A hyperbranched fluorescent supramolecular polymer with aggregation induced emission (AIE) properties

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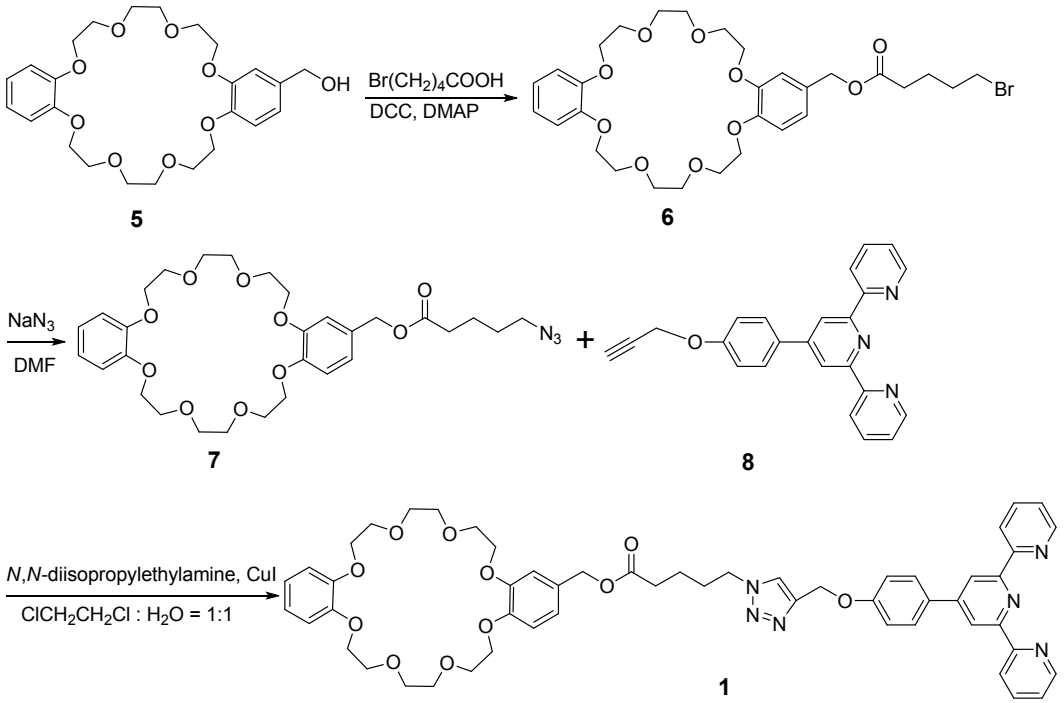
Supporting Information (24 pages)

1. Materials and methods

5-Bromovaleric acid, 4-dimethylaminopyridine (DMAP), 1,6-dibromohexane, 4-hydroxybenzaldehyde, di-tert-butyl dicarbonate, sodium borohydride, *N*,*N*-diisopropylethylamine, dicyclohexylcarbodiimide (DCC), zinc triflate ($Zn(OTf)_2$) and potassium trifluoromethanesulfonate (KCF_3SO_3) were purchased from Aldrich and used without further purification. Compounds **5**[S1], **8**[S2] and **11**[S3] were synthesized according to the published procedure.

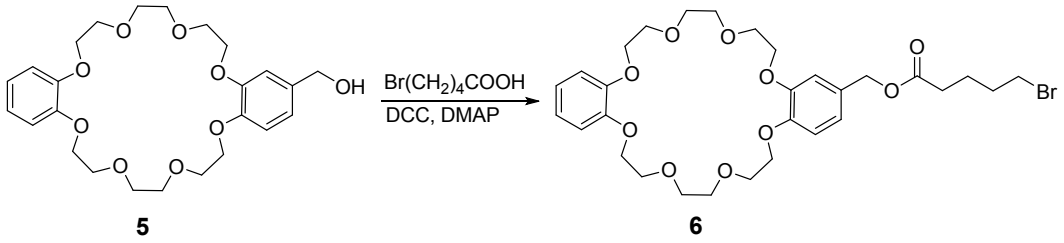
1D (^1H, ^{13}C) and 2D (^1H–^1H NOESY, DOSY) nuclear magnetic resonance (NMR) spectra were operated at room temperature on a Bruker Avance 500 operating at a frequency of 500 MHz for ^1H and 125 MHz for ^{13}C. High-resolution mass data were obtained with an Agilent Technologies 6530 Accurat-Mass Q-TOF LC/MC instrument. UV/Vis absorption spectra were recorded on a Perkin Elmer Lambda 750 UV/Vis spectrophotometer. The fluorescence spectra were recorded on a HITACHI F7000 fluorescence spectrophotometer. Viscosity measurements were carried out with Ubbelohde dilution viscometers (Julabo Technology Corporation visco-170, 0.47 mm inner diameter) in $CHCl_3/CH_3CN$ (1/1, *v*/*v*). Transmission electron microscopy (TEM) were recorded on a HT7700 instrument. Dynamic light scattering (DLS) measurements were carried out on Mastersizer 2000 Malvern Zetasizer.

2. *Synthetic routes to monomer **1***



Scheme S1. Synthetic routes of monomer **1**.

2.1. *Synthesis of compound **6***



5 (300 mg, 0.63 mmol), 5-bromovaleric acid (228 mg, 1.26 mmol) and DMAP (4.00 mg, 3.2 mmol) were dissolved in 30 mL of dry THF. After the mixture solution was stirred for 30 minutes at 0 °C, DCC (258 mg, 1.26 mmol) in 10 mL of dry THF were added. The reaction mixture was stirred for another 24 h at room temperature, then filtered and concentrated. The residue was dissolved into 50 mL of CH_2Cl_2 and washed with H_2O (30 mL × 3). The organic layer was combined, dried over anhydrous Na_2SO_4, filtered and the solvent was removed. The obtained crude product was purified by flash column chromatography (ethyl acetate/petroleum ether, 3:1 v/v) to afford **6** as a pale yellow solid (304 mg, 76%). ^{1}H NMR (500 MHz, $CDCl_3$, 293K) δ (ppm): 6.89–6.81 (m, 7H), 5.00 (s, 2H), 4.15–4.12 (m, 8H), 3.90–3.89 (m, 8H), 3.81–3.80 (m, 8H), 3.37

(t, J = 6.5 Hz, 2H), 2.35 (t, J = 7.3 Hz, 2H), 1.89–1.83 (m, 2H), 1.79–1.75 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 293K) δ (ppm): 172.6, 148.9, 148.8, 129.0, 121.8, 121.5, 114.5, 114.2, 113.8, 71.1, 69.8, 69.3, 66.2, 33.3, 33.1, 31.9, 23.4. HRMS $[M + Na]^+$: calcd. for $C_{30}H_{41}BrO_{10}Na$ 663.1775, found 663.1776.

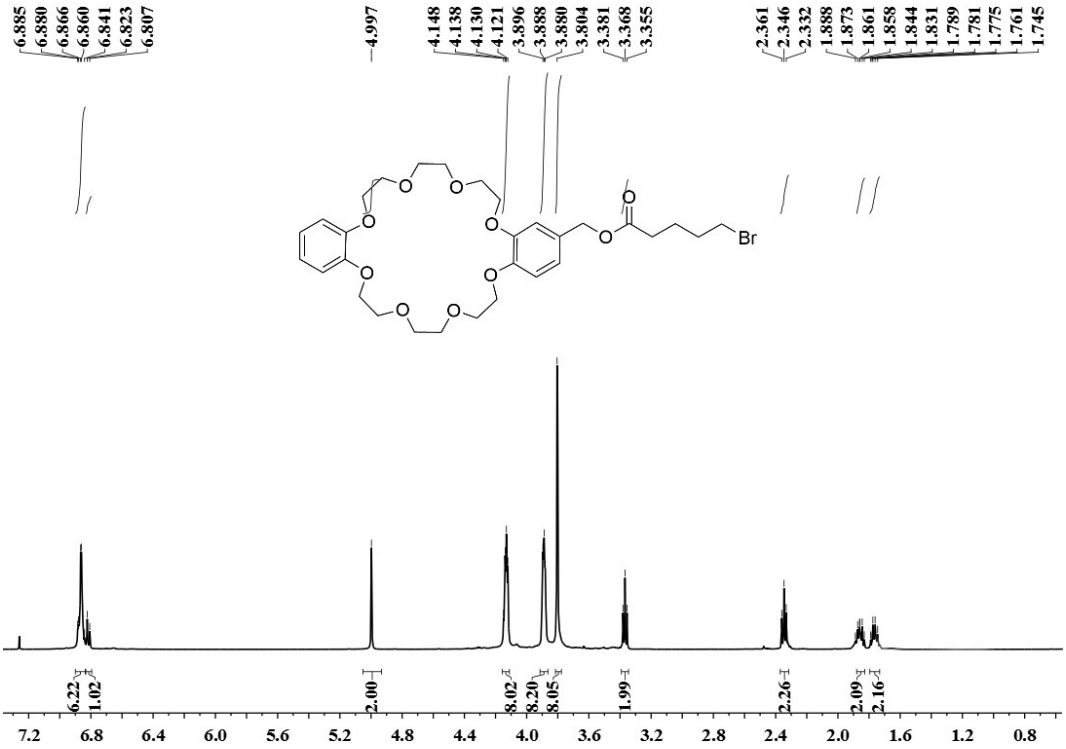


Fig S1. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 293K) of compound **6**.

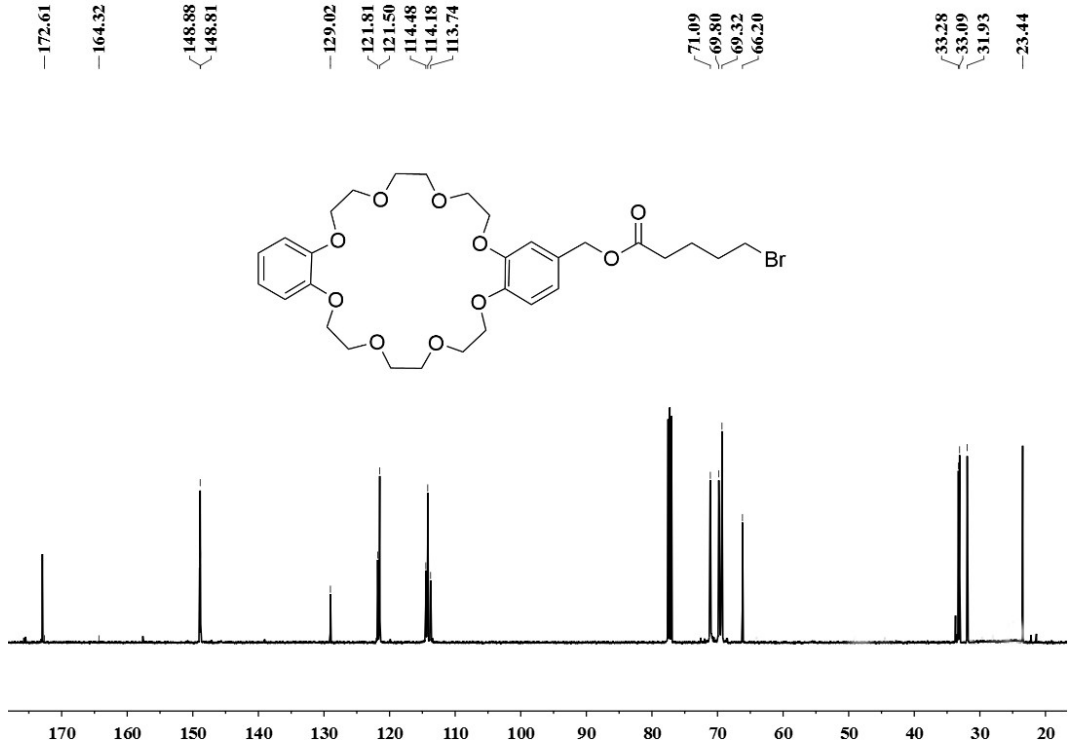
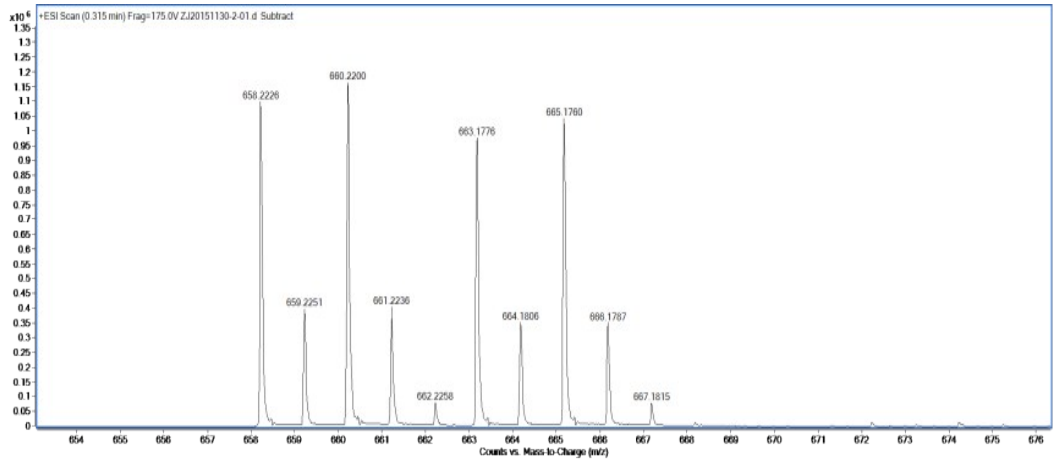


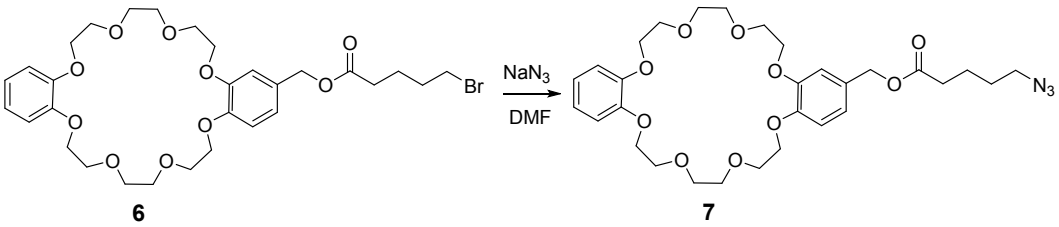
Fig S2. ^{13}C NMR spectrum (500 MHz, $CDCl_3$, 293K) of compound **6**.



Formula (M)	Score (MFG)	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)	DBE	m/z
C30 H41 Br O10	100	640.1884	640.1883	663.1775	-0.11	10	663.1776

Fig S3. HRMS spectrum of compound **6**.

2.2. Synthesis of compound 7



6 **7**

6 (256 mg, 0.4 mmol) and NaN_3 (260 mg, 4.0 mmol) were dissolved in 20 mL of DMF. The mixture solution was heated at 80 °C for 16 h. After removal of solvent under reduced pressure, the obtained residue was dissolved in 50 mL of ethyl acetate, and extracted with water (30 mL × 3). The organic phase was combined, washed with brine (50 mL × 2) and then the solvent was removed to obtain compound **7** as a white solid (240 mg, 100%). ^{1}H NMR (500 MHz, $CDCl_3$, 293K) δ (ppm): 6.90–6.81 (m, 7H), 5.01 (s, 2H), 4.16–4.13 (m, 8H), 3.92–3.90 (m, 8H), 3.83–3.82 (m, 8H), 3.27 (t, J = 6.8 Hz, 2H), 2.36 (t, J = 7.3 Hz, 2H), 1.74–1.68 (m, 2H),1.64–1.60 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 293K) δ (ppm): 172.8, 149.0, 148.9, 148.8, 128.9, 121.8, 121.2, 114.4, 114.1, 113.6, 71.2, 69.9, 69.4, 66.2, 50.8, 33.5, 28.2, 21.9. HRMS $[M + Na]^+$: calcd. for $C_{30}H_{41}N_3O_{10}Na$ 626.2684, found 626.2672.

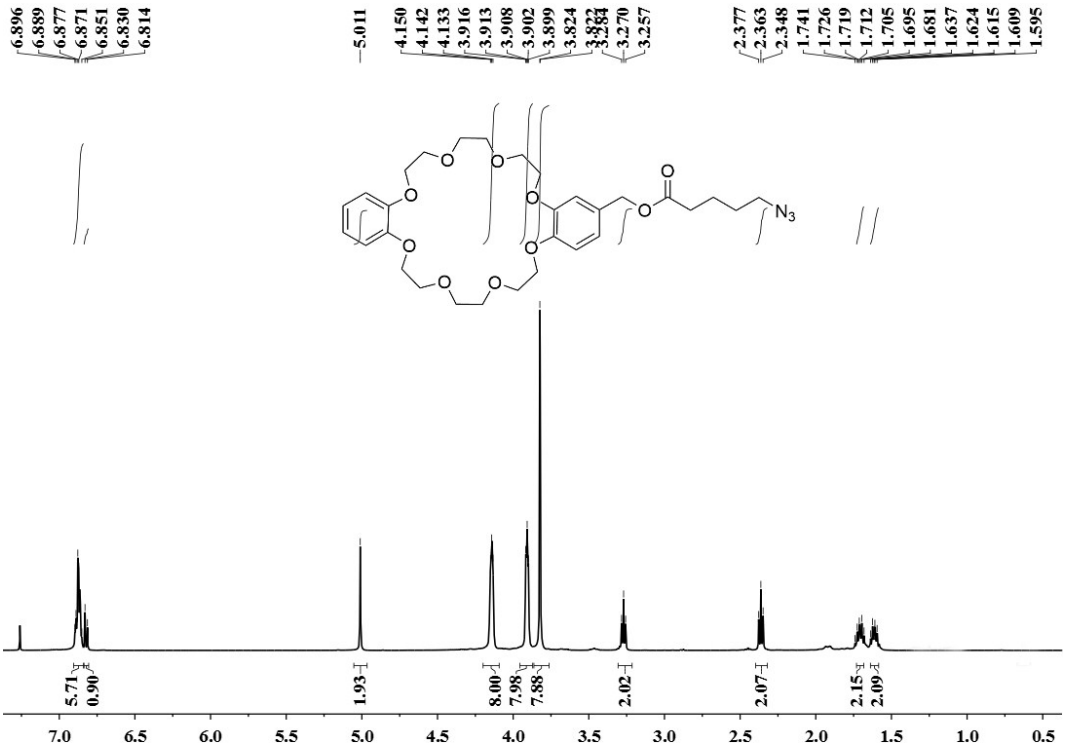


Fig S4. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 293K) of compound **7**.

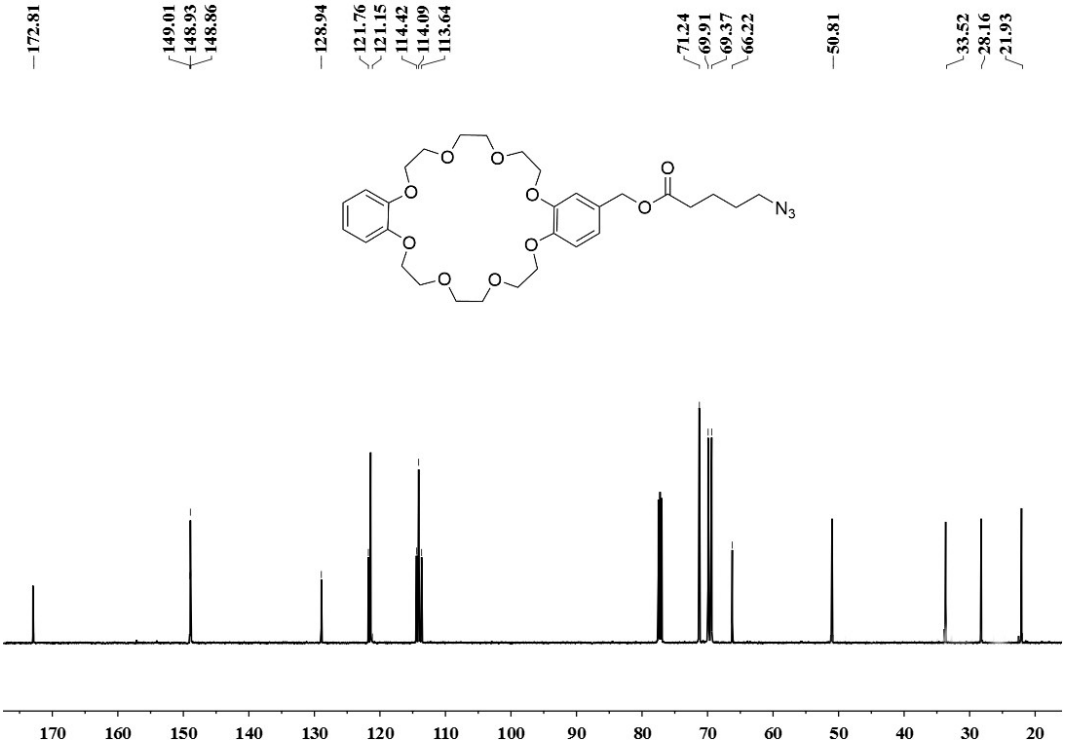
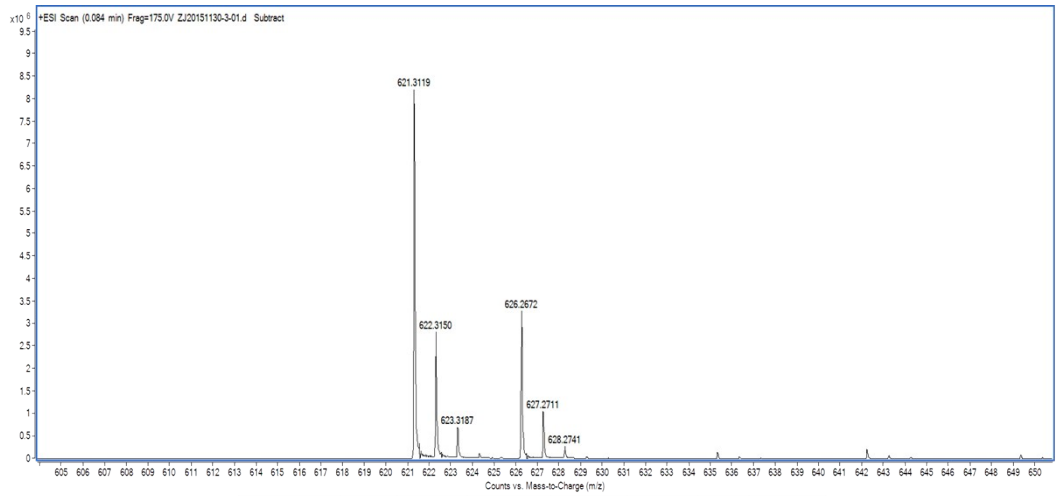


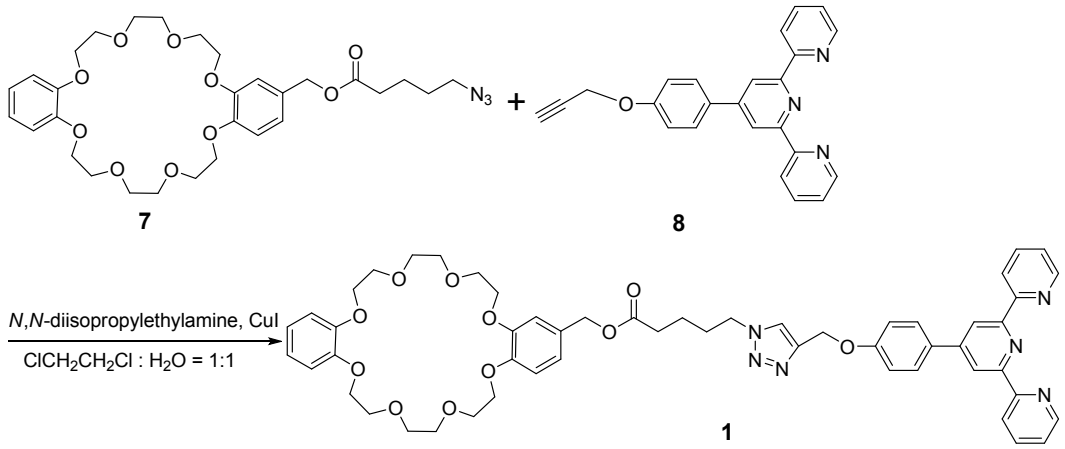
Fig S5. ^{13}C NMR spectrum (500 MHz, $CDCl_3$, 293K) of compound **7**.



Formula (M)	Score (MFG)	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)	DBE	m/z
C30 H41 N3 O10	100	603.278	603.2792	626.2684	2.02	12	626.2672

Fig S6. HRMS spectrum of compound **7**.

*2.3. Synthesis of monomer **1***



A mixture of **7** (100 mg, 0.145 mmol), **8** (121 mg, 0.333 mmol), CuI (16.0 mg, 0.083 mmol), *N*,*N*-diisopropylethylamine (15.0 mg, 0.116 mmol) was added to $ClCH_2CH_2Cl/H_2O$ (1:1, 10 mL) and stirred at 50 ºC for 24 h. After the solvent was removed, the residue was poured into 50 mL of water and extracted with CH_2Cl_2 (30 mL × 3). The organic layer was combined, dried over anhydrous Na_2SO_4, filtered and the solvent was removed. The crude product was purified by flash column chromatography (ethyl acetate) to afford **1** as a white solid (87.5 mg, 55%). ^{1}H NMR (500 MHz, $CDCl_3$, 293K) δ (ppm): 8.73 (d, J = 4.0 Hz, 2H), 8.71 (s, 2H), 8.67 (d, J = 8.0 Hz, 2H), 7.88 (d, J = 7.5 Hz, 2H), 7.62 (s, 1H), 7.37–7.35 (m, 2H), 7.12 (d, J = 8.0 Hz, 2H), 6.88–6.81 (m, 7H), 5.29 (s, 2H), 5.01 (s, 2H), 4.38 (t, J = 7.0 Hz, 2H), 4.13–4.10 (m, 8H), 3.93–3.88 (m, 8H), 3.83–3.80 (m, 8H), 3.29 (t, J = 6.5 Hz, 2H), 2.39 (t,

J = 7.3 Hz, 2H), 2.00–1.94 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, 293K) δ (ppm): 171.7, 158.1, 155.2, 154.8, 148.6, 148.1, 147.8, 142.9, 135.9, 130.3, 127.8, 127.5, 122.8, 121.7, 120.8, 120.4, 120.3, 117.3, 114.2, 113.4, 113.0, 112.6, 70.2, 68.9, 68.3, 65.3, 61.1, 48.9, 33.4, 32.3, 28.5, 20.7, 13.8. HRMS $[M + H]^+$: calcd. for $C_{54}H_{59}N_6O_{11}$ 967.4236, found 967.4223.

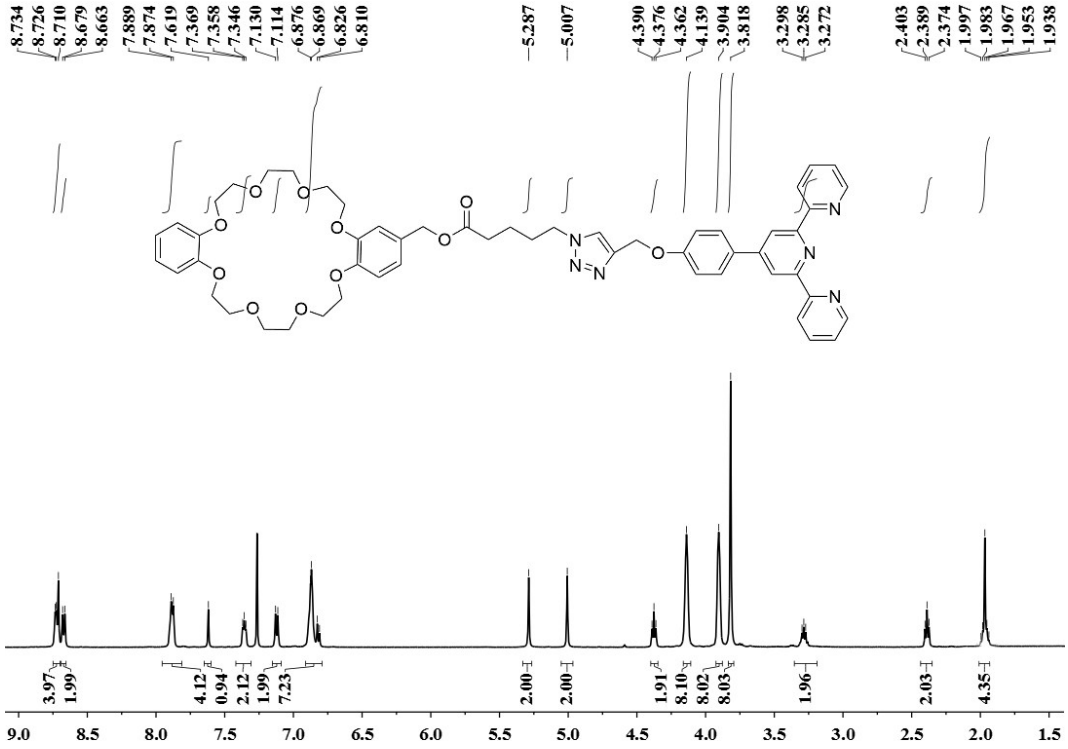


Fig S7. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 293K) of monomer **1**.

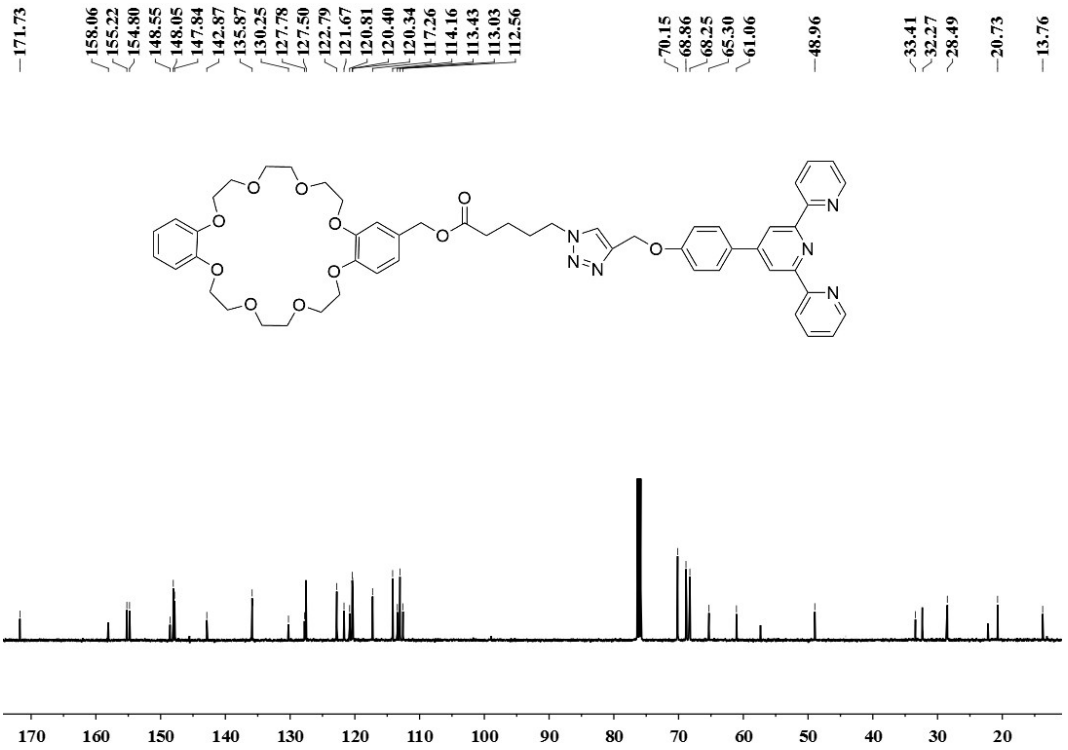
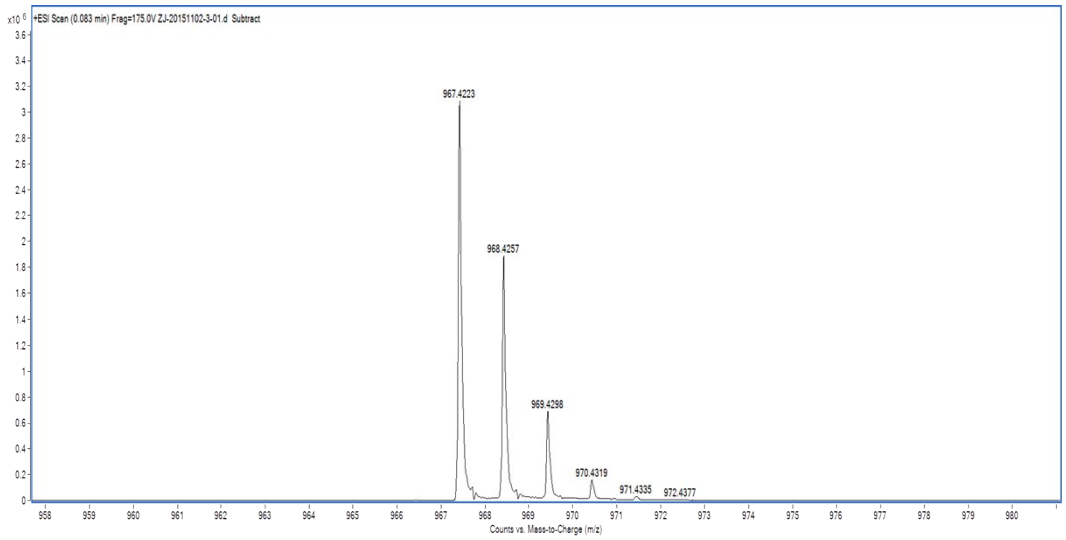


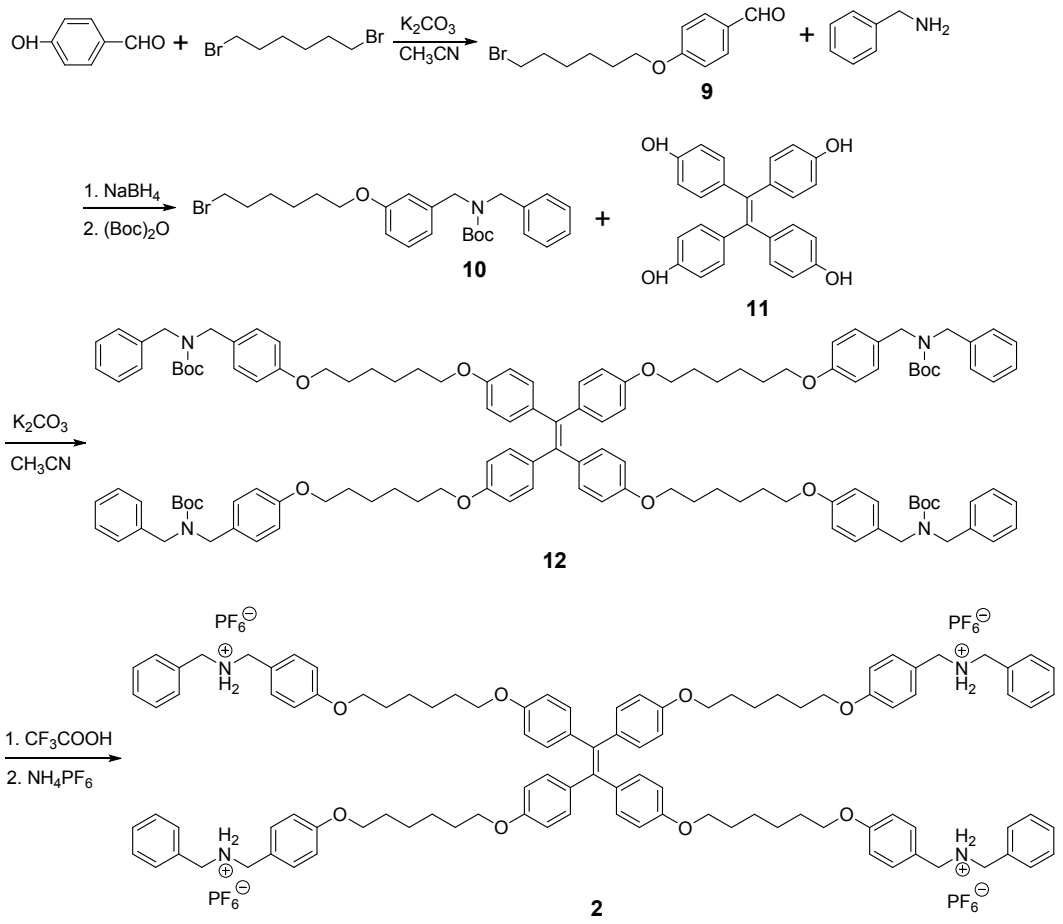
Fig S8. ^{13}C NMR spectrum (500 MHz, $CDCl_3$, 293K) of monomer **1**.



Formula (M)	Score (MFG)	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)	DBE	m/z
C54 H58 N6 O11	100	966.415	966.4164	967.4236	1.38	29	967.4223

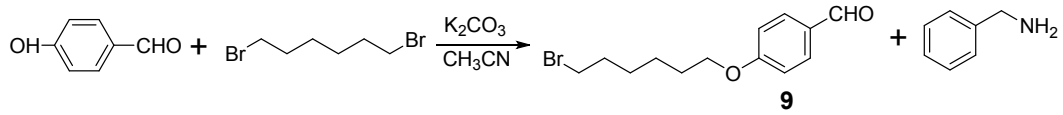
Fig S9. HRMS spectrum of monomer **1**.

3. *Synthetic routes of monomer* ***2***



Scheme S2. Synthetic routes of monomer **2**.

3.1. Synthesis of compound ***9***



4-Hydroxybenzaldehyde (1.22 g, 0.01 mol), 1,6-dibromohexane (24.4 g, 0.10 mol) and K_2CO_3 (5.52 g, 0.04 mol) were dissolved in 100 mL of CH_3CN. The mixture solution was refluxed for 12 h. After filtration, the solvent was removed with a rotary evaporator and the residue was poured into 200 mL of water and extracted with CH_2Cl_2 (100 mL × 3). The organic phase was collected, thoroughly dried and then the solvent was removed, the crude was further purified by flash column chromatography (dichloromethane/petroleum ether, 1:1 v/v) to afford **9** as a pale yellow solid (2.22 g, 78%). ^{1}H NMR (500 MHz, $CDCl_3$, 293K) δ (ppm): 9.87 (s, 1H), 7.82 (d, J = 8.5 Hz, 2H), 6.98 (d, J = 8.5 Hz, 2H), 4.04 (t, J = 6.3 Hz, 2H), 3.42 (t, J = 6.8 Hz, 2H), 1.92–

1.87 (m, 2H), 1.85–1.80 (m, 2H), 1.55–1.48 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, 293K) δ (ppm): 190.7, 164.1, 132.0, 129.8, 114.7, 68.1, 33.8, 32.6, 28.9, 27.9, 25.2. HRMS $[M + H]^+$: calcd. for $C_{13}H_{18}BrO_2$ 285.0485, found 285.0479.

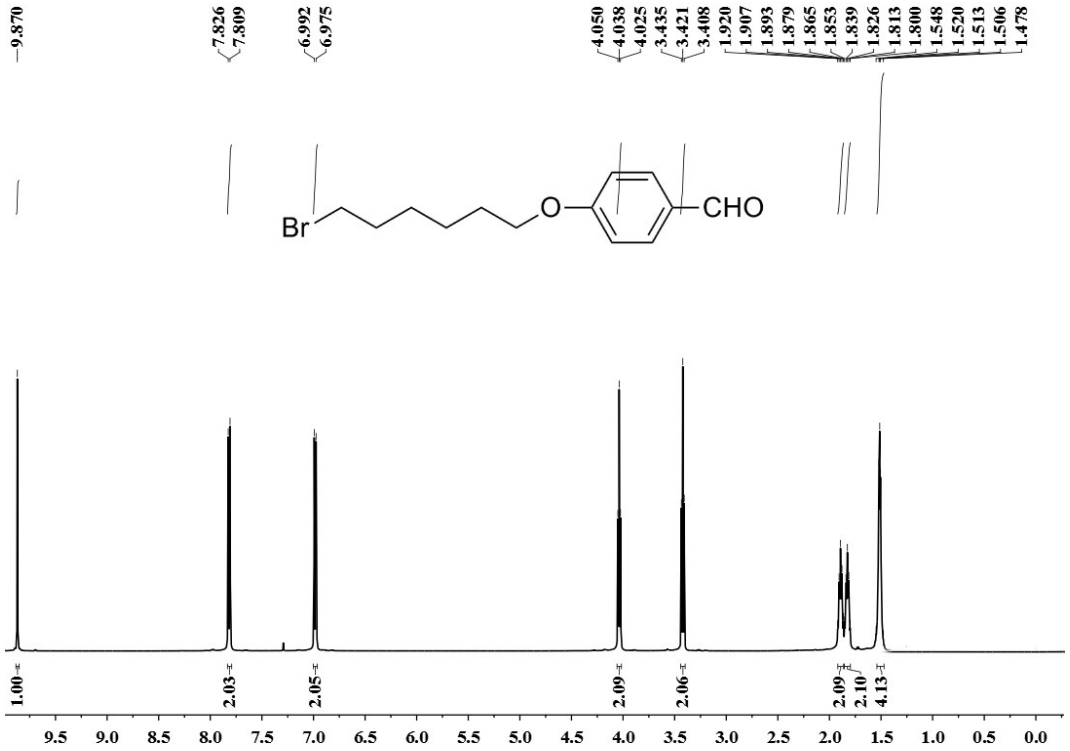


Fig S10. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 293K) of compound **9**.

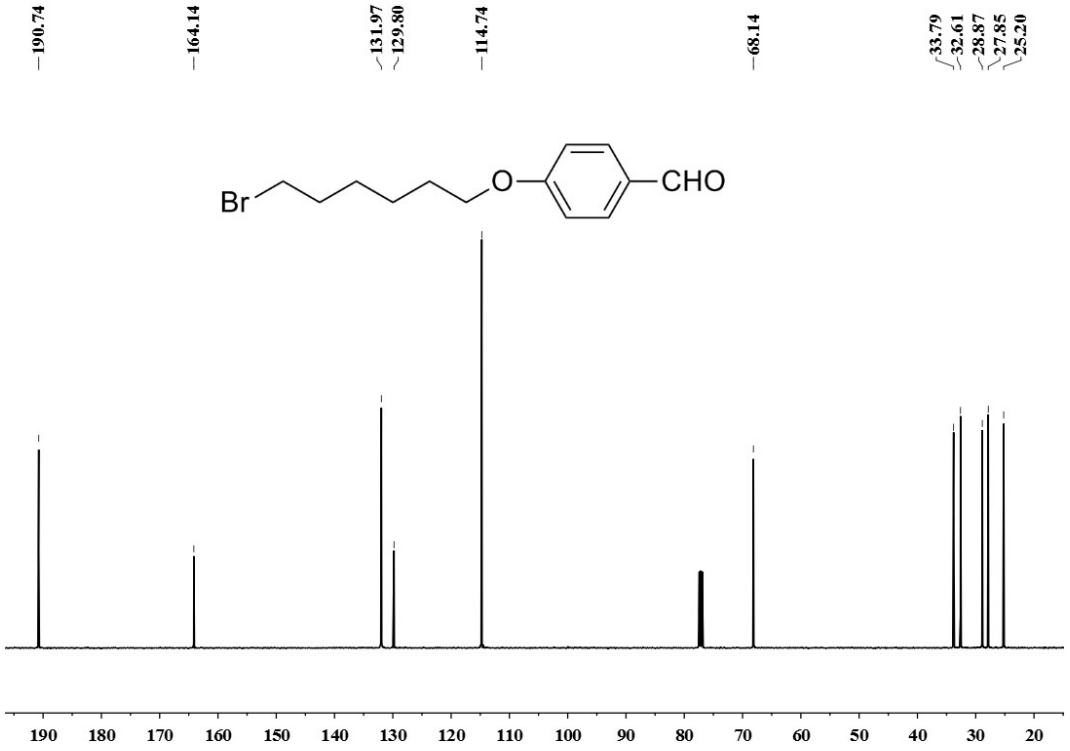
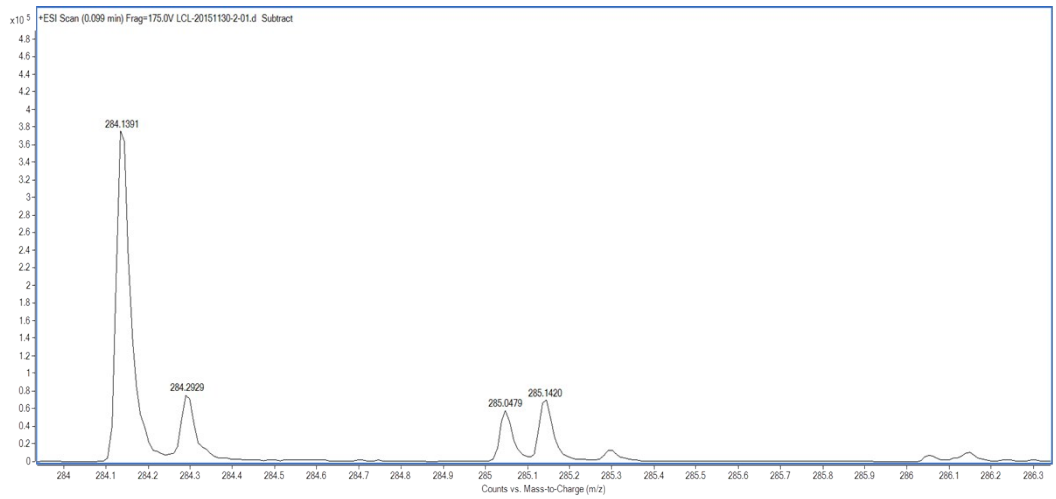


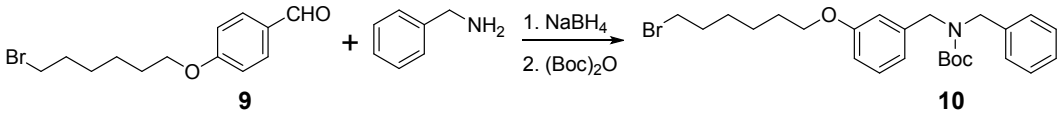
Fig S11. ^{13}C NMR spectrum (500 MHz, $CDCl_3$, 293K) of compound **9**.



Formula (M)	Score (MFG)	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)	DBE	m/z
C13 H17 Br O2	100	284.0406	284.0412	285.0485	2	5	285.0479

Fig S12. HRMS spectrum of compound **9**.

*3.2. Synthesis of compound **10***



9 **10**

9 (570 mg, 2.0 mmol), dry benzylamine (220 mg, 2.0 mmol) were dissolved in 10 mL of dry toluene. The mixture solution were refluxed for 20 h. After the solvent was removed, the residue was dissolved in 40 mL of methanol. To this solution, $NaBH_4$ (150 mg, 4.0 mmol) was added. After the mixture were stirred at 40 ºC for 5 h, 2.0 mol/L aqueous NaOH (100 mL) was quenched the reaction, and then extracted with CH_2Cl_2 (50 mL × 3). The organic layer was combined, dried over anhydrous Na_2SO_4, filtered and the solvent was removed. The residue was dissolved in 20 mL of CH_2Cl_2. Di-tert-butyl dicarbonate (570 mg, 2.6 mmol) and DMAP (11.0 mg) were added to the above solution, and the mixture solution were refluxed for another 12 h. After then, the solvent was removed. The obtained crude product was further purified by flash column chromatography (ethyl acetate/petroleum ether, 1:8 v/v) to afford **10** as a light yellow liquid (456 mg, 48%). ^{1}H NMR (500 MHz, $CDCl_3$, 293K) δ (ppm): 7.31–7.10 (m, 7H), 6.84 (d, J = 8.5 Hz, 2H), 4.39–4.26 (m, 4H), 3.92 (t, J = 6.3 Hz, 2H), 3.38 (t, J = 6.8 Hz, 2H), 1.88–1.83 (m, 2H), 1.79–1.74 (m, 2H), 1.49–1.45 (m, 13H). ^{13}C NMR (125 MHz, $CDCl_3$, 293K) δ (ppm): 158.4, 156.0, 129.9, 129.5, 128.9, 128.6, 128.0, 127.5, 127.2, 114.5, 79.9, 67.8, 33.8, 32.7, 29.2, 28.5, 28.0, 25.4. HRMS $[M + Na]^+$: calcd. for $C_{25}H_{34}BrNO_3Na$ 498.1614, found 498.1604.

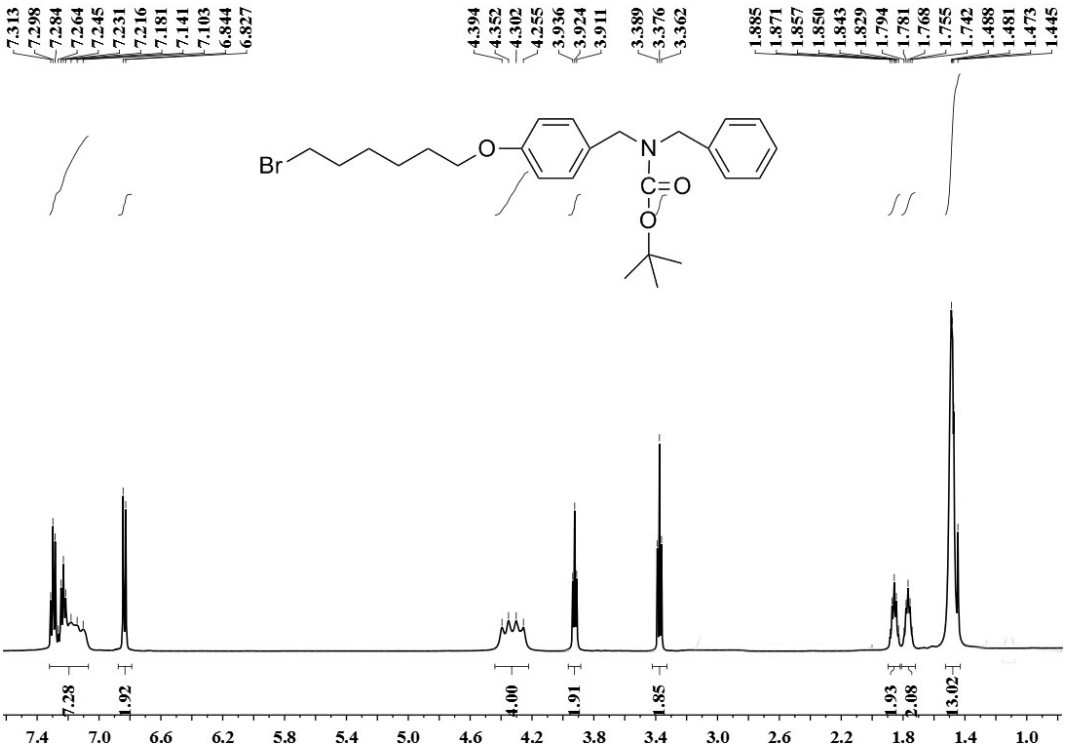


Fig S13. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 293K) of compound **10**.

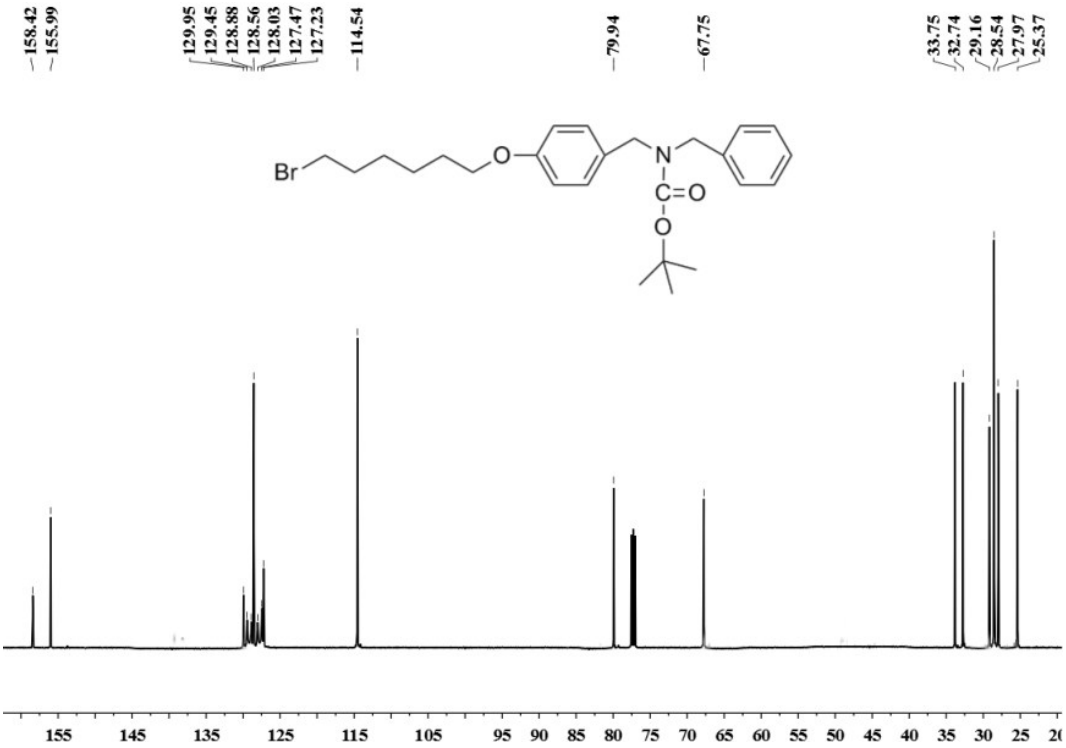
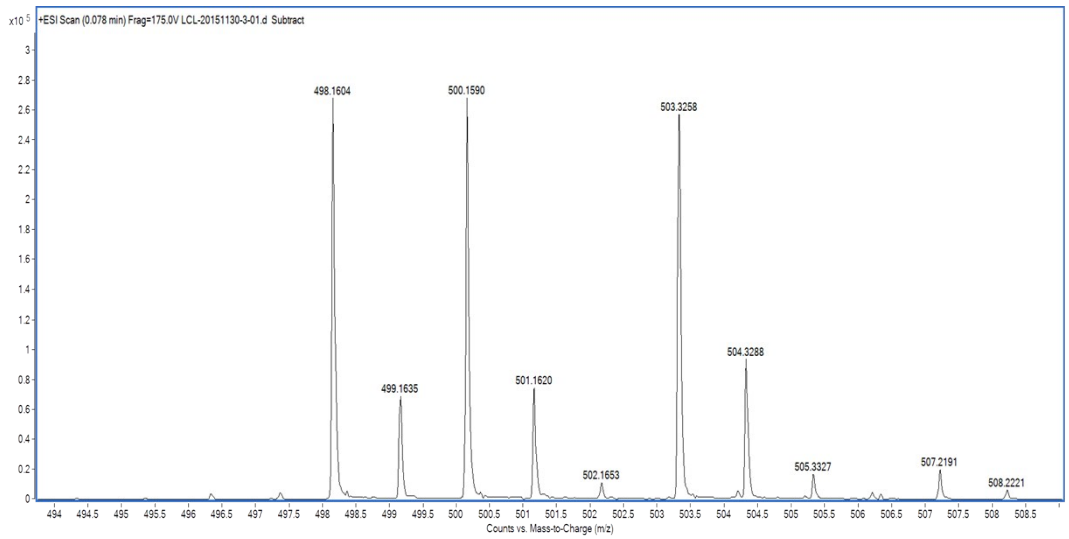


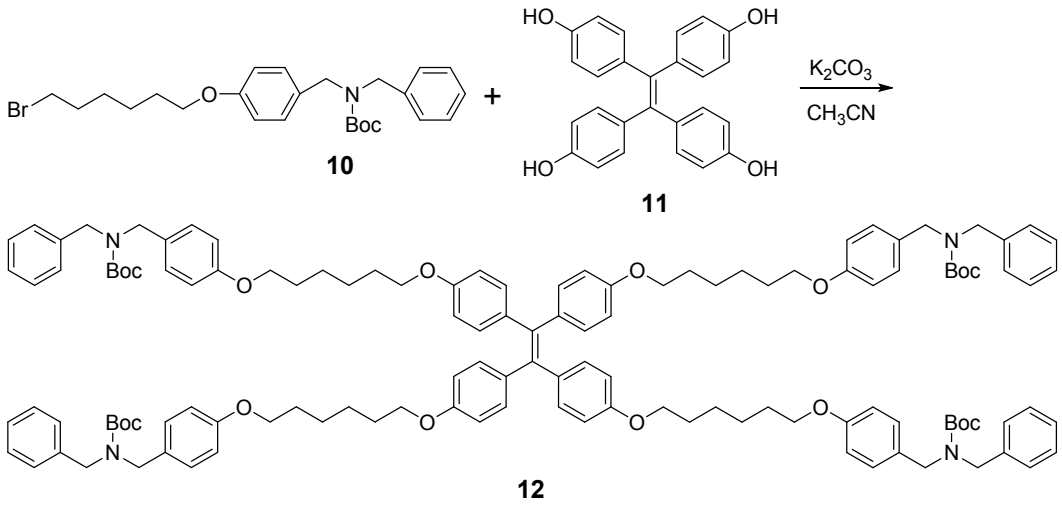
Fig S14. ^{13}C NMR spectrum (500 MHz, $CDCl_3$, 293K) of compound **10**.



Formula (M)	Score (MFG)	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)	DBE	m/z
C25 H34 Br N O3	100	475.1712	475.1722	498.1614	2.16	9	498.1604

Fig S15. HRMS spectrum of compound **10**.

*3.3. Synthesis of compound **12***



10 (1.92 g, 4.0 mmol), **11** (0.40 g, 1.0 mmol) and K_2CO_3 (6.00 g, 0.04 mol) were dissolved in 250 mL of acetonitrile. The mixture was refluxed for 24 h. After then, the solvent was removed with a rotary evaporator, the residue was dissolved in 200 mL of H_2O and extracted with CH_2Cl_2 (100 mL × 3). The organic layer was combined, dried over anhydrous Na_2SO_4, filtered and the solvent was removed. The crude product was purified by flash column chromatography (ethyl acetate/petroleum ether, 1:1 v/v) to afford **12** as a yellow oil (1.27 g, 64%). ^{1}H NMR (500 MHz, $CDCl_3$, 293K) δ (ppm): 7.20–6.52 (m, 52H), 4.30–4.09 (m, 16H), 3.92–3.77 (t, 16H), 1.69–1.68 (d, J = 4.5 Hz, 16H), 1.39 (s, 52H). ^{13}C NMR (125 MHz, $CDCl_3$, 293K) δ (ppm): 157.3, 156.2, 154.9,

135.8, 131.5, 128.8, 128.3, 127.7, 127.4, 126.9, 126.3, 126.1, 113.4, 112.5, 78.8, 66.7, 28.6, 28.1, 27.4, 24.8. HRMS $[M + Na]^+$: calcd. for $C_{126}H_{152}N_4O_{16}Na$ 2000.1096, found 2000.1101.

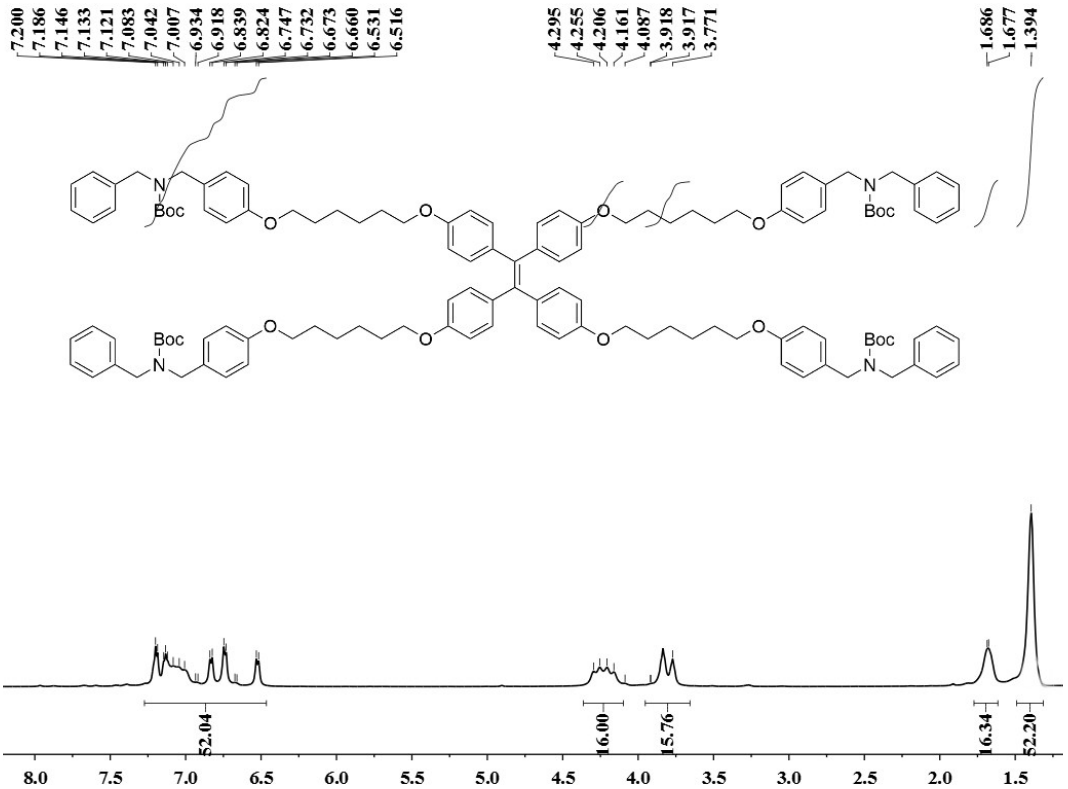


Fig S16. ^1H NMR spectrum (500 MHz, $CDCl_3$, 293K) of compound **12**.

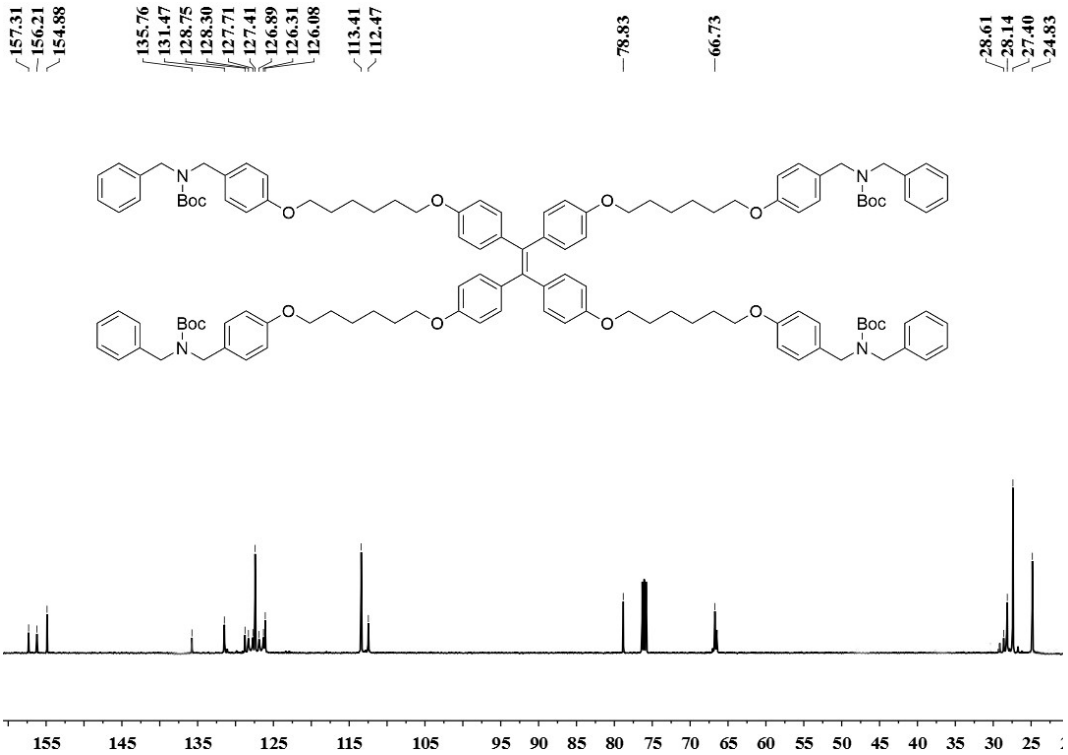
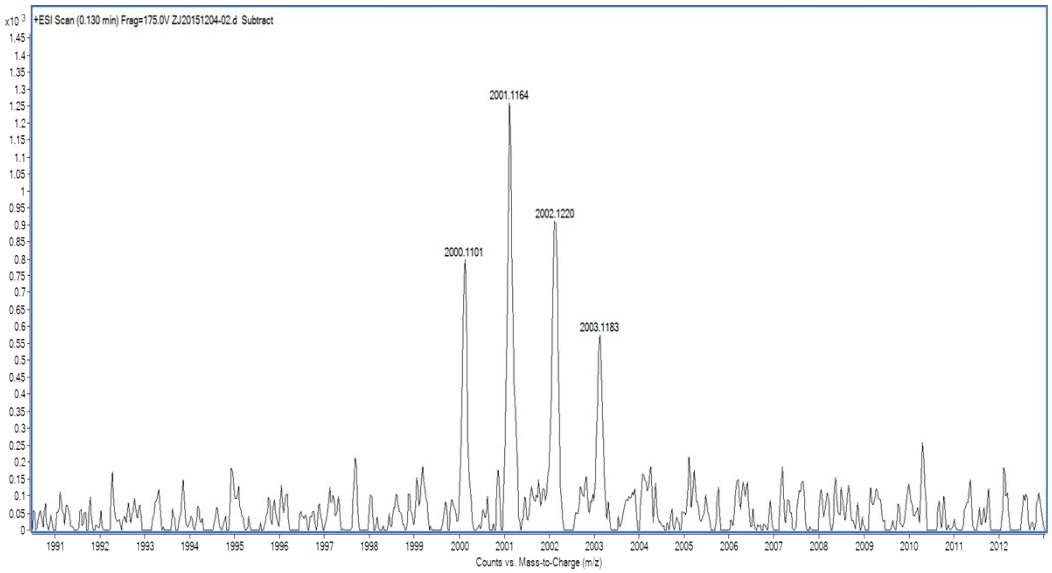


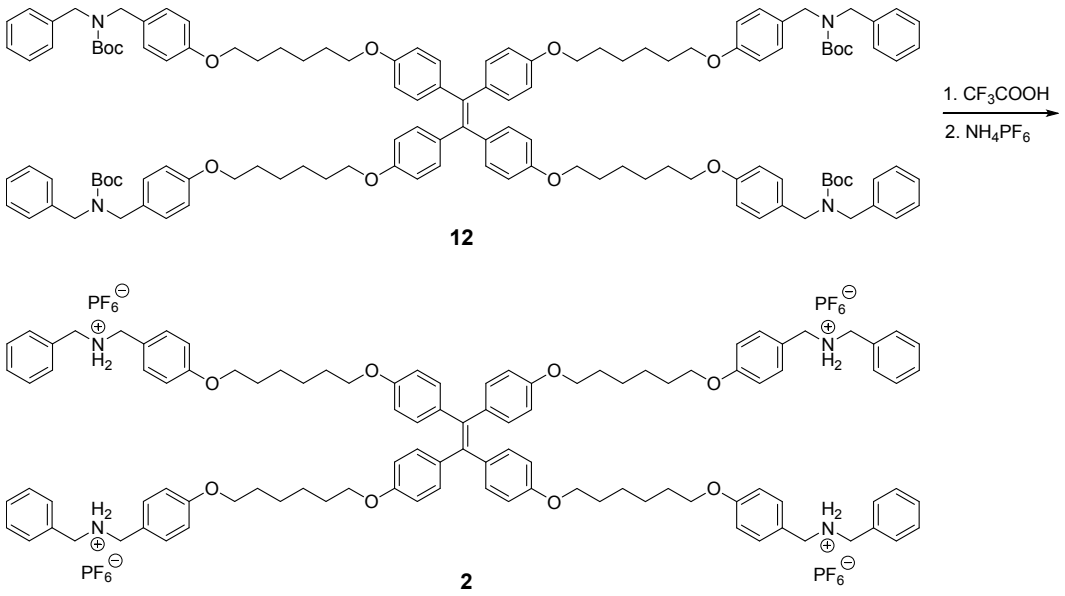
Fig S17. ^{13}C NMR spectrum (500 MHz, $CDCl_3$, 293K) of compound **12**.



Formula (M)	Score (MFG)	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)	DBE	m/z
C126 H152 N4 O16	100	1977.1209	1977.1203	2000.1096	-0.28	53	2000.1101

Fig S18. HRMS spectrum of compound **12**.

*3.4. Synthesis of compound **2***



12

2

To the solution of **12** (1.29 g, 0.65 mmol) in 100 mL of CH_2Cl_2, trifluoroacetic acid (1.92 g, 16.90 mmol) was added and the mixture was stirred at room temperature for 10 h. The saturated aqueous solution of NH_4PF_6 (20 mL) was added and stirred at room temperature for another 3 h. After then, the solvent was removed with a rotary evaporator. The residue was dissolved into 200 mL H_2O and extracted with CH_2Cl_2 (100 mL × 3). The organic phase was dried with anhydrous Mg_2SO_4, filtrated, and concentrated. The crude product was washed with ether three times to give **2** as a yellow

solid (1.02 g, 73 %). ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 293K) δ (ppm): 7.46–7.43 (m, 20H), 7.36 (d, *J* = 8.5 Hz, 8H), 6.94 (d, *J* = 8.5 Hz, 8H), 6.88 (d, *J* = 8.5 Hz, 8H), 6.64 (d, *J* = 9.0 Hz, 8H), 4.17 (s, 8H), 4.13 (s, 8H), 3.99 (t, *J* = 6.5 Hz, 8H), 3.89 (t, *J* = 7.5 Hz, 8H), 1.78–1.71 (m, 16H), 1.49–1.43 (m, 16H). ^{13}C NMR (125 MHz, 1:1 $CDCl_3$/CD_3CN, 293K) δ (ppm): 160.7, 158.0, 132.9, 132.4, 131.3, 130.7, 130.2, 129.6, 122.9, 115.4, 114.1, 68.5, 51.6, 29.4, 26.1. HRMS $[M - 4PF_6]^{4+}$: calcd. for $[C_{106}H_{124}N_4O_8]^{4+}$ 395.2349, found 395.2348.

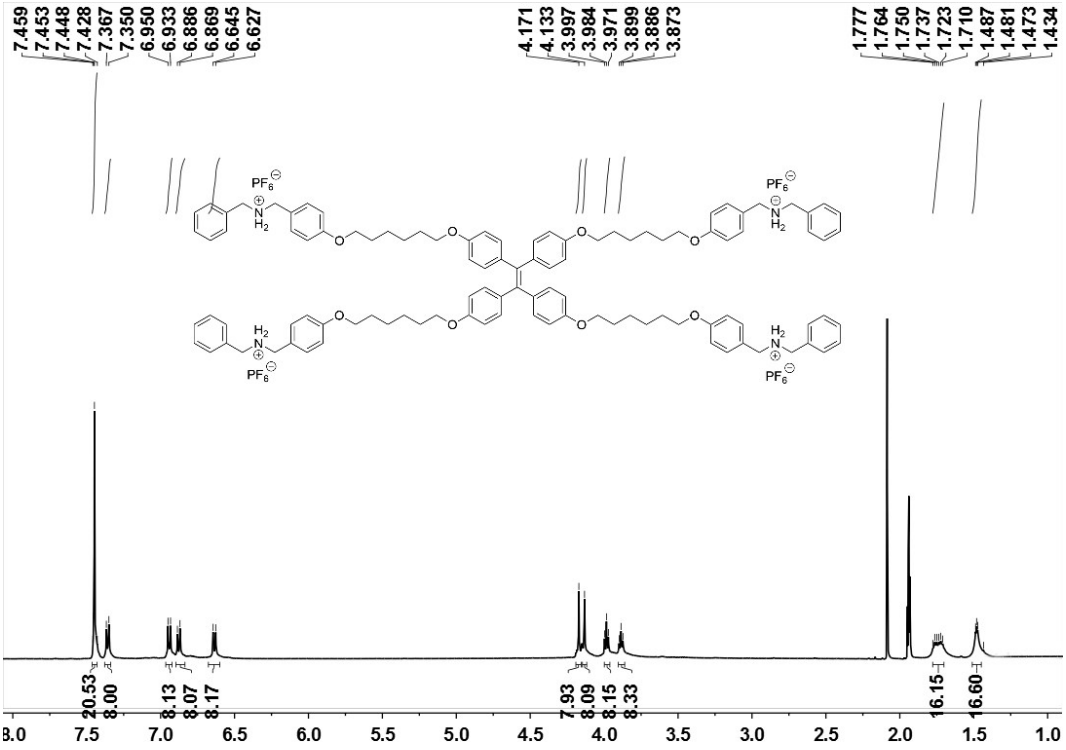


Fig S19. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 293K) of compound **2**.

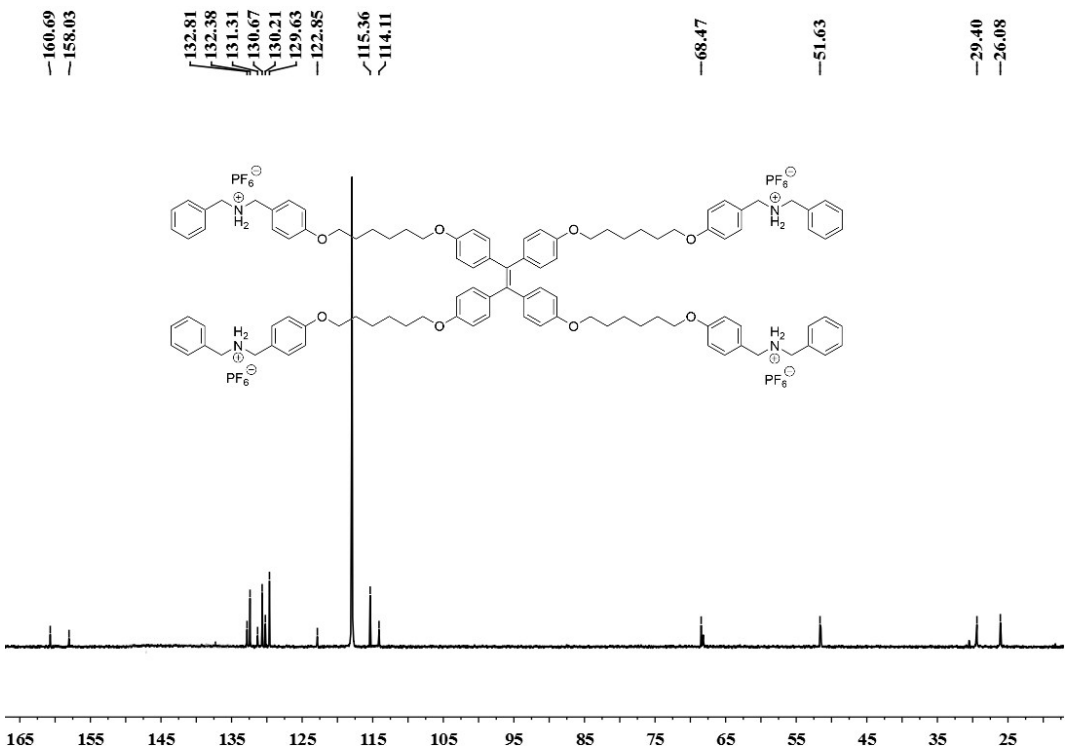
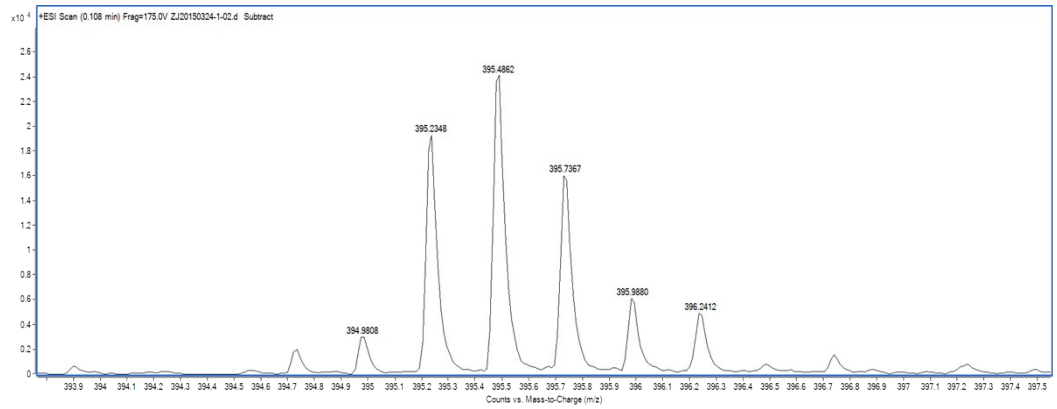


Fig S20. ^{13}C NMR spectrum (500 MHz, $CDCl_3$, 293K) of compound **2**.



Formula (M)	Score (MFG)	Mass	Mass (MFG)	m/z (Calc)	Diff (ppm)	DBE	m/z
C106 H124 N4 O8	100	1580.94	1580.9419	395.2349	0.33	47	395.2348

Fig S21. HRMS spectrum of compound **2**.

4. *Characterization of dimer **4** and tetramer **5***

4.1. *UV/Vis absorbance spectra of complexation between monomer **1** and Zn(OTf)$_2$*

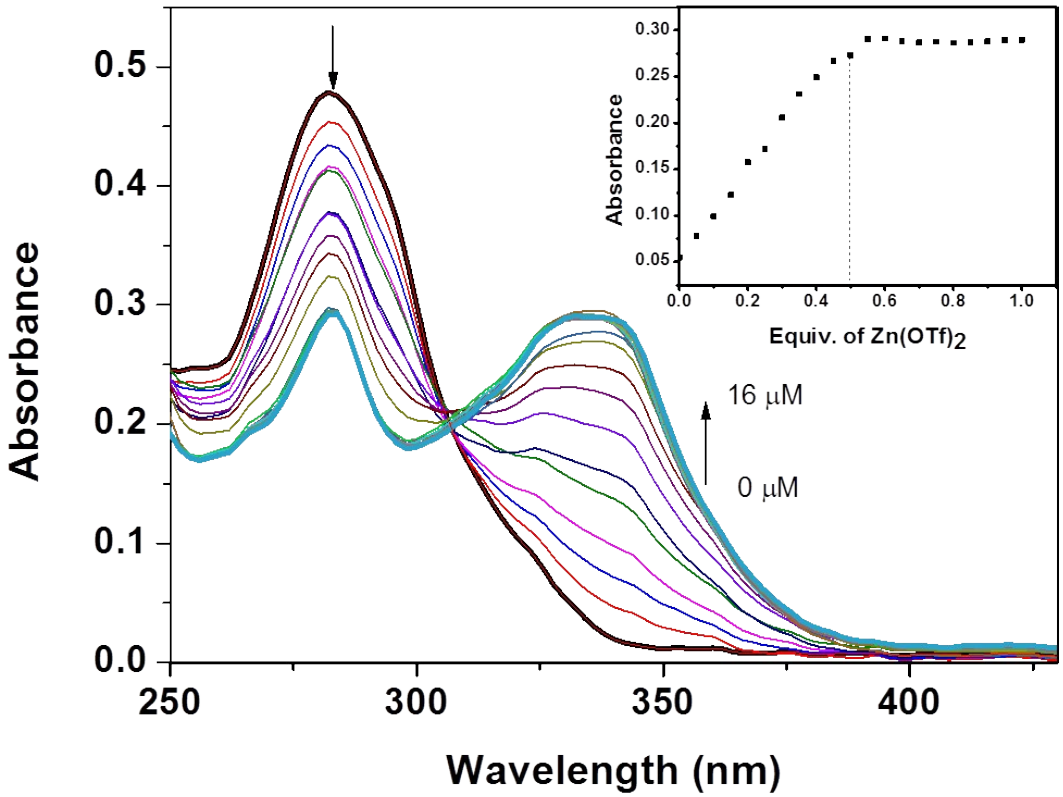


Fig S22. Change in the UV/Vis absorbance intensity upon stepwise addition of $Zn(OTf)_2$ to monomer **1** in $CHCl_3/CH_3CN$ (1/1, v/v); Inset: Plot of the absorbance intensity at 330 nm versus the amount of $Zn(OTf)_2$.

*4.2. [1]HNMR spectra of complexation between monomer **1** and $Zn(OTf)_2$*

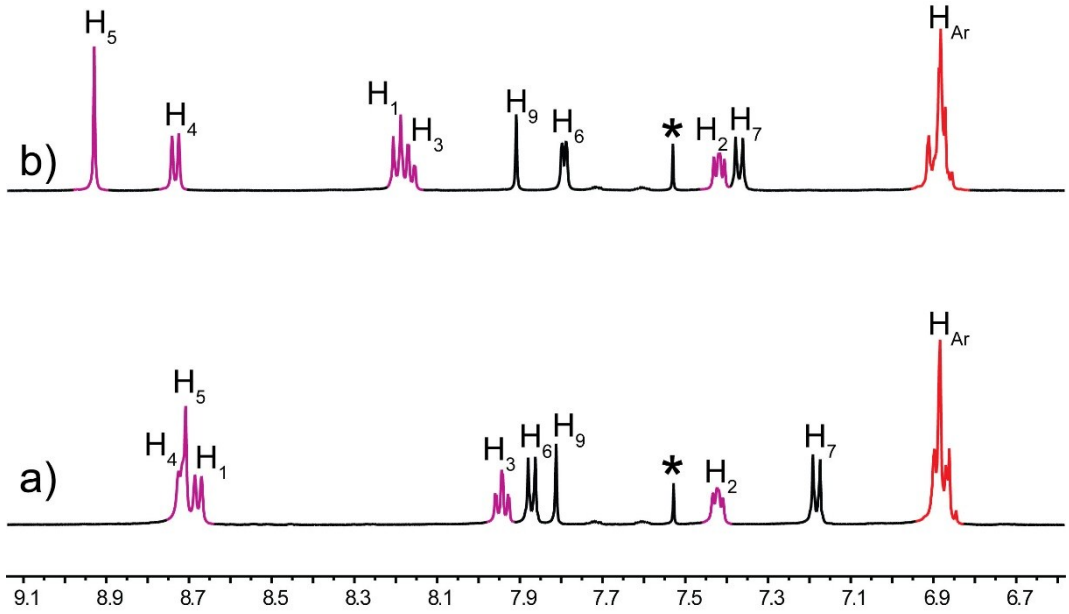


Fig S23. Partial ^{1}H NMR spectra (500 MHz, $CDCl_3/CD_3CN$ (1/1, v/v), 293 K) of (a) 8.00 mM **1**, (b) 8.00 mM **1** and 4.00 mM $Zn(OTf)_2$. The solvent peaks are marked with asterisks.

*4.3. [1]HNMR spectra of complexation between monomers **1** and **2***

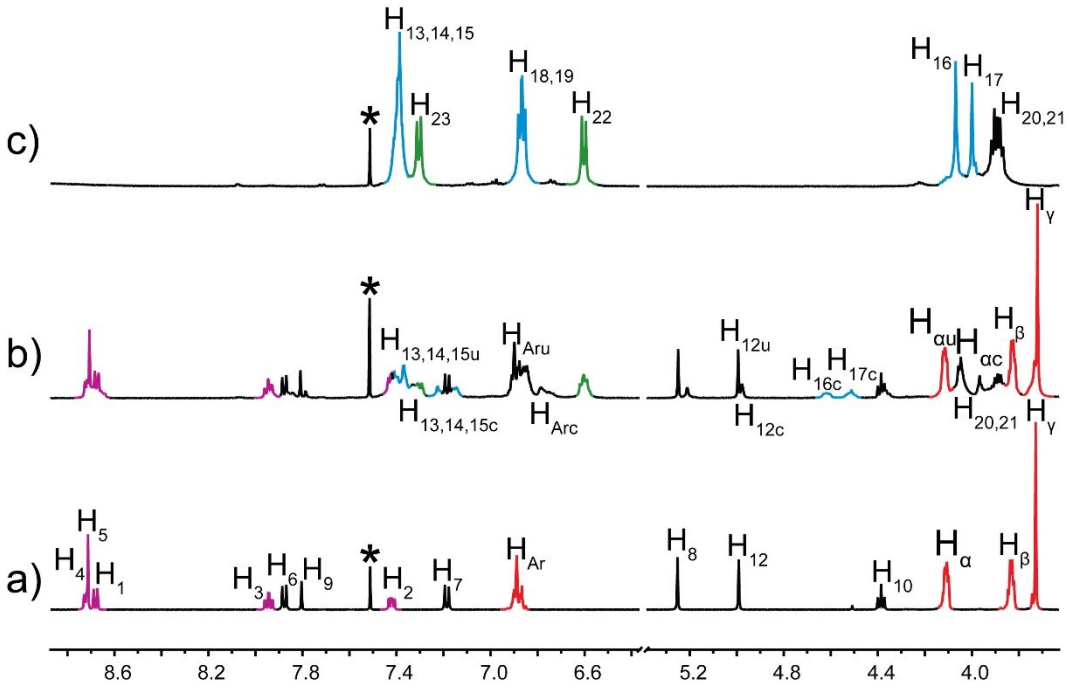


Fig S24. Partial ^{1}H NMR spectra (500 MHz, $CDCl_3/CD_3CN$ (1/1, v/v), 293K) of (a) 8.00 mM **1**, (b) 8.00 mM **1** and 2.00 mM **2**, and (c) 8.00 mM **2**. Peaks associated with

the complexed and uncomplexed species are designated by “c” and “u”, respectively. The solvent peaks are marked with asterisks.

*4.4. NOESY spectrum of complexation between monomers **1** and **2***

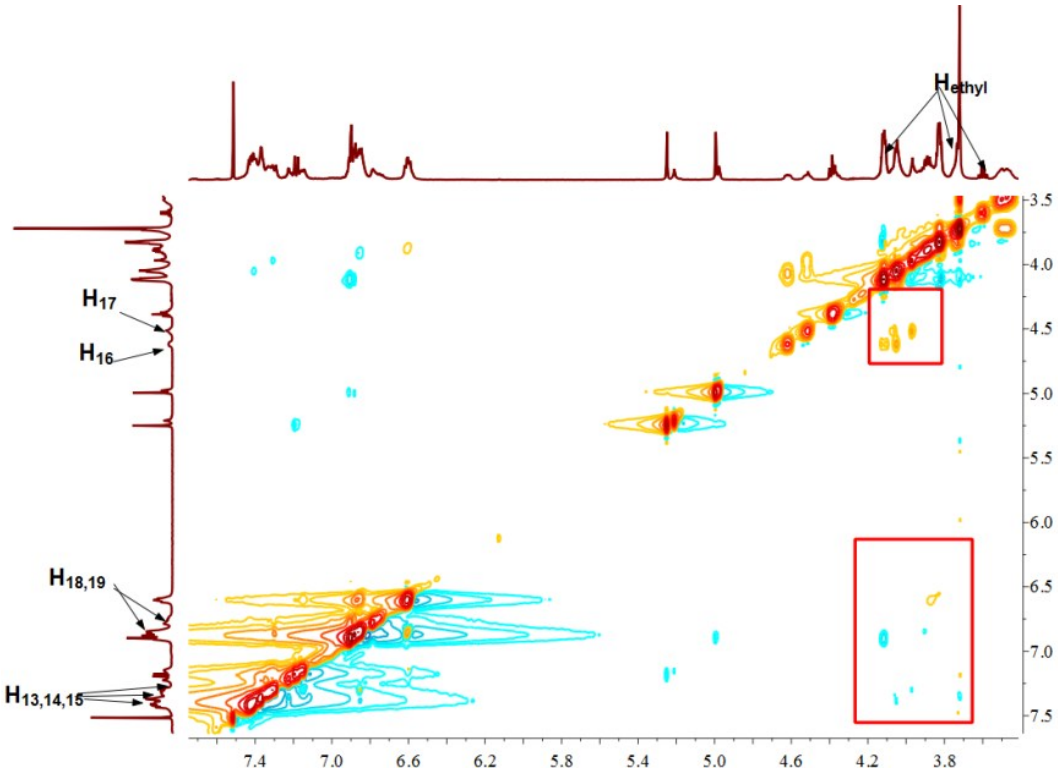


Fig S25. NOESY spectrum (500 MHz, 1:1 $CDCl_3/CD_3CN$, 293 K) of supramolecular tetramer **5** formed by mixing 8.00 mM monomer **1** and 2.00 mM monomer **2**.

5. *Multiple stimuli-responsiveness of hyperbranched supramolecular polymer **3***

5.1. *UV/Vis titration spectra of hyperbranched supramolecular polymer **3** with increasing amount of cyclen and then $Zn(OTf)_2$*

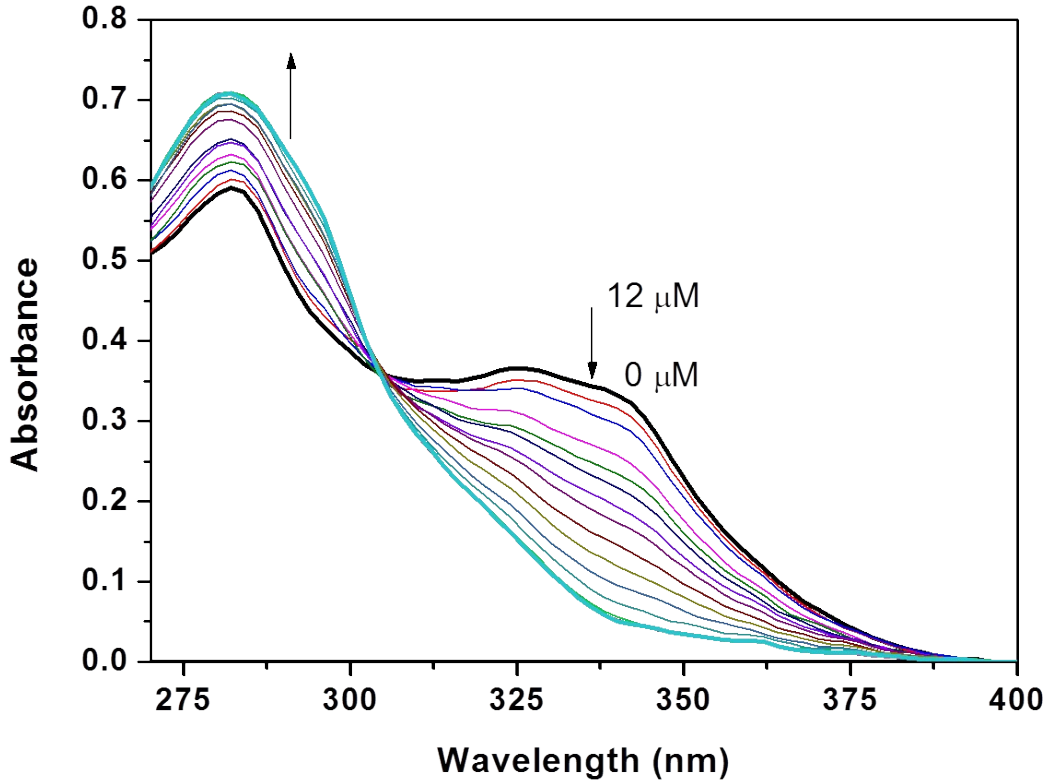


Fig S26. UV/Vis titration curve of hyperbranched supramolecular polymer **3** constructed by **1**, **2** and $Zn(OTf)_2$ (4 : 1 : 2 in molar ratio) at monomer **1** concentration of 50 mM with increasing amount of cyclen in $CHCl_3/CH_3CN$ (1/1, v/v).

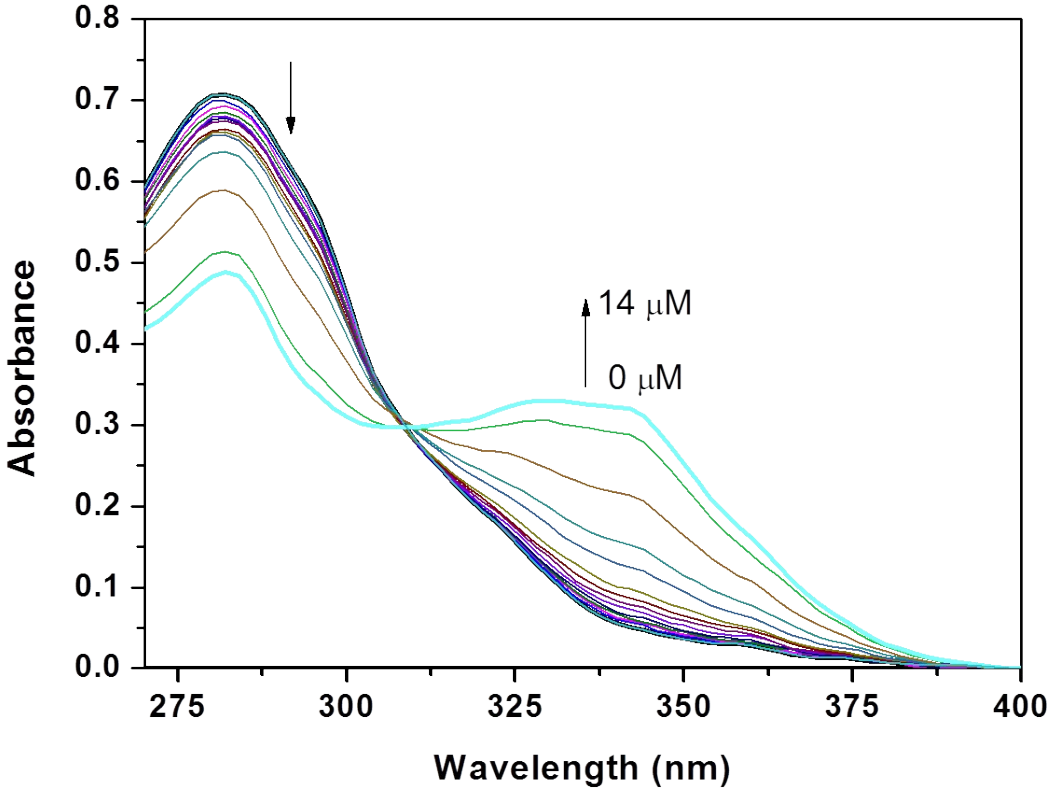


Fig S27. UV/Vis titration curve of hyperbranched supramolecular polymer **3** constructed by **1**, **2** and $Zn(OTf)_2$ (4 : 1 : 2 in molar ratio) at monomer **1** concentration of 50 mM with cyclen (12 μM), then addition of different amounts of $Zn(OTf)_2$ in $CHCl_3/CH_3CN$ (1/1, v/v).

*5.2. ^1H NMR spectra of hyperbranched supramolecular polymer **3** with Et_3N and then CF_3COOH*

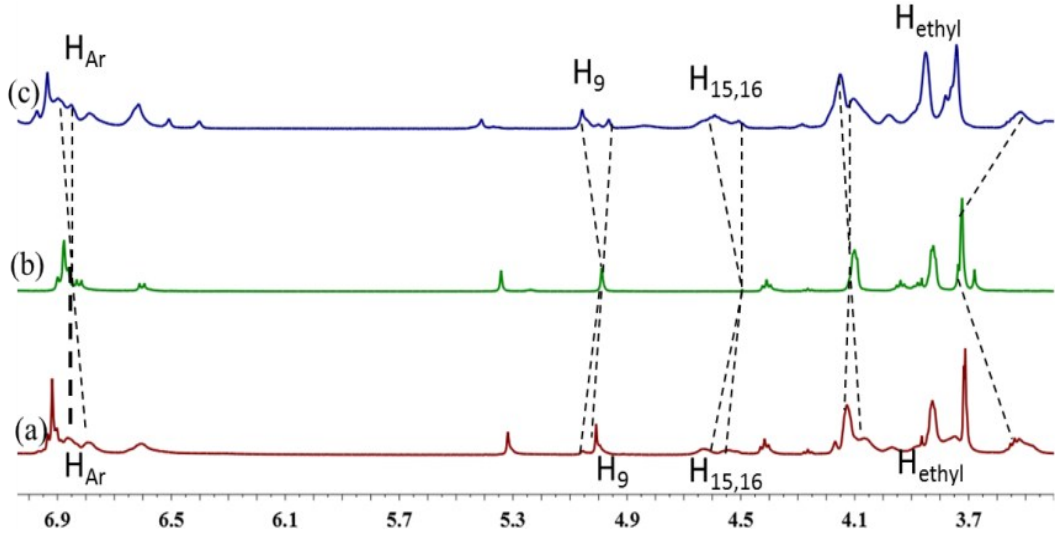


Fig S28. Partial ^1H NMR spectra (500 MHz, $CHCl_3/CH_3CN$ (1/1, v/v), 293 K) of (a)

hyperbranched supramolecular polymer **3** constructed by **1**, **2** and $Zn(OTf)_2$ (4 : 1 : 2 in molar ratio) at monomer **1** concentration of 8 mM; (b) treating the mixture with 1.5 equiv. of Et_3N to (a); (c) then addition of 2.8 equiv. of CF_3COOH to (b).

References

S1. H. W. Gibson, N. Yamaguchi and J. W. Jones, *J. Am. Chem. Soc.*, 2003, **125**, 3522.

S2. Y. Tian, F. Wang, *Macromol. Rapid Commun.*, 2014, **35**, 337.

S3. L. Zhao, Y. Chen, J. Yuan, M. Chen, H. Zhang and X. Li, *ACS Appl. Mater. Interf.*, 2015, **7**, 5177.