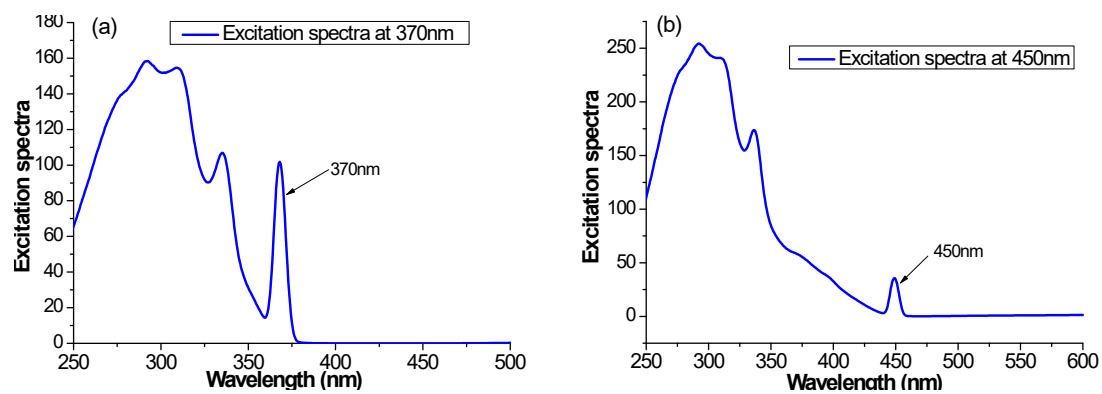
## 1. Figures referenced in the manuscript



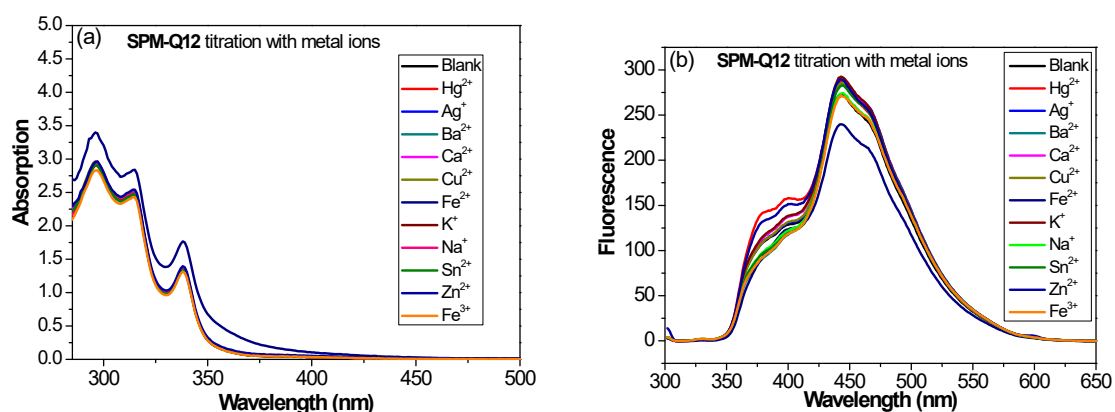
**Fig. S1.** The optimized structure for SPM-Q12-NH<sub>2</sub>, (a) “Twisted” model with highly distortion and (b) “Planar” model, with  $\pi$ - $\pi$  stacking at the cross connection, respectively.



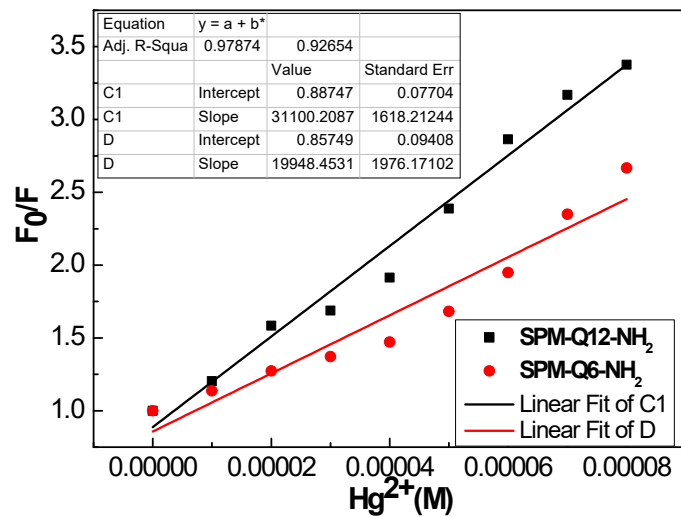
**Fig. S2.** Large-scale(100nm\*100nm) STM image of SPM-Q12 self-assembly and a small domain.



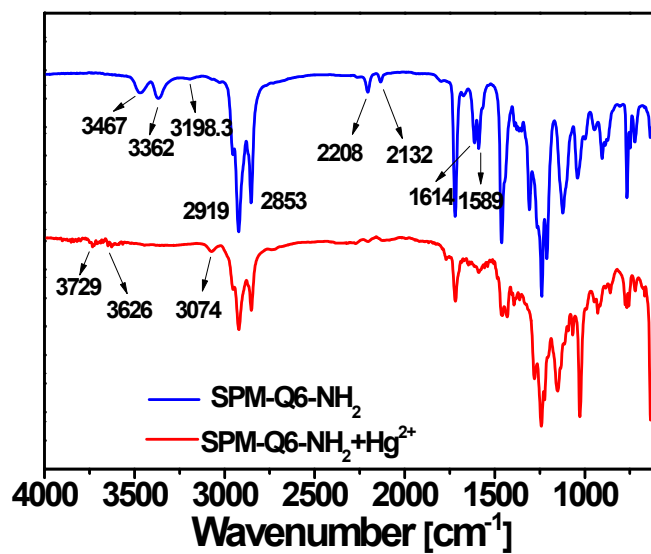
**Fig S3.** Fluorescence excitation spectra of SPM-Q12 in THF (a) monitored at 370nm and (b) 450nm, respectively.



**Fig. S4.** UV-vis absorption spectra (a) and fluorescence responses(b) of SPM-Q12 (10  $\mu$ M) in THF addition of different metal ions (10 eq);.



**Fig. S5.** Plot of fluorescence intensity change of SPM-Q6-NH<sub>2</sub> and SPM-Q12-NH<sub>2</sub> (10 μM) against varied concentrations of Hg<sup>2+</sup>.



**Fig. S6.** FT-IR spectra for SPM-Q6-NH<sub>2</sub> before and after adding Hg<sup>2+</sup>.

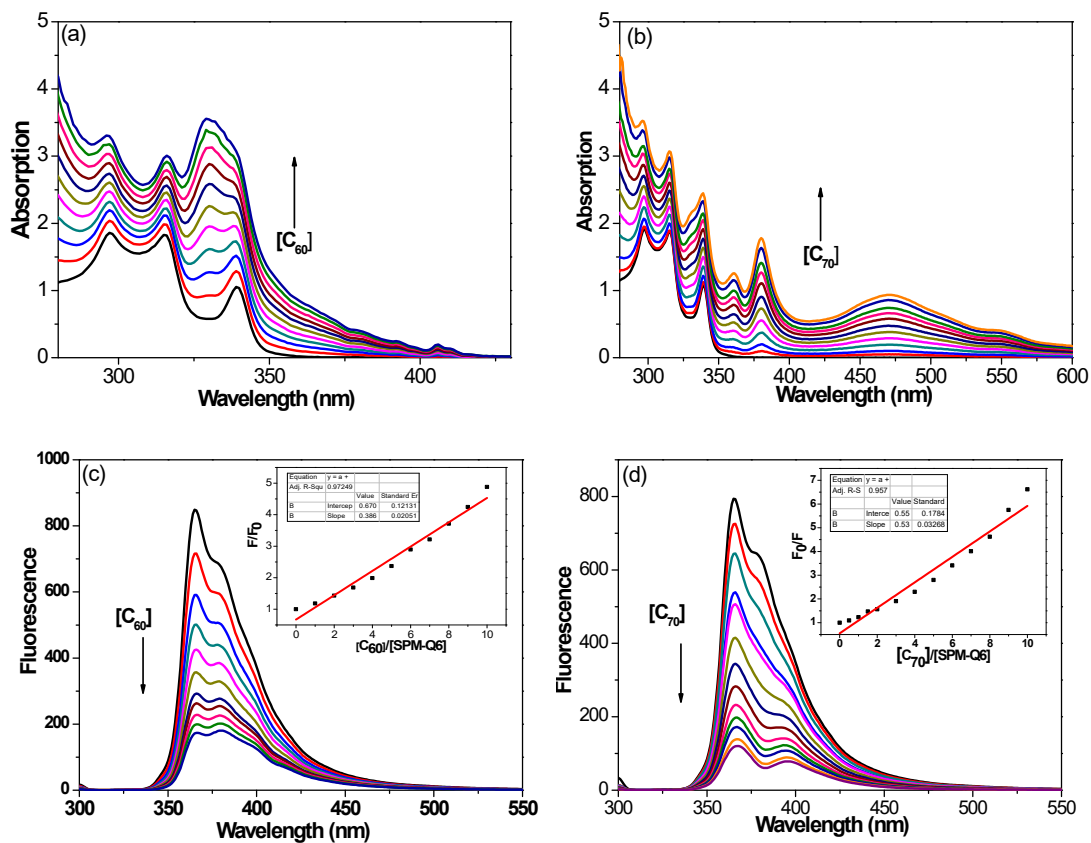


Fig. S7. UV-vis absorption spectra of SPM-Q6 to (a) C<sub>60</sub> and (b) C<sub>70</sub> (from 0 to 10 eq); Fluorescence responses of SPM-Q6 to (c) C<sub>60</sub> and (d) C<sub>70</sub> (from 0 to 10 eq) in 1,1,2,2-tetrachloroethane solution. Inset: the inset is the variation of fluorescence intensity F<sub>0</sub>/F of SPM-Q6 with increasing fullerene concentration.

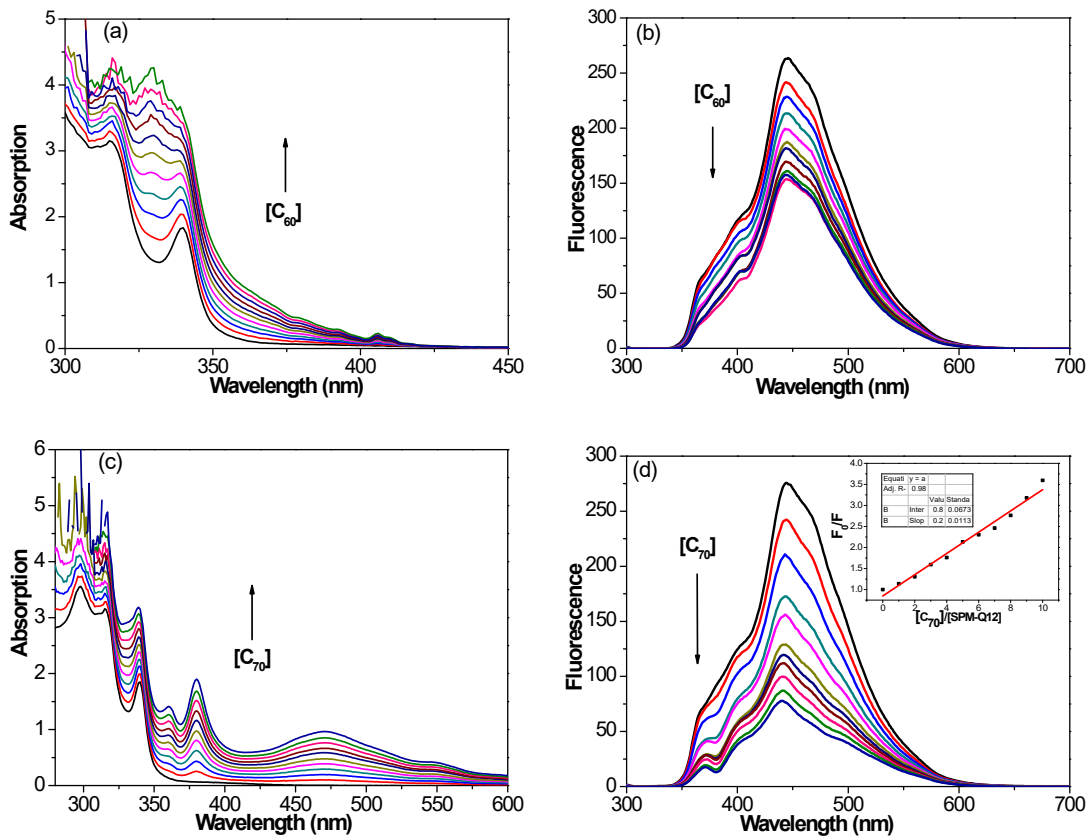


Fig. S8. UV-vis absorption spectra of SPM-Q12 to (a) C<sub>60</sub> and (b) C<sub>70</sub> (from 0 to 10 eq); Fluorescence responses of SPM-Q12 to (c) C<sub>60</sub> and (d) C<sub>70</sub> (from 0 to 10 eq) in 1,1,2,2-tetrachloroethane solution. Inset: the inset is the variation of fluorescence intensity  $F_0/F$  of SPM-Q12 with increasing fullerene concentration.

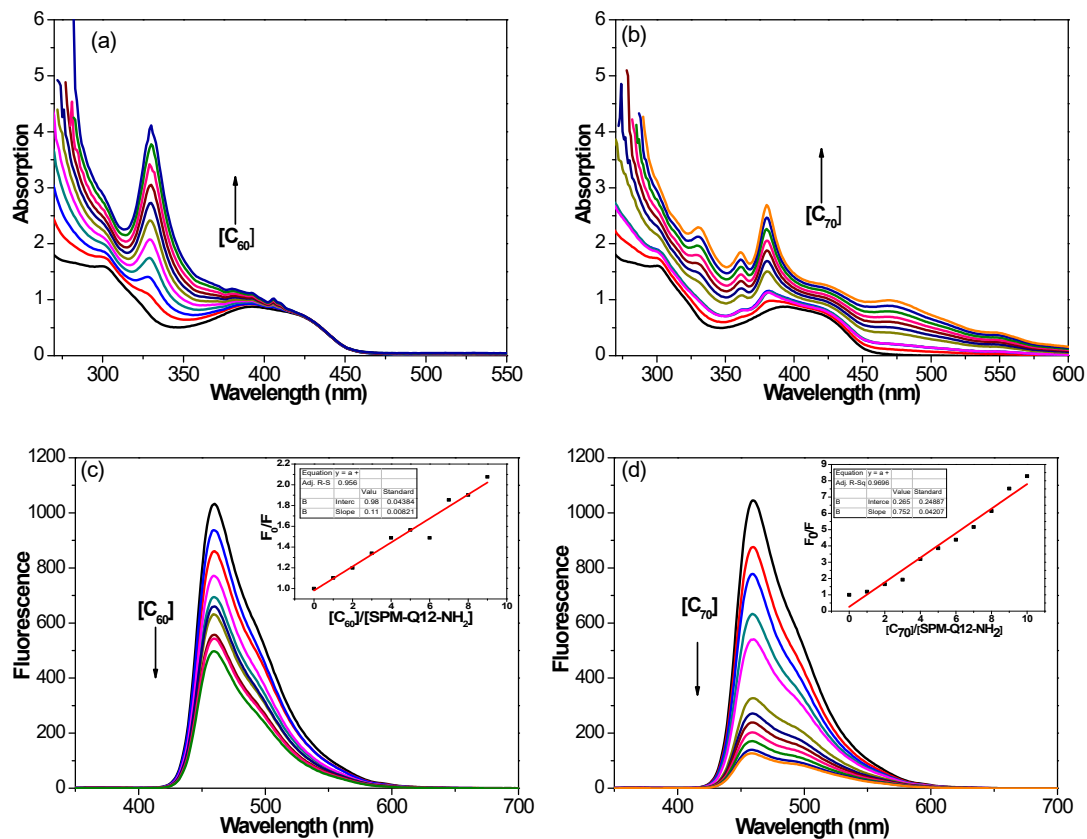


Fig. S9. UV-vis absorption spectra of **SPM-Q12-NH<sub>2</sub>** to (a) **C<sub>60</sub>** and (b) **C<sub>70</sub>** (from 0 to 10 eq); Fluorescence responses of **SPM-Q12-NH<sub>2</sub>** to (c) **C<sub>60</sub>** and (d) **C<sub>70</sub>** (from 0 to 10 eq) in 1,1,2,2-tetrachloroethane solution. Inset: the inset is the variation of fluorescence intensity  $F_0/F$  of **SPM-Q12-NH<sub>2</sub>** with increasing fullerene concentration.

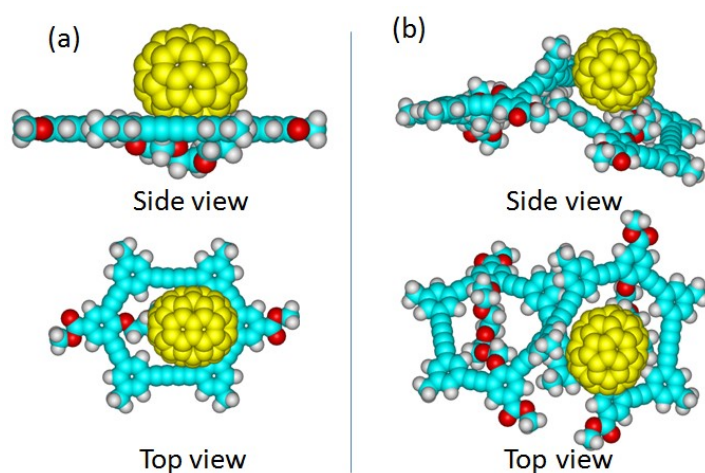


Fig. S10. The macrocycles interact with **C<sub>70</sub>** models, (a) **SPM-Q6/C<sub>70</sub>**, (b) **SPM-Q12/C<sub>70</sub>**.

## 2. Tables Referenced in the Manuscript

**Table S1.** Optimization of substrate concentration for the cyclization (**SPM-Q6-NH<sub>2</sub>**).

<b>C/mol/L (10<sup>-4</sup>)<sup>a</sup></b>	2	3	6	10	20
<b>SPM-Q6-NH<sub>2</sub> Yield(%)<sup>b</sup></b>	33.3	26.7	20.6	18.7	16.4
<b>SPM-Q12-NH<sub>2</sub> Yield(%)<sup>b</sup></b>	6.7	8.6	11.2	16.3	18.4

<sup>a</sup>. The concentration of **SPM-NH<sub>2</sub>** in reaction solution. <sup>b</sup>. The isolated yield.

**Table S2.** The unit cell parameters for assembled monolayer on HOPG.

	<i>a</i> (nm)	<i>b</i> (nm)	deg
<b>SPM-Q6</b>	2.17	2.79	90.0
<b>SPM-Q12</b>	4.10	3.15	89.0

**Table S3.** Total energy and energy per unit area for the macrocycles by DFT calculations. The total energy includes the interaction between molecules and the interaction between molecules and HOPG.

	Inter	Sub	Total	Energy per unit area kcal mol <sup>-1</sup> Å <sup>-2</sup>
<b>SPM-Q6</b>	-24.907	-189.508	-214.415	-0.348
<b>SPM-Q12</b>	-17.395	-114.759	-132.154	-0.102



### 3. Experimental details:

#### 3.1. General remarks.

All reagents were obtained from commercial suppliers and used as received. Toluene, tetrahydrofuran (THF), dioxane and diisopropylamine were dried over sodium/benzophenoneketyl and freshly distilled prior to use. Compound **7** and SPM-NH<sub>2</sub> were prepared according to literature methods<sup>S1,S2</sup>. All reactions were carried out under nitrogen atmosphere unless otherwise noted.

**Measurements and Instruments.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker AV-400 spectrometer with residual solvent peaks (CDCl<sub>3</sub>: <sup>1</sup>H: δ= 7.26, <sup>13</sup>C: δ = 77.23). The mass spectra was obtained using an Ion-Spec 4.7 T HiRes MALDI instrument. UV absorption spectra was obtained using a Scinco S-3150 UV/vis spectrophotometer. The GPC analysis was performed on Waters1525 gel permeation chromatography (GPC) with refractive index (RI) detector, using polystyrene as a standard and toluene as mobile phase.

**Calculation in the gas phase.** All calculations were carried out using density functional theory (DFT) method as implemented in the DMol3 program.<sup>S3</sup> Geometries were optimized using the local spin density approximation and Perdew and Wang parameterization(PWC) as the local exchange correlation.<sup>S4</sup> The double numerical plus polarization (DNP) was employed as the basis set. The all-electron calculations were performed with medium grid (0.25 Å grid interval). The convergence criterions of the energy and electron density in the self-consistent field procedure were set at 10<sup>-5</sup> au. The force criteria 0.004 au Å<sup>-1</sup> and displacement criteria 0.005 Å was adopted for structural optimization.

#### STM measurements.

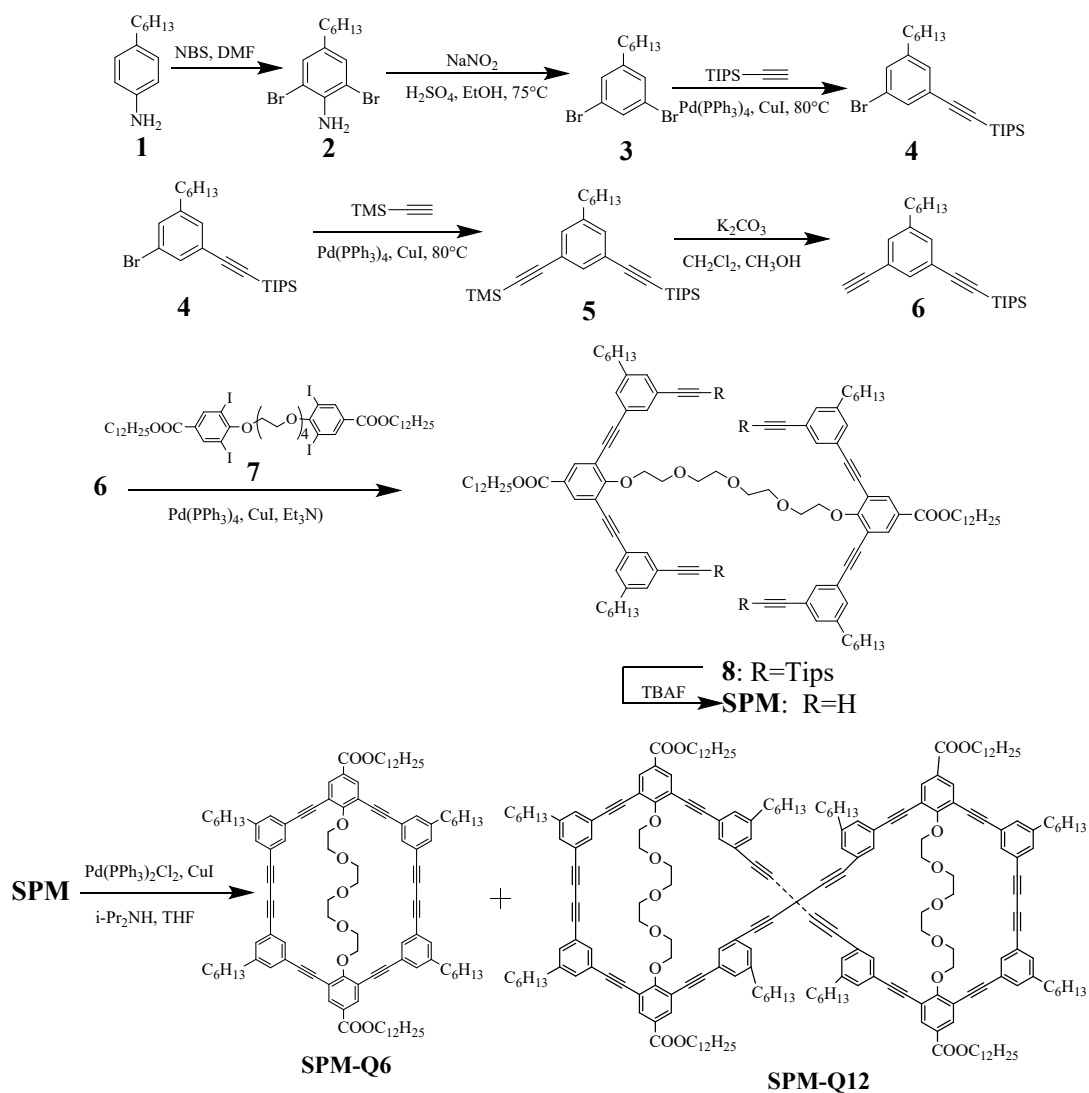
**Sample Preparation.** All the studied samples were dissolved in 1-phenyloctane (Aldrich). Highly oriented pyrolytic graphite (HOPG, grade ZYB) purchased from Agilent (U.S.A.) were used as substrates. The samples were prepared by depositing a droplet of the above solution on a basal plane of freshly cleaved HOPG substrate. The samples were studied by STM with the scanning tips immersed directly into the droplet.

**STM Measurement.** All STM experiments were performed with a NanoscopeIIIa scanning probe microscope system (Bruker, USA) in constant current mode under ambient conditions. STM tips were

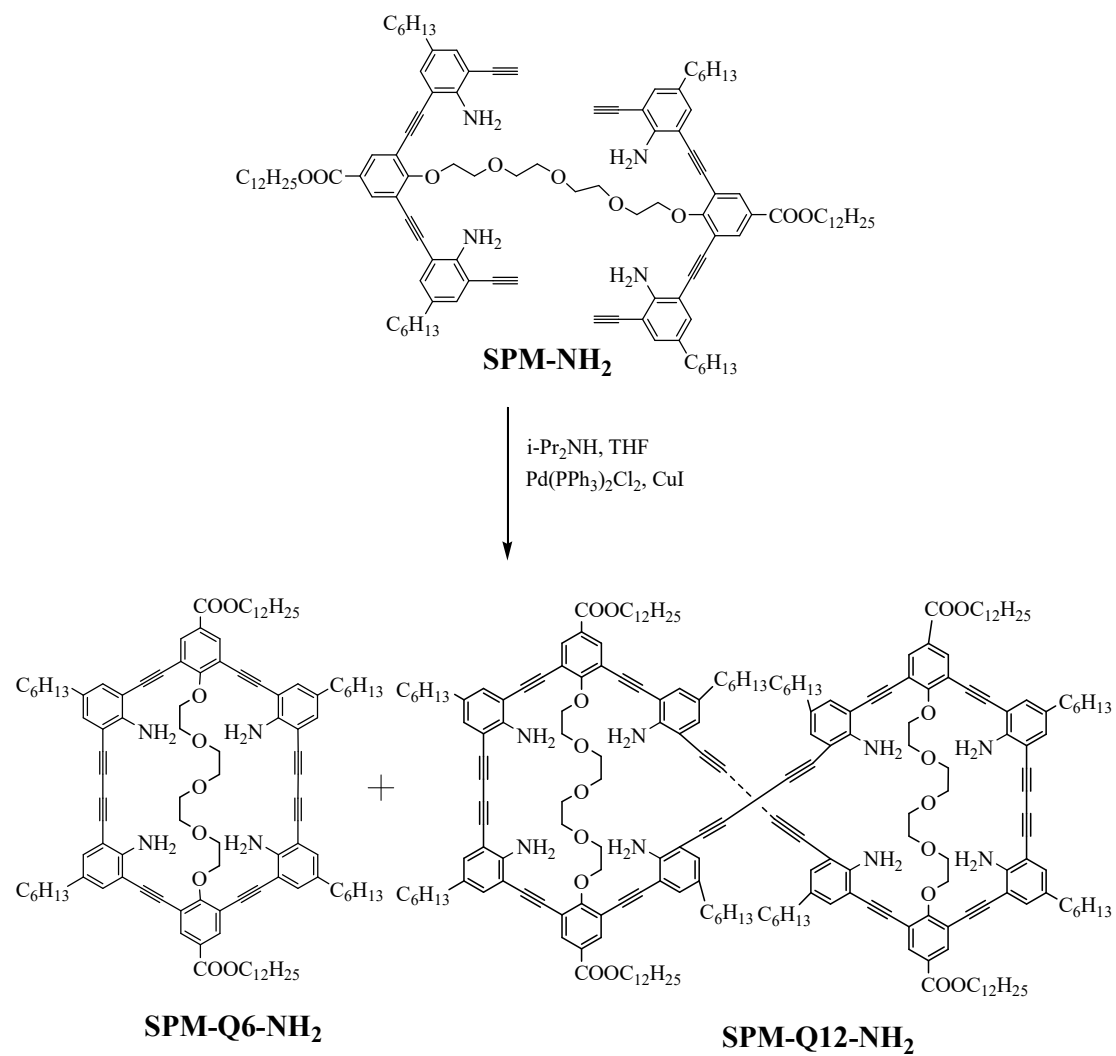
prepared by mechanically cutting of Pt/Ir wire (80/20). All the STM images provided are raw data and were calibrated by referring the underlying graphite lattice. Detailed tunneling conditions were given in the corresponding figure captions.

**Calculation in the self-assemblies.** All the calculations for the self-assemblies on HOPG were performed by using the DMol3 code.<sup>S3</sup> The periodic molecular structures were applied with periodic boundary conditions (PBC). Geometries were optimized using the local spin density approximation and Perdew and Wang parameterization(PWC) as the local exchange correlation.<sup>S4</sup> The double numerical plus polarization (DNP) was employed as the basis set. The all-electron calculations were employed with medium grid(0.25 Å grid interval). The convergence criterions of the energy and electron density in the self-consistent field procedure were set at  $10^{-5}$  au. The force criteria  $0.004 \text{ au } \text{Å}^{-1}$  and displacement criteria  $0.005 \text{ Å}$  was adopted for structural optimization. We applied the infinite graphene monolayer to investigate the interactions between the substrate and the adsorbed molecules. Superlattice was utilized, and the vacuum layer along z axis was separated by  $40 \text{ Å}$ . The Brillouin zone was sampled by a  $4 \times 4 \times 1$  k-point mesh. The calculated interaction energy of the adsorbates  $E_{\text{inter}}$  were determined by the equation:  $E_{\text{inter}} = E_{\text{tot(adsorbates/graphene)}} - E_{\text{tot(isolated adsorbates in vacuum)}} - E_{\text{tot(graphene)}}$ .

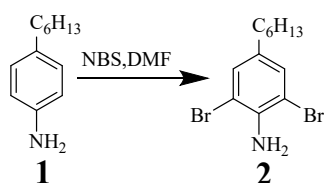
### 3.2 Synthetic procedure



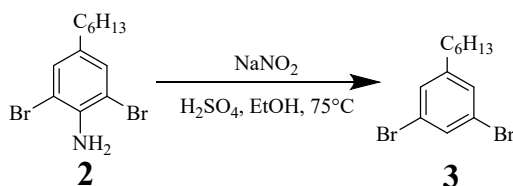
Scheme S1: Synthesis of target compound SPM-Q6 and SPM-Q12.



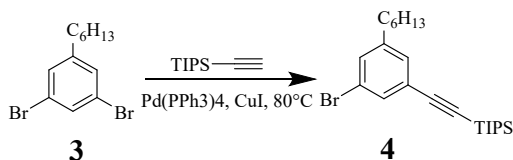
Scheme S2: Synthesis of target compound **SPM-Q6-NH<sub>2</sub>** and **SPM-Q12-NH<sub>2</sub>**.



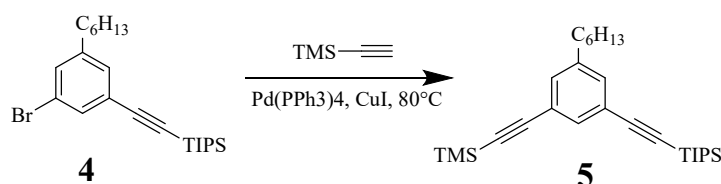
**Compound 2.** To a stirred mixture of **1** (10g, 0.056mol) in 10mL DMF, NBS (21.56g, 0.121mol) was added dropwise at 0°C. The resulting reaction was stirred at room temperature for 4 hours and was quenched with 20 ml water. The layers were separated and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. The combined organic phase was washed with brine, and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether) to afford compound **2** as a pale white solid (17.9 g, 96.2%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): δ 0.87 (t, J = 4Hz, 3H), 1.28 (s, 6H), 1.54 (m, 2H), 4.02 (br, 2H), 7.20 (s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm): 14.05, 22.58, 28.78, 31.37, 31.66, 34.44, 108.78, 131.58, 134.65, 139.65. MALDI-TOF MS: m/z; [M]<sup>+</sup>, calcd for C<sub>12</sub>H<sub>17</sub>Br<sub>2</sub>N :335.07; found: 335.75



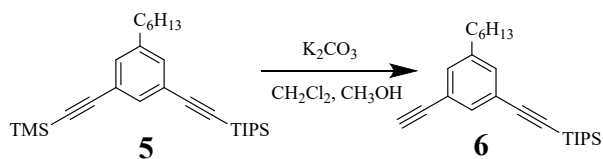
**Compound 3.** A mixture of compound **2** (4.38 g, 0.0131 mol), concentrated sulfuric acid (5 mL), and ethanol (80 mL) were heated to reflux at 75°C, then NaNO<sub>2</sub> (2.735 g, 0.040 mol) was slowly added. The reaction mixture was continually stirred at this temperature for 2 h. After cooled down to room temperature, ice water was added and then was extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. The combined organic phase was washed with brine, and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether) to afford compound **3** as a colorless liquid (3.22g, 72.5%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): δ 7.48 (s, 1H), 7.26 (s, J = 1.5 Hz, 2H), 2.55 (t, 2H), 1.59 (m, 2H), 1.30 (m, 6H), 0.90 (t, 3H). MALDI-TOF MS: m/z; [M]<sup>+</sup>, calcd for C<sub>12</sub>H<sub>16</sub>Br<sub>2</sub> :320.06; found: 319.24.



**Compound 4.** To a degassed solution of **3** (3.0 g, 9.435mmol) in triethylamine (50 mL), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.32 g, 2.83 mmol), CuI (0.09 g, 0.472 mmol), (triisopropylsilyl)acetylene ( 1.7 g, 9.435 mmol) was added. The resulting mixture was stirred under nitrogen at 80 °C for 12 h and then cooled down to room temperature. The reaction was quenched with water, and the layers were separated. The combined organic phase was washed with brine, and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether) to afford compound **4** as a colorless oil(1.58g, 40.0%).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm):δ 7.44 (s, 1H), 7.26 (d, J = 1.6 Hz, 1H), 7.21 (s, 1H), 2.55 (t, 2H), 1.59 (m, 2H), 1.31 (m, 6H), 1.14 (d, 18H), 0.90 (t, 3H).MALDI-TOF MS: m/z; [M]<sup>+</sup>, calcd for C<sub>23</sub>H<sub>37</sub>BrSi :420.18; found: 429.20.

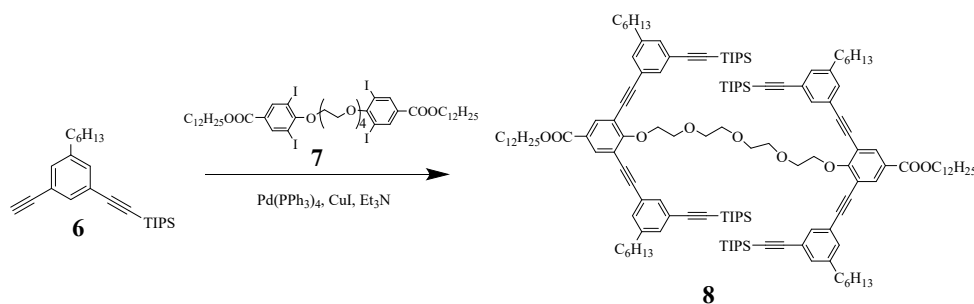


**Compound 5.** To a degassed solution of **4** (2.25 g, 5.354 mmol) in triethylamine (50 mL), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.186 g, 0.161 mmol), CuI (0.051 g, 0.267 mmol), trimethylsilylacetylene ( 0.876 g, 8.948 mmol) was added. The reaction mixture was stirred under nitrogen at 80 °C for 12 h and then cooled down to room temperature. The reaction was quenched with water, and the layers were separated. The combined organic phase was washed with brine, and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether) to afford compound **5** as a colorless oil (1.99 g, 84.9%).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.24 (s, 1H), 7.06 (s, 2H), 2.36 (t, 2H), 1.42 (m, 2H), 1.13 (m, 6H), 0.96 (d, 18H), 0.72 (t, 3H), 0.08 (s, 9H).<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.09, 132.84, 132.08, 131.86, 123.57, 123.15, 106.48, 104.55, 94.25, 90.64, 35.51, 31.67, 31.14, 28.94, 22.57, 22.57, 18.68, 14.05, 11.36.MALDI-TOF MS: m/z; [M]<sup>+</sup>, calcd for C<sub>28</sub>H<sub>46</sub>Si<sub>2</sub> :438.31; found: 437.79.

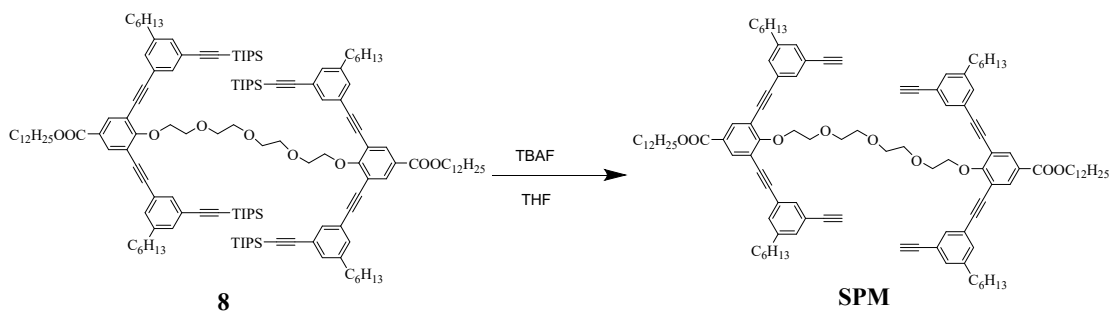


**Compound 6.** To a solution of **5** (2 g, 3.83 mmol) in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (1:1) 50mL, K<sub>2</sub>CO<sub>3</sub> (5.0 g, 36.0

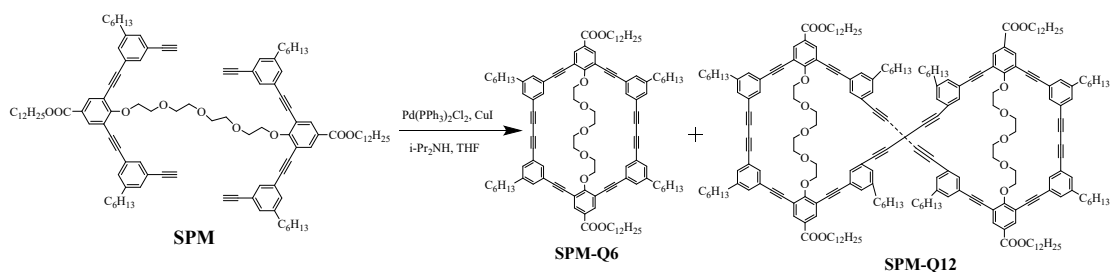
mmol) was added. After stirring for 5h at RT, removal of solvent under reduced pressure and purification by column chromatography on silica gel (hexane as eluent) yielded compound **6** as a colorless oil (1.284 g, 91.6%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45 (s, 1H), 7.28 (s, 1H), 7.27 (s, 1H), 3.06 (s, 1H), 2.56 (t, 2H), 1.61 (m, 2H), 1.32 (m, 6H), 1.16 (d, 18H), 0.91 (t, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.22, 133.02, 132.33, 131.99, 123.70, 122.16, 106.34, 90.89, 83.10, 77.19, 35.46, 31.66, 31.10, 28.91, 22.57, 18.66, 14.04, 11.35. MALDI-TOF MS: m/z; [M]<sup>+</sup>, calcd for C<sub>25</sub>H<sub>38</sub>Si :366.27; found: 364.87.



**Compound 8.** To a degassed solution of **7** (0.5 g, 0.3924 mmol) in triethylamine (20 mL), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.027 g, 0.023 mmol), CuI (0.007 g, 0.039 mmol) and **6** (0.71 g, 1.962 mmol) was added. The reaction mixture was stirred under nitrogen at 45°C for 12h and cooled to room temperature. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, 100:1) to afford compound **8** as a yellow oil (0.681 g, 78.1%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 8.05 (s, 4H), 7.41 (s, 4H), 7.23 (s, 4H), 7.20 (s, 4H), 4.51 (t, 4H), 4.26 (t, 4H), 3.82 (t, 4H), 3.58 (t, 4H), 3.43 (t, 4H), 2.50 (t, 8H), 1.72 (m, 8H), 1.54 (m, 8H), 1.38 (m, 4H), 1.24 (s, 56H), 1.20 (s, 12H), 1.07 (s, 72H), 0.83 (s, 18H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm): 164.95, 164.58, 145.78, 143.71, 135.53, 132.51, 132.27, 131.90, 131.44, 130.51, 126.32, 125.00, 123.79, 122.91, 122.39, 117.70, 106.34, 94.17, 93.49, 91.03, 85.52, 84.80, 84.69, 73.42, 70.73, 70.60, 65.59, 35.52, 35.44, 29.64, 29.62, 29.60, 29.55, 29.33, 29.30, 28.94, 28.85, 28.74, 26.00, 22.67, 22.54, 18.68, 14.05, 11.34. MALDI-TOF MS: m/z; [M]<sup>+</sup>, calcd for C<sub>146</sub>H<sub>218</sub>O<sub>9</sub>Si<sub>4</sub> :2250; found: 2249.58.



**Compound SPM.** To a stirred solution of **8** (0.2 g, 0.0898 mmol) in THF (20 mL) was added dropwise a solution of tetrabutylammonium fluoride (TBAF) (0.05 g, 0.019 mmol) in THF (2.5 ml) in 30 minutes. The resulted mixture was stirred at room temperature for 1 h. After removal of the solvent under reduced pressure at 0°C, the residue was purified by column chromatography on silica gel (hexane/THF =10:1) to afford **SPM** (0.13 g, 0.0826 mmol) as a orange solid in 90.3 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 8.10 (s, 4H), 7.48 (s, 4H), 7.32 (s, 4H), 7.28 (s, 4H), 4.58 (t, 4H), 4.31 (t, 4H), 3.91 (t, 4H), 3.66 (t, 4H), 3.52 (t, 4H), 3.07 (s, 4H), 1.78 (d, 4H), 1.60 (d, 8H), 1.44 (s, 4H), 1.29 (s, 56H), 1.26 (s, 23H), 1.05 (s, 30H), 0.88 (s, 18H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm): 164.99, 164.15, 143.49, 134.91, 132.40, 131.94, 125.80, 123.04, 122.41, 93.91, 84.92, 82.97, 77.59, 70.74, 70.62, 65.54, 35.46, 31.90, 31.64, 31.04, 29.64, 29.61, 29.59, 29.52, 29.33, 29.29, 28.87, 28.73, 26.00, 22.67, 22.55, 17.69, 14.04, 12.32. MALDI-TOF MS: calcd for C<sub>110</sub>H<sub>138</sub>O<sub>9</sub> + Na<sup>+</sup> (M+Na<sup>+</sup>) : 1626.03; found: 1626.2



**SPM-Q6 and SPM-Q12.** A mixture of **SPM**(0.1 g, 0.062 mmol), diisopropylamine (1 g, 7.7 mmol), CuI (6 mg, 0.03 mmol) and dry THF (250mL) was carefully degassed for 20 min before and after the addition of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (5 mg, 0.007 mmol). The reaction mixture was stirred under nitrogen at room temperature for 3 days. The solvent was removed under reduced pressure. The residue was purified by gel permeation chromatography (GPC) to afford **SPM-Q6** (30.76 mg) in 30.76% yield and **SPM-Q12** (5.31mg) in 5.31% yield as colorless solid, respectively.

**SPM-Q6:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 8.02 (s, 4H), 7.53 (d, 4H), 7.29 (s, 4H), 7.25 (s, 4H), 4.64 (d, 4H), 4.35 (t, 4H), 4.15 (t, 4H), 4.10 (t, 8H), 2.58 (t, 8H), 1.83 (m, 4H), 1.64 (m, 12H), 1.48 (m, 4H), 1.36



(m, 28H), 1.29 (m, 24H), 0.94 (s, 18H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm): 164.89, 164.59, 143.42, 134.37, 132.96, 132.18, 132.01, 125.62, 123.23, 121.98, 117.28, 93.72, 85.12, 80.95, 74.48, 74.29, 71.61, 71.34, 71.13, 65.46, 35.45, 31.88, 31.66, 30.96, 29.64, 29.61, 29.53, 29.32, 28.89, 28.72, 25.98, 22.65, 22.57, 14.08. MALDI-TOF MS: , calcd for C<sub>110</sub>H<sub>134</sub>O<sub>9</sub> + Na<sup>+</sup> [M+Na]<sup>+</sup>: 1623.2; found: 1624.7.

**SPM-Q12**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96 (s, 4H), 7.91 (s, 4H), 7.56 (s, 4H), 7.32 (s, 8H), 7.26 (s, 4H), 7.19 (s, 4H), 7.16 (s, 4H), 7.14 (s, 4H), 4.57 (t, 8H), 4.18 (t, 8H), 4.07 (t, 8H), 3.99 (t, 16H), 2.55 (t, 8H), 2.47 (t, 8H), 1.69 (m, 8H), 1.56 (m, 8H), 1.50 (m, 8H), 1.27 (m, 48H), 1.18 (m, 96H), 0.82 (t, *J* = 14.5 Hz, 36H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.81, 164.25, 143.76, 134.64, 134.43, 133.27, 132.53, 132.41, 132.35, 132.26, 132.14, 125.85, 123.39, 123.04, 122.02, 121.93, 117.34, 117.18, 94.15, 93.72, 85.23, 85.05, 81.22, 81.11, 74.55, 74.38, 73.86, 71.45, 71.25, 71.15, 65.59, 31.91, 31.67, 31.65, 31.04, 30.90, 29.69, 29.64, 29.59, 29.35, 29.03, 28.87, 28.73, 25.97, 22.67, 22.60, 22.57, 14.07, 14.06, 14.04. MALDI-TOF MS: *m/z*; M<sup>+</sup>, calcd for C<sub>220</sub>H<sub>268</sub>O<sub>18</sub>: 3198.00; found: 3194.9. HRMS(MALD): calcd for C<sub>220</sub>H<sub>269</sub>O<sub>18</sub>(M+H<sup>+</sup>): 3199.0134; found: 3199.01336.

**SPM-Q6-NH<sub>2</sub>** and **SPM-Q12-NH<sub>2</sub>**. The same synthetic procedure of **SPM-Q6** and **SPM-Q12** was employed. A mixture of **SPM-NH<sub>2</sub>** (0.1 g, 0.06 mmol), diisopropylamine (1.25 g, 8.5 mmol), CuI (6 mg, 0.03 mmol) and dry THF (250 mL) was carefully degassed for 20 min before and after the addition of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (5 mg, 0.007 mmol). The reaction mixture was then stirred under nitrogen at room temperature for 3 days. The solvent was removed under reduced pressure. The residue was purified by gel permeation chromatography (GPC) to afford **SPM-Q6-NH<sub>2</sub>** (16.41 mg) in 16.4% yield and **SPM-Q12-NH<sub>2</sub>** (18.35 mg) in 18.4% yield as colorless solid, respectively.

**SPM-Q6-NH<sub>2</sub>** <sup>56</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 8.09 (s, 4H), 7.20 (d, *J* = 1.6 Hz, 4H), 7.14 (s, 4H), 5.02 (br, 8H), 4.47 (d, *J* = 3.7 Hz, 4H), 4.34 (t, *J* = 6.8 Hz, 4H), 3.98 (d, *J* = 3.3 Hz, 4H), 3.88 (t, *J* = 5.1 Hz, 4H), 3.82 (t, *J* = 5.0 Hz, 4H), 2.46 (t, *J* = 7.6 Hz, 8H), 1.80 (m, 4H), 1.57 (m, 8H), 1.47 (m, 4H), 1.38 (m, 4H), 1.31 (m, 28H), 1.27 (s, 24H), 0.89 (m, 18H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm): 164.80, 162.79, 148.71, 133.76, 133.05, 132.69, 131.51, 126.08, 117.67, 107.14, 105.82, 91.26, 90.10, 79.52, 78.91, 77.23, 76.91, 76.59, 73.59, 71.37, 70.91, 70.02, 65.46, 34.54, 31.81, 31.64, 31.20, 29.57, 29.54, 29.47, 29.26, 28.78, 28.63, 25.91, 22.59, 22.53, 14.04. MALDI-TOF MS: calcd for C<sub>110</sub>H<sub>138</sub>N<sub>4</sub>O<sub>9</sub>: 1659.04; found: 1659.4.

**SPM-Q12-NH<sub>2</sub>**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) : 8.02 (s, 8H), 8.00 (s, 8H), 7.17 (s, 4H), 7.13 (s, 4H),

7.08 (s, 8H), 5.38 (m, 1H), 4.45 (s, 8H), 4.30 (s, 8H), 3.91 (s, 16H), 3.82 (s, 8H), 2.44 (s, 8H), 2.37 (s, 8H), 1.78 (s, 8H), 1.56 (s, 8H), 1.48 (s, 8H), 1.32 (s, 48H), 1.26 (s, 96H), 0.88 (t, 7.4Hz, 36H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 164.90, 163.09, 149.39, 149.17, 134.11, 133.65, 133.47, 133.20, 133.00, 132.82, 131.65, 131.41, 126.26, 117.88, 117.32, 106.98, 105.61, 105.56, 91.57, 91.52, 90.28, 90.12, 80.26, 79.76, 79.21, 78.96, 73.36, 71.27, 71.12, 70.42, 65.63, 31.92, 31.74, 31.72, 31.36, 31.25, 29.68, 29.65, 29.58, 29.35, 28.94, 28.85, 28.75, 26.00, 22.68, 22.62, 14.10. MALDI-ToF MS:  $m/z$ ;, calcd for  $\text{C}_{220}\text{H}_{276}\text{N}_8\text{O}_{18}$   $[\text{M}-\text{H}]^+$ : 3317.07; found: 3317.0.

### 3.3. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra

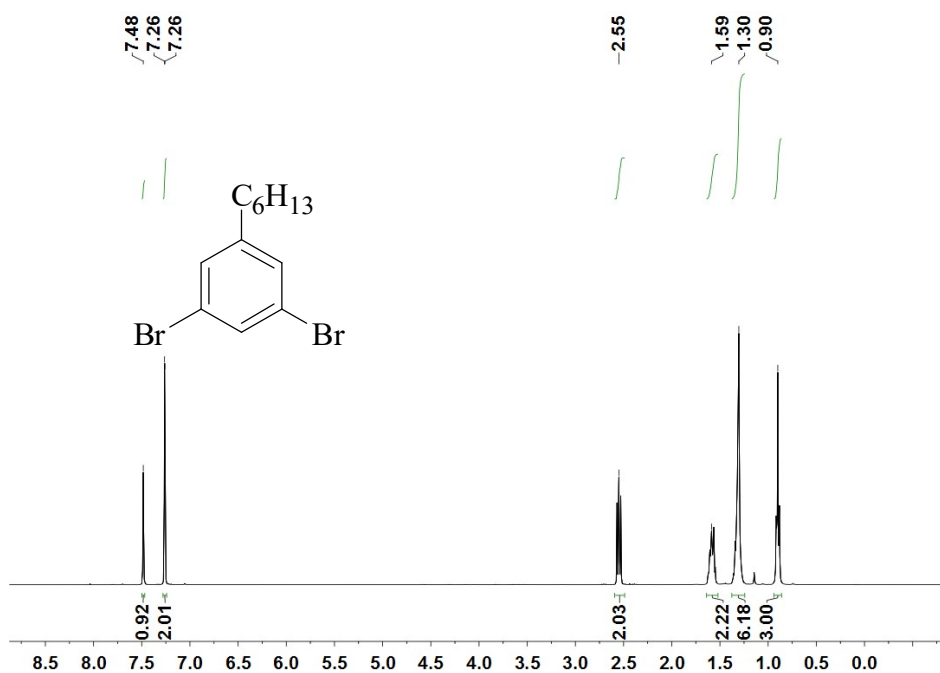


Fig. S11.  $^1\text{H}$  NMR of compound 3.

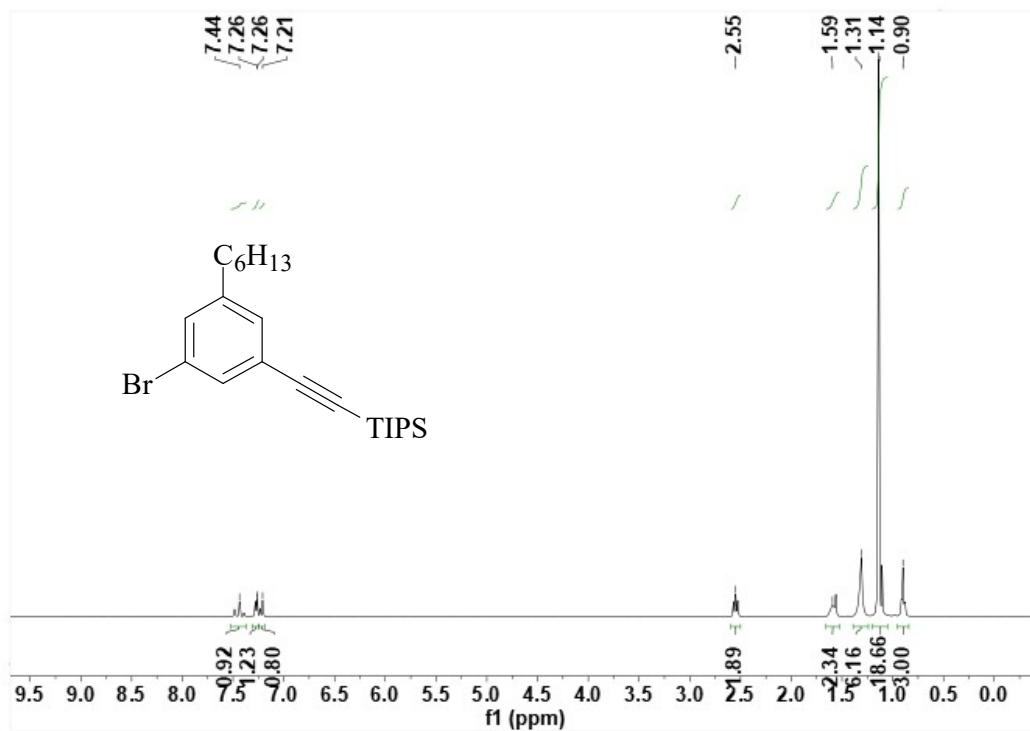


Fig. S12.  $^1\text{H}$  NMR of compound 4.

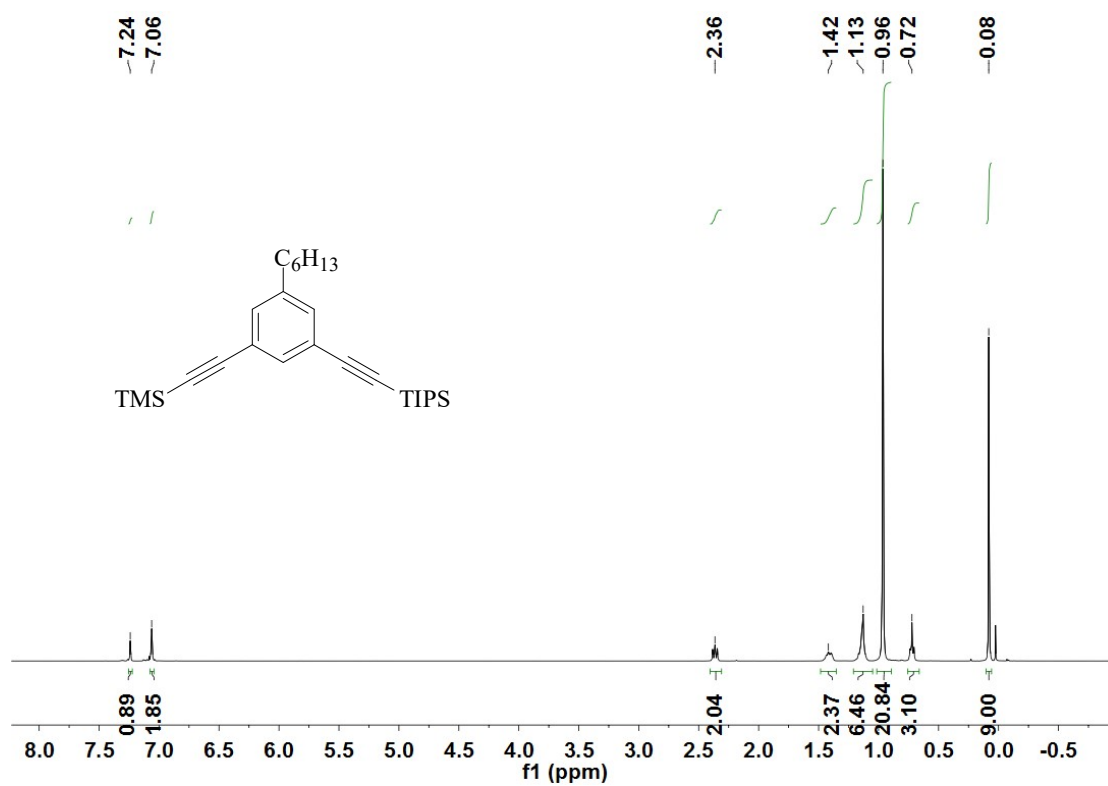


Fig. S13.  $^1\text{H}$  NMR of compound 5.

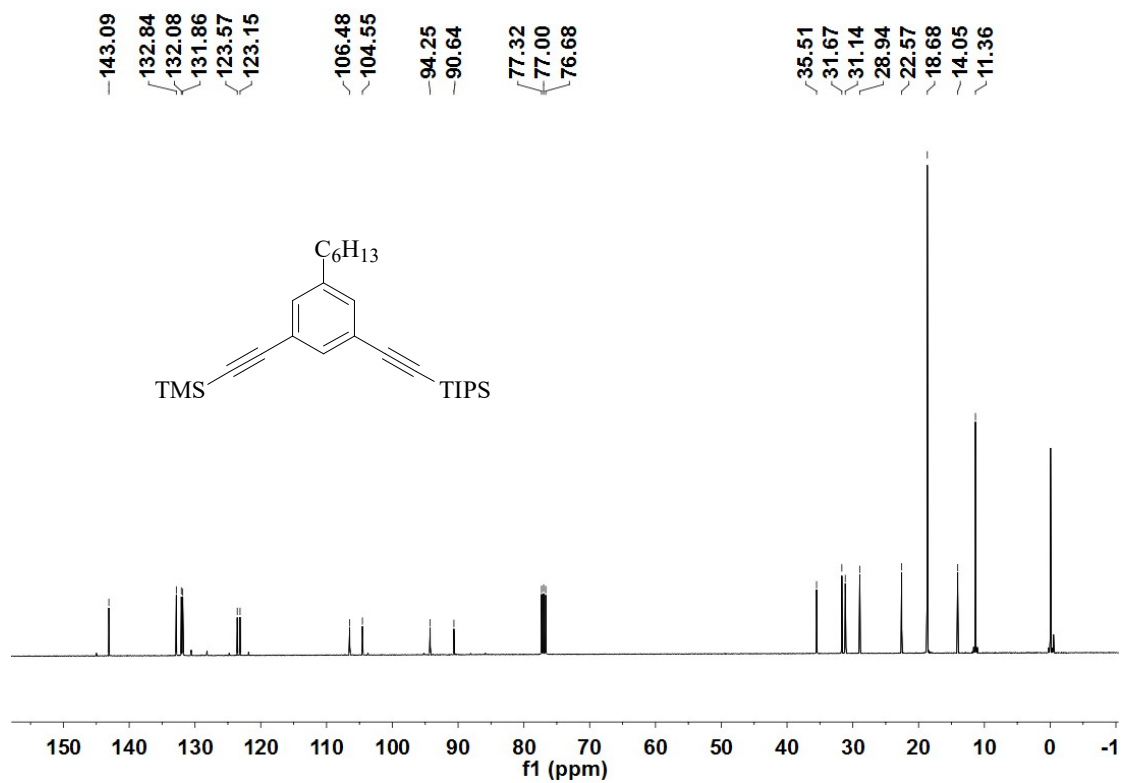


Fig. S14.  $^{13}\text{C}$  NMR of compound 5.

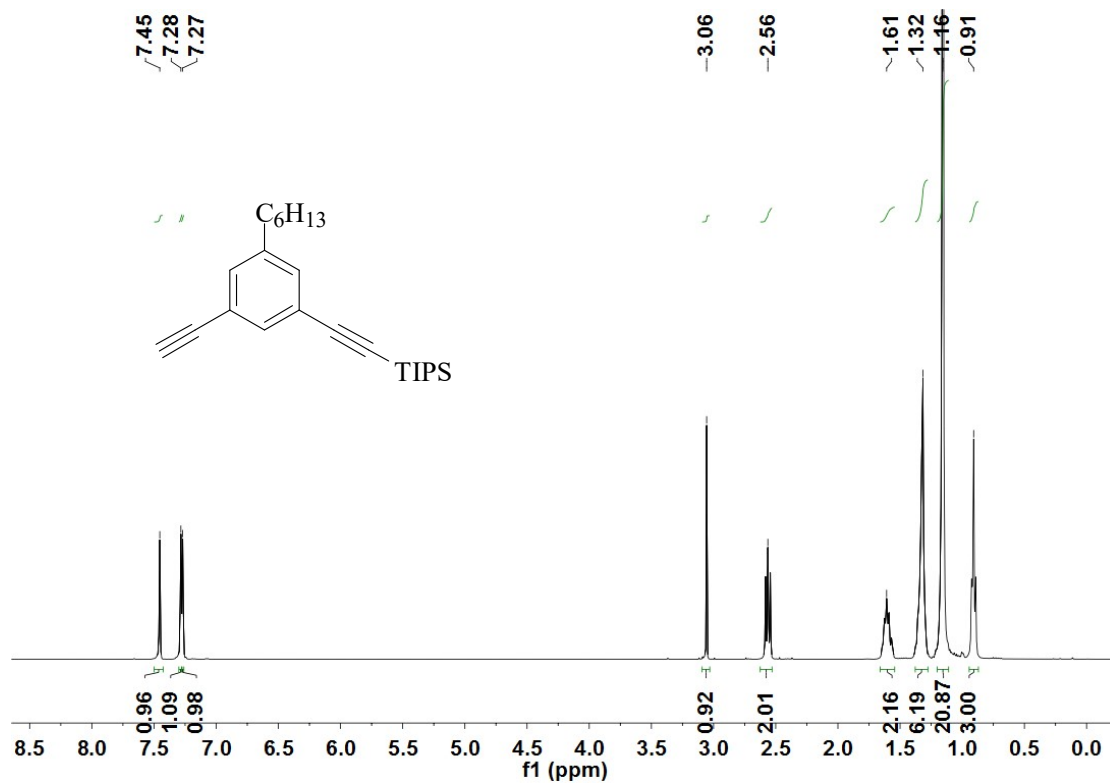


Fig. S15.  $^1\text{H}$  NMR of compound 6.

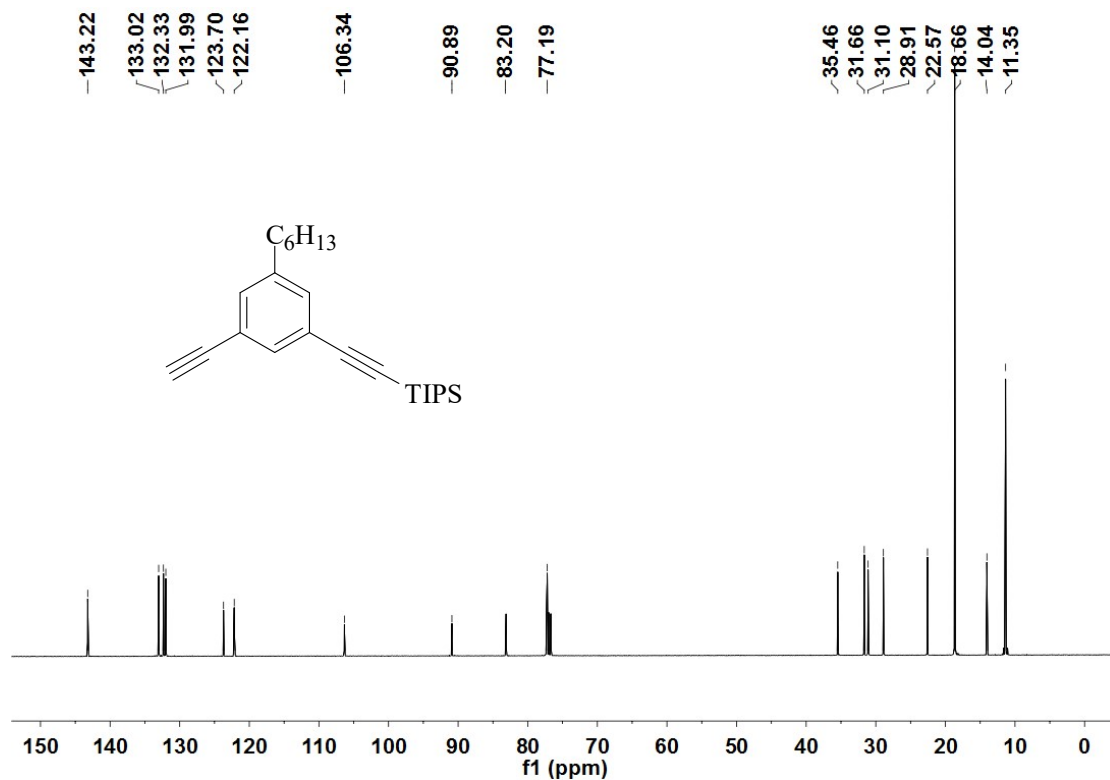


Fig. S16.  $^{13}C$  NMR of compound 6.

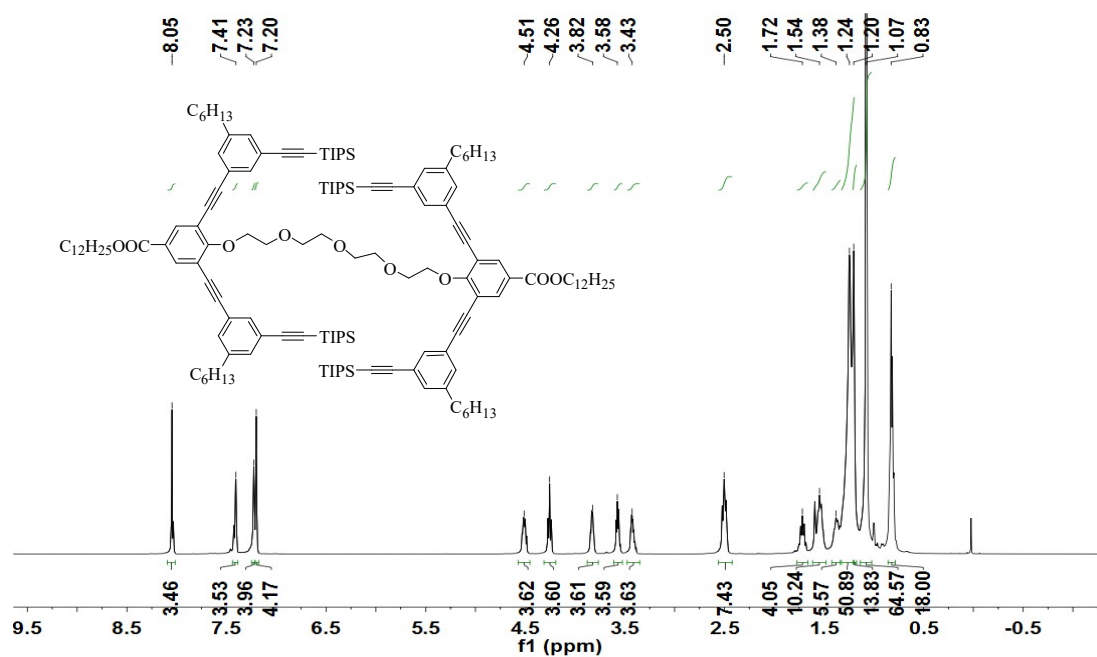


Fig. S17.  $^1H$  NMR of compound 8.



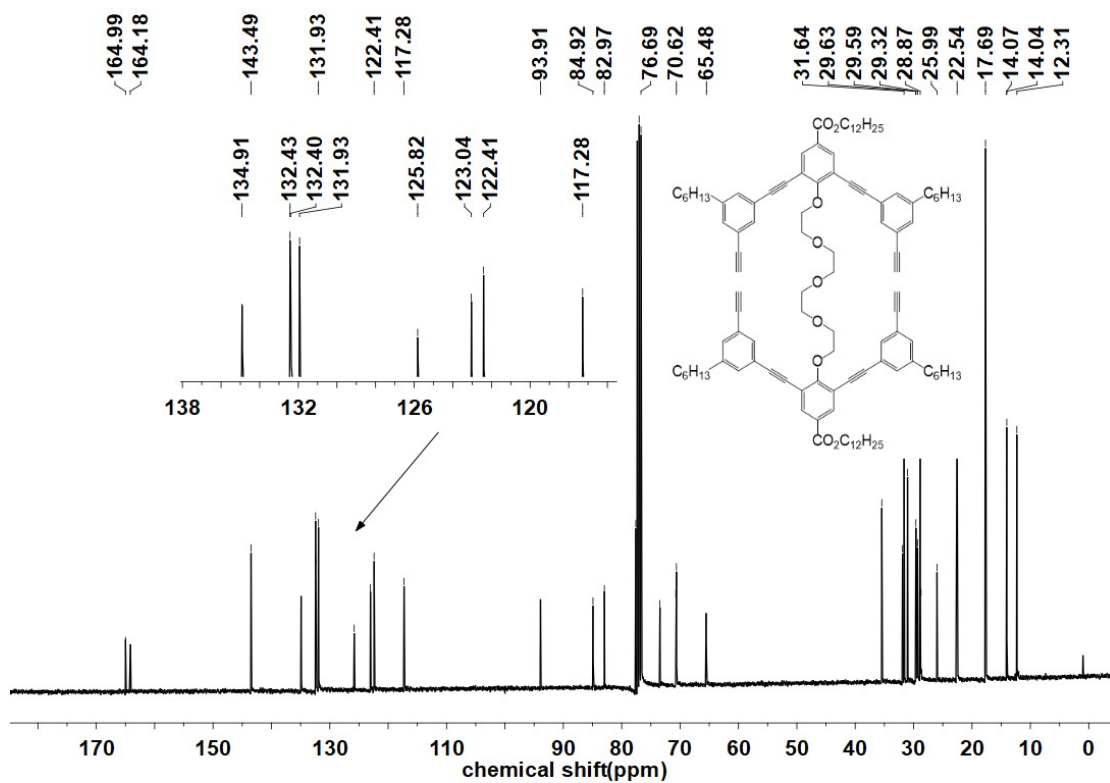


Fig. S20.  $^{13}C$  NMR of compound SPM.

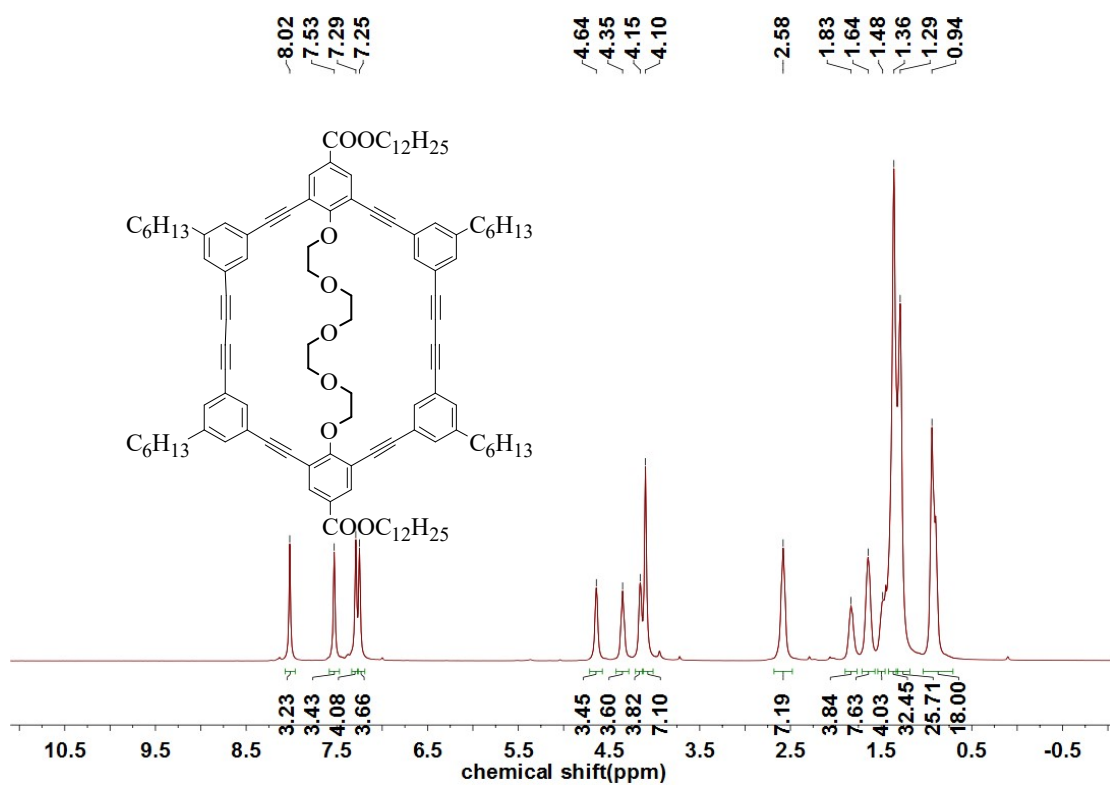


Fig. S21.  $^1H$  NMR of compound SPM-Q6.

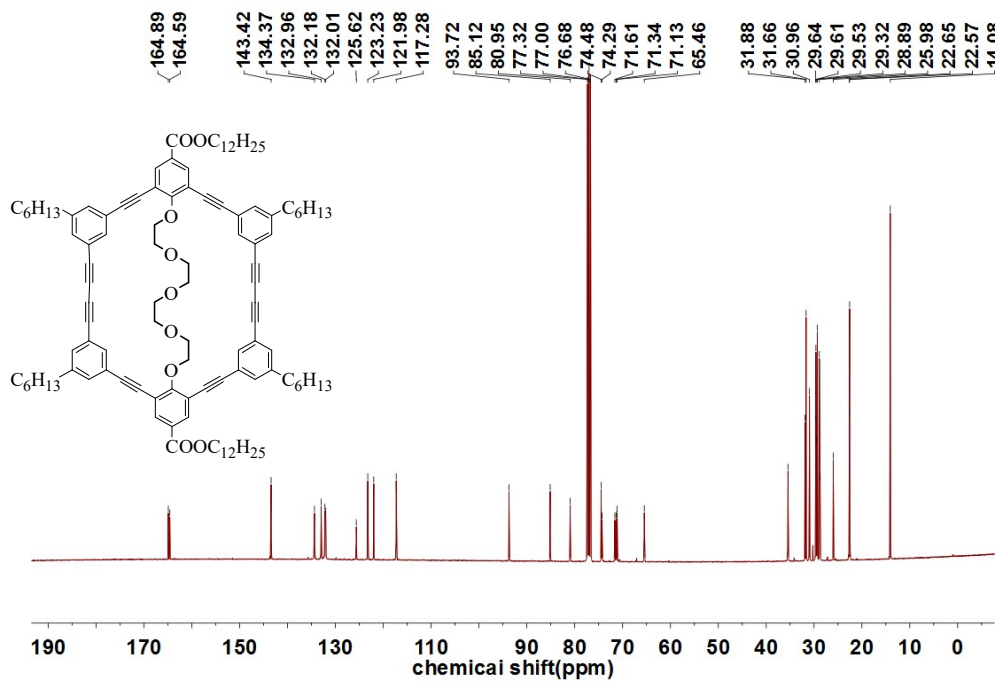


Fig. S22.  $^{13}\text{C}$  NMR of compound **SPM-Q6**.

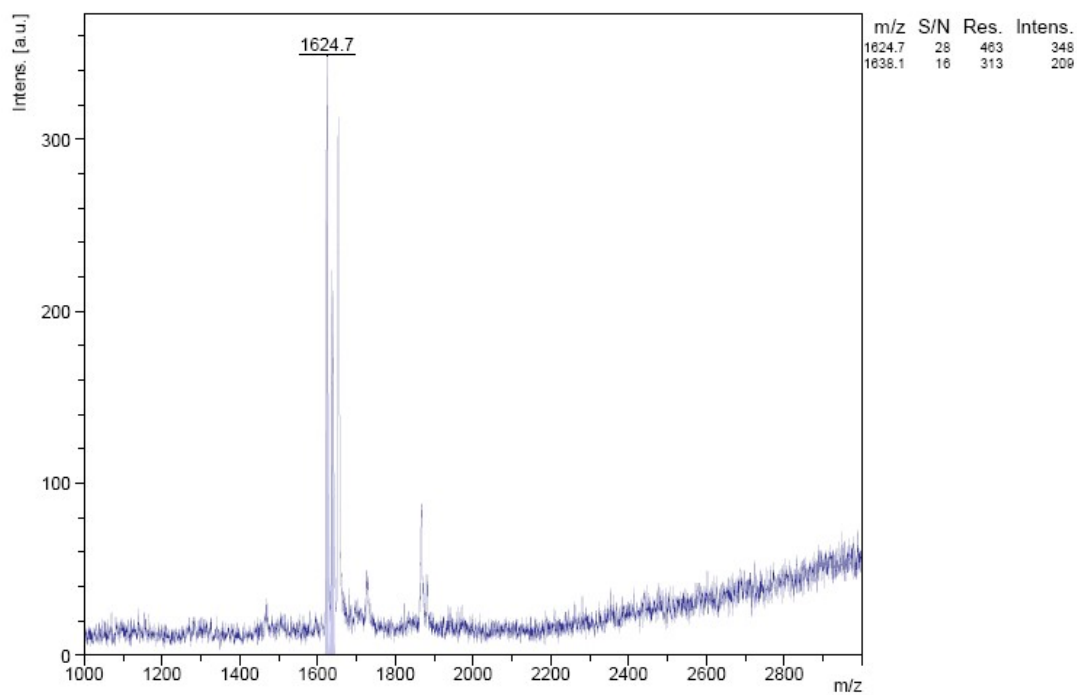


Fig. 23. Maldi-TOF MS for **SPM-Q6** ( $\text{M}+\text{Na}^+$ ).



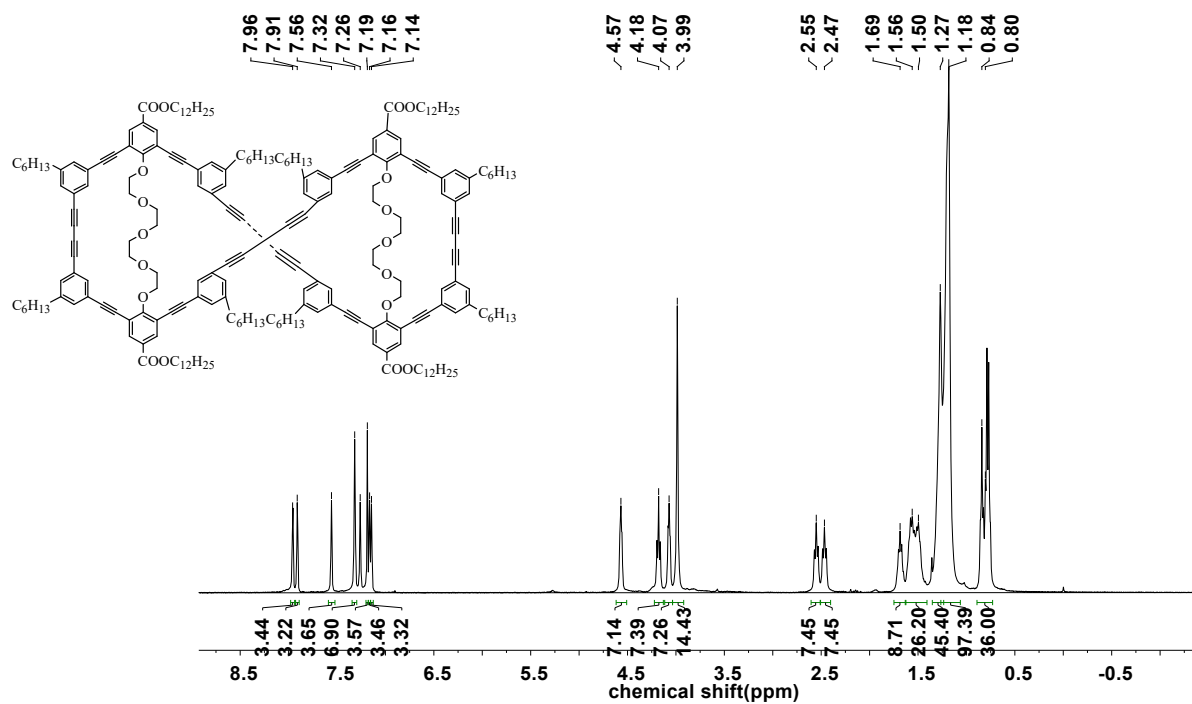


Fig. S24. <sup>1</sup>H NMR of compound SPM-Q12.

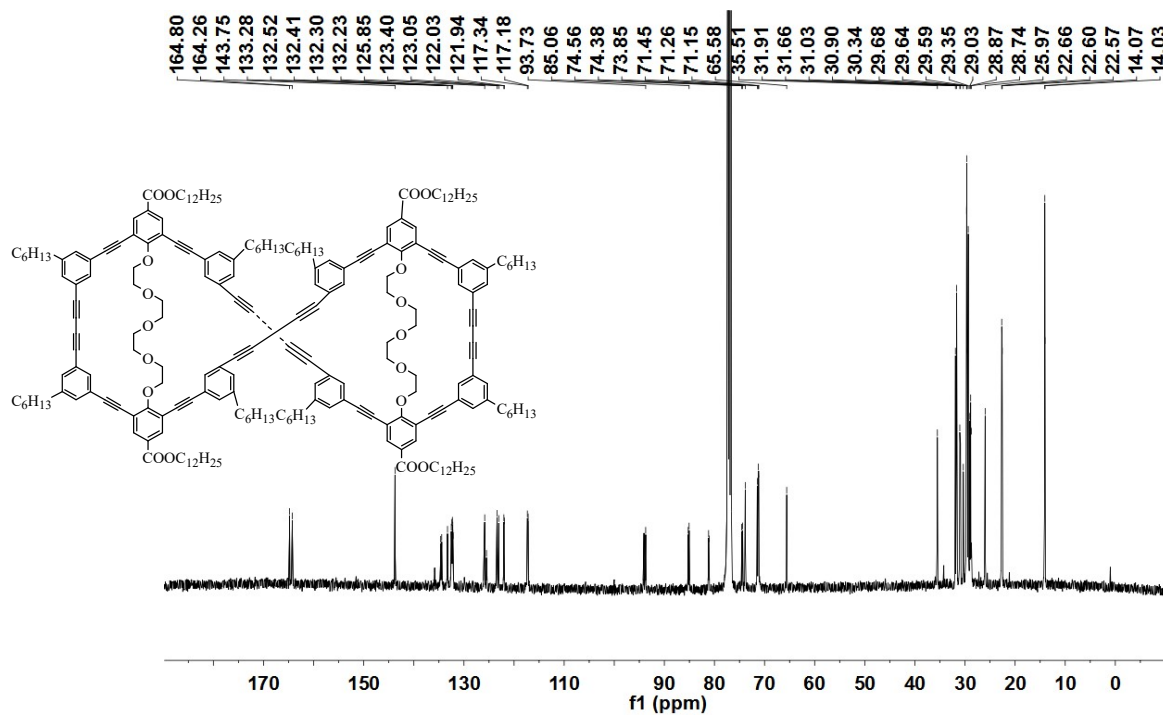


Fig. S25. <sup>13</sup>C NMR of compound SPM-Q12.

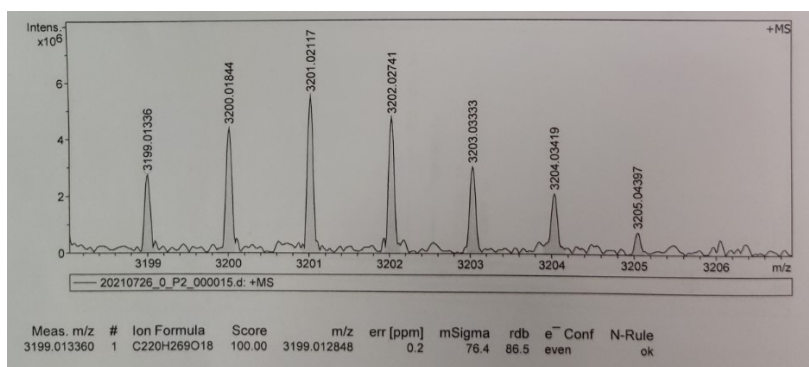
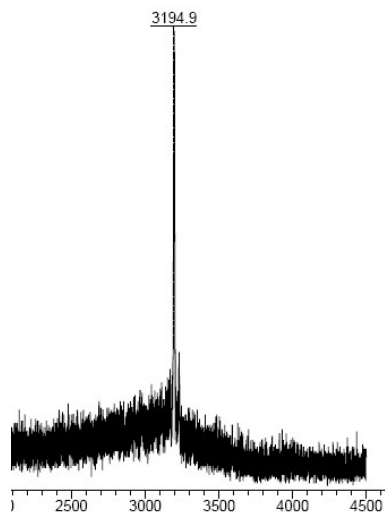


Fig. 26. Maldi-TOF MS for **SPM-Q12** (up) and high-resolution MS(Bottom).

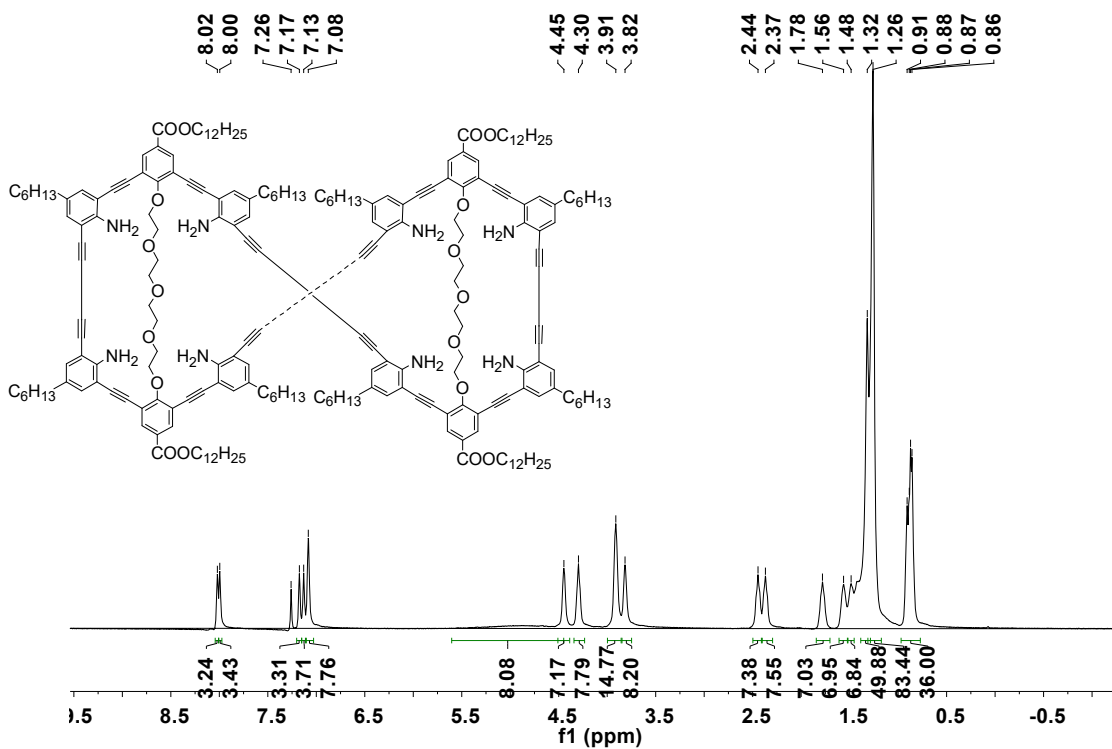


Fig. 27. <sup>1</sup>H NMR spectra of **SPM-Q12-NH<sub>2</sub>**

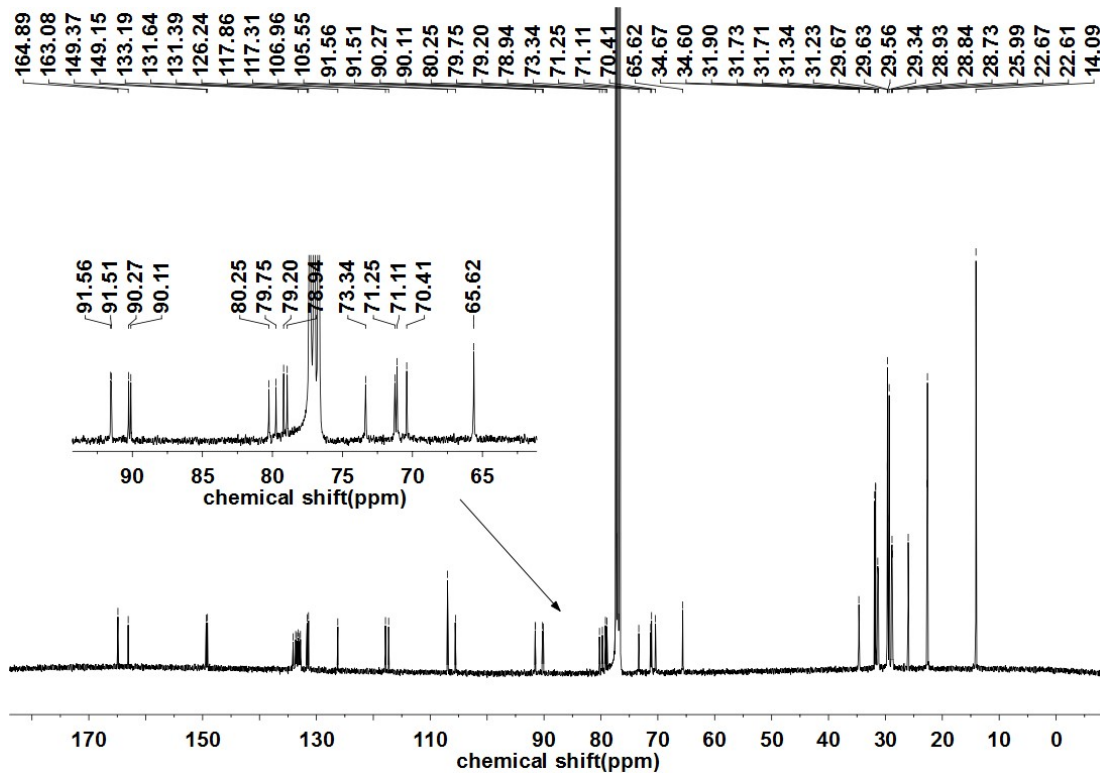


Fig. 28.  $^{13}\text{C}$  NMR spectra of SPM-Q12-NH<sub>2</sub>

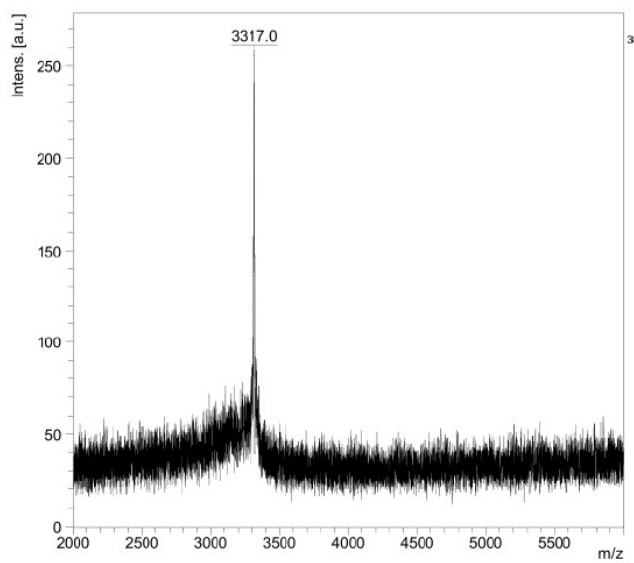
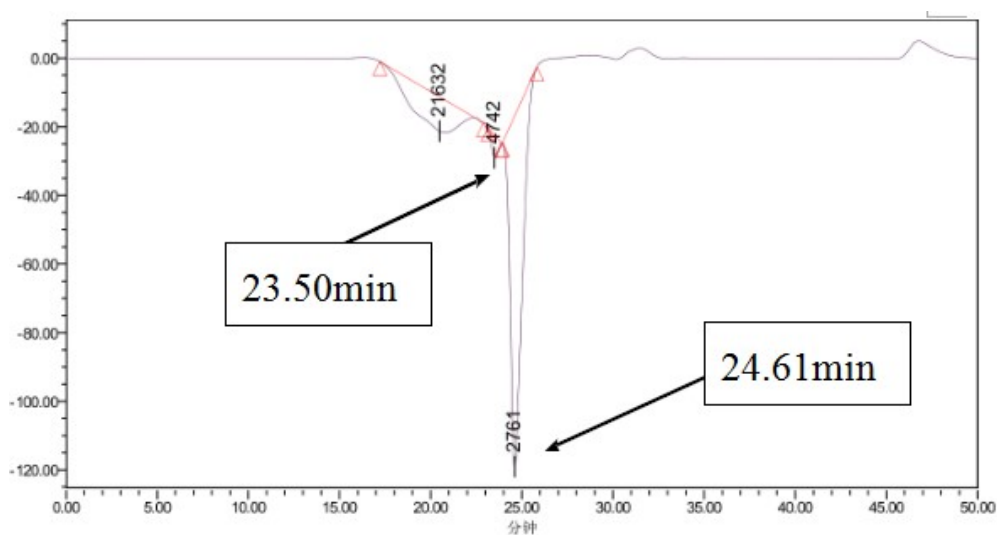


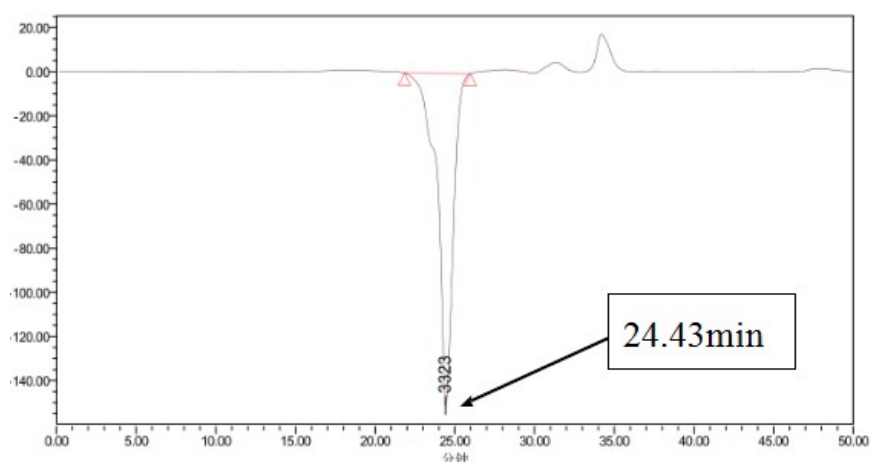
Fig. 29. Maldi-TOF MS for SPM-Q12-NH<sub>2</sub>

#### 4 · GPC plots of SPM-Q6 and SPM-Q12

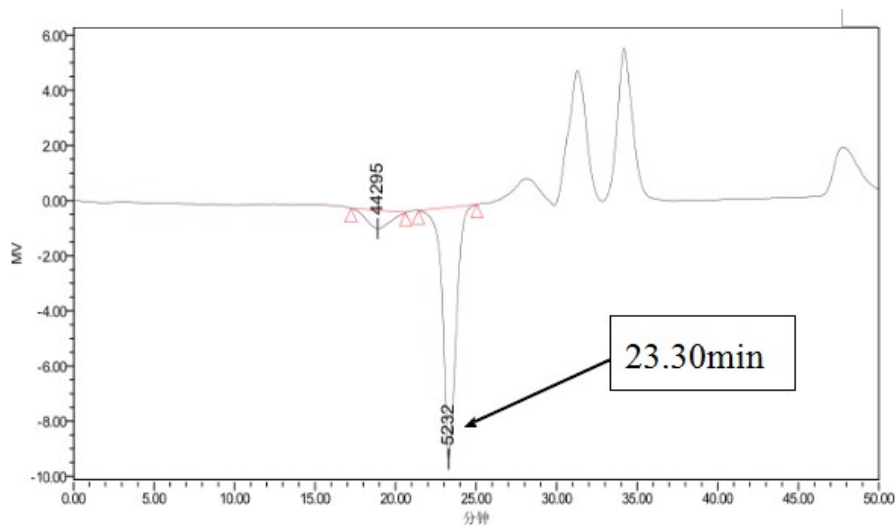
As shown in Fig. S29, after the cyclization reaction of compound **SPM**, the reaction mixture contained several components. The broad peak at 19.50 min corresponds to polymers with average molecular weight  $M_p$  about 21632. The other two peaks at 23.50 min and 24.61 min originated from two oligomers with different molecular weight. After purified with size-exclusion chromatography, the obtained pure **SPM-Q6** and **SPM-Q12** macrocycles were also characterized by GPC and the GPC plots were shown in Fig. S30 and S31, respectively. Based on the comparison, we can confirm that the two components with peaks at 23.50 min and 24.61 min in Fig.32-34 correspond to macrocycle **SPM-Q12** and macrocycle **SPM-Q6**, respectively. So, we can estimate the ratio of the two macrocycles from cyclization reaction of SPM with different concentrations by GPC measurement.



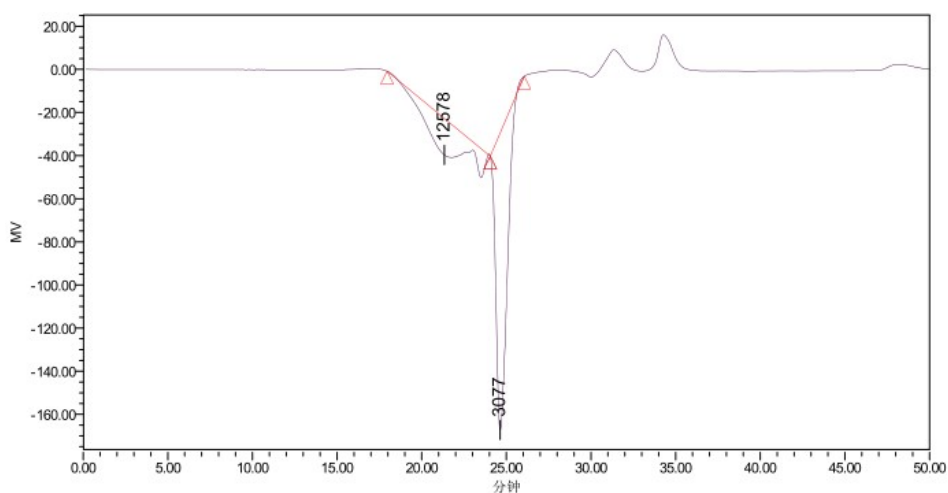
**Fig. S30.** GPC plots of reaction solution of cyclization reaction of **SPM** before being purified by size-exclusion chromatography.



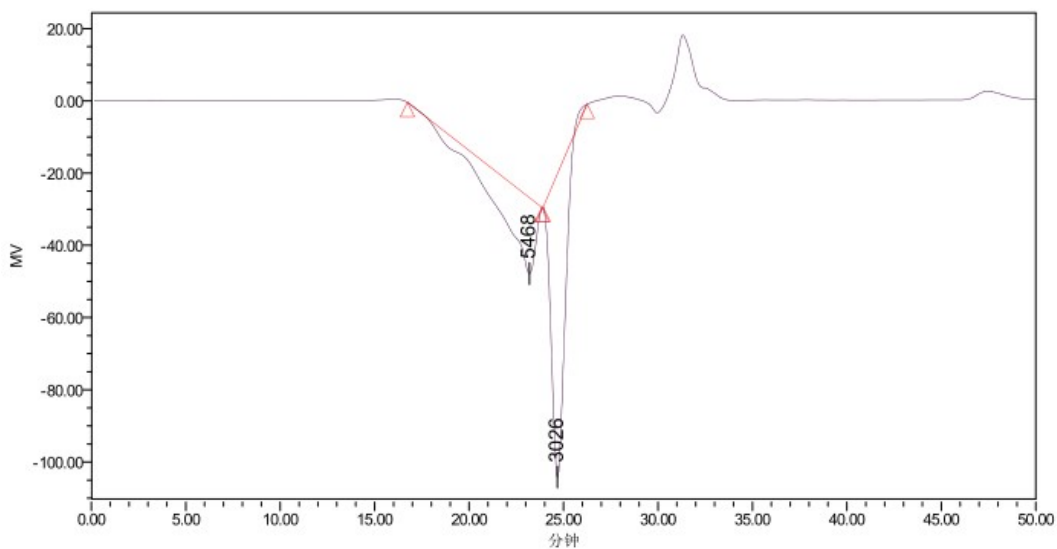
**Fig. S31.** GPC plots of pure **SPM-Q6**.



**Fig. S32.** GPC plots of pure SPM-Q12.



**Fig. S33.** GPC diagram of coupling reaction of SPM with the concentration of  $3 \times 10^{-4}$  mol/L.



**Fig. S34.** GPC diagram of coupling reaction of SPM with the concentration of  $6 \times 10^{-4}$  mol/L.

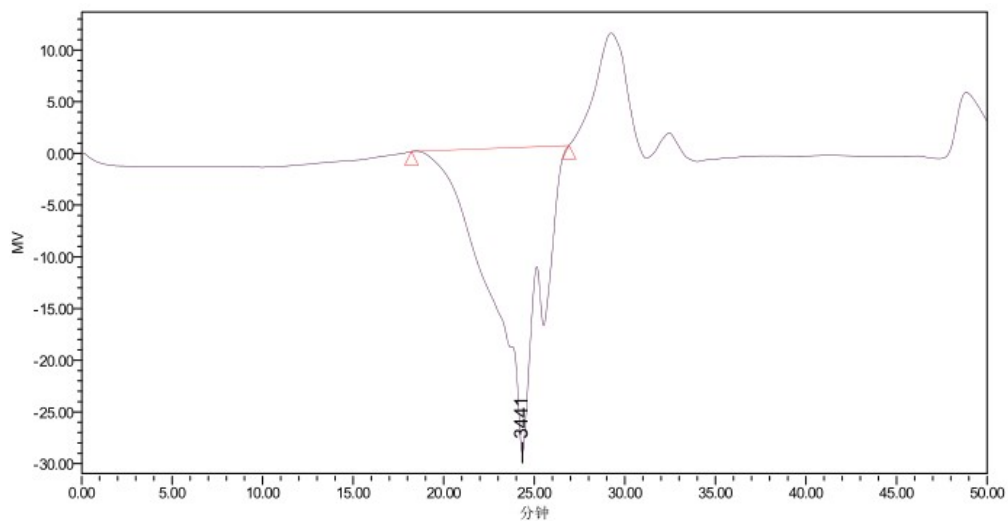


Fig. S35. GPC diagram of coupling reaction of SPM with the concentration of  $20 \times 10^{-4}$  mol/L.

## 5. Reference.

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- S6. Nie H, Geng YF, Luo DP, Liu MQ, Wang YF, Liu ZY, Zeng QD, Shu LJ. *Asian J. Org. Chem.* **2015**, 4, 788 – 793.