A supramolecular hyperbranched polymer constructed by host-guest interaction and complementary metal-coordination interaction

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Supporting information

1. The ^{1}H NMR spectra of the model compounds

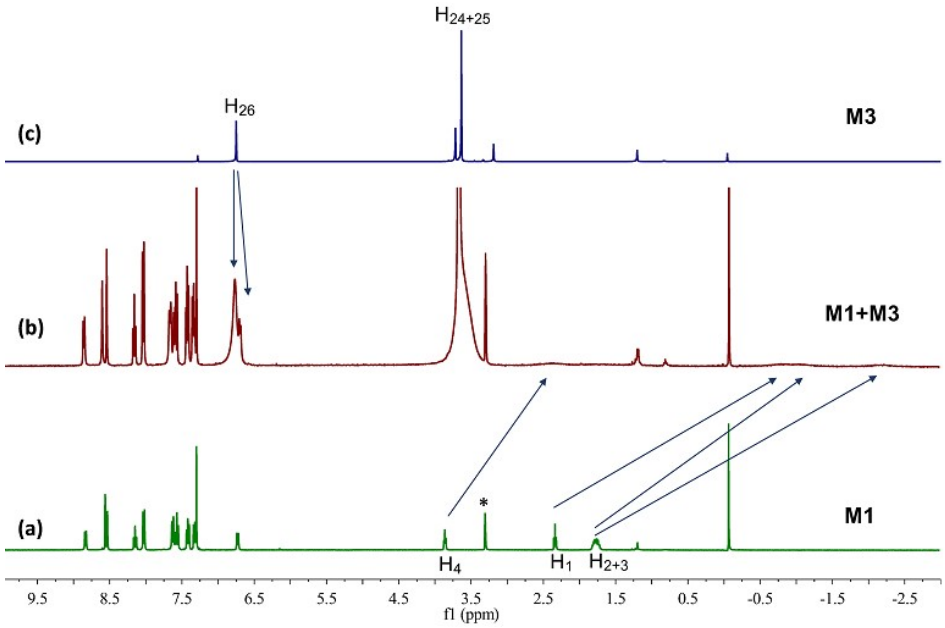


Fig. S1 The ^{1}H NMR of model compound (400 MHz, $CDCl_3$-CD_3OD = 3/1, v/v, 298 K): (a) M1；(b) M1+M3；(c) M3.

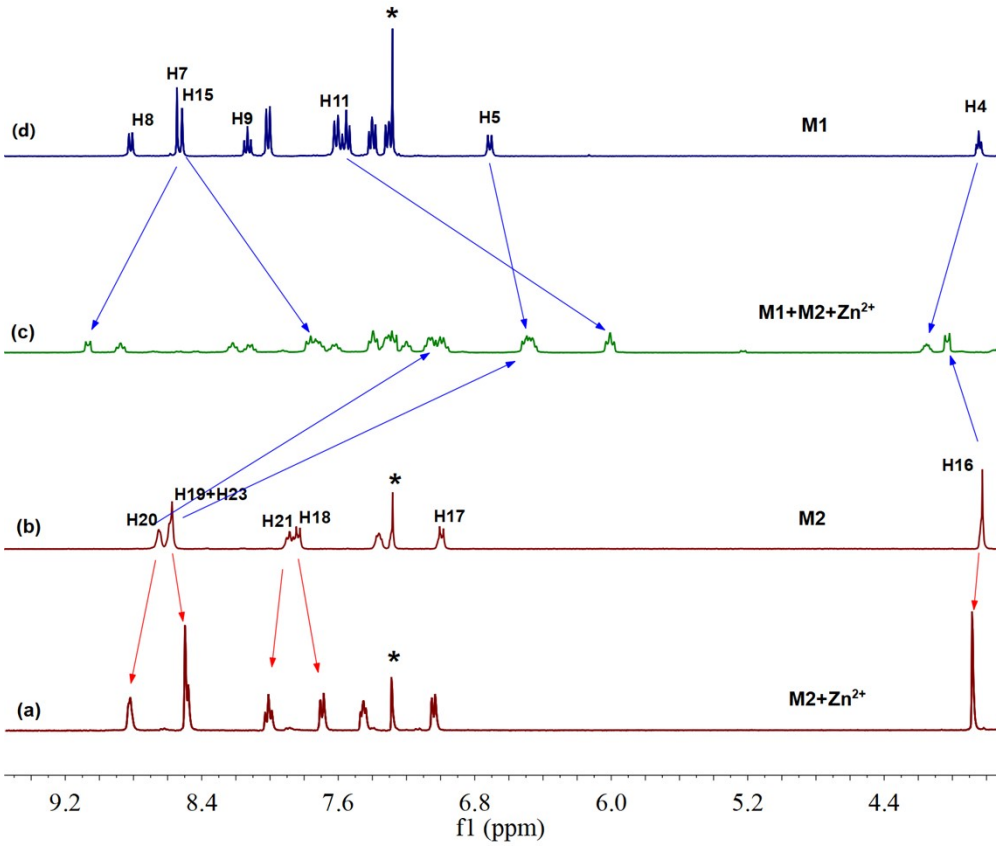


Fig. S2 The ^{1}H NMR of model compound (400 MHz, $CDCl_3$-CD_3OD = 3/1, v/v, 298 K): (a) M2+$Zn(OTf)_2$; (b) M2; (c) M1+M2+$Zn(OTf)_2$, (d) M1.

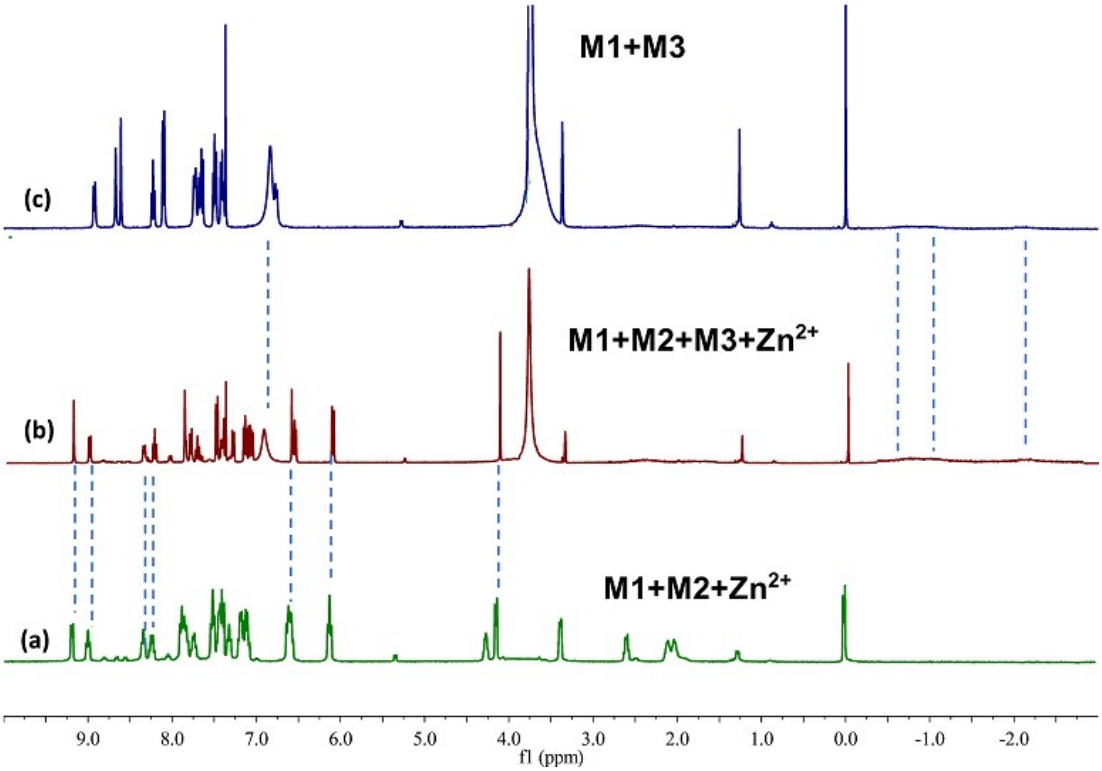


Fig. S3 The ^{1}H NMR of model compounds (400 MHz, $CDCl_3$-CD_3OD = 3/1, v/v, 298 K): (a) M1 +M2+$Zn(OTf)_2$; (b) M1+M2+M3+$Zn(OTf)_2$; (c) M1+M3.

2. The ^{1}H-^{1}H COSY and NOESY NMR spectra

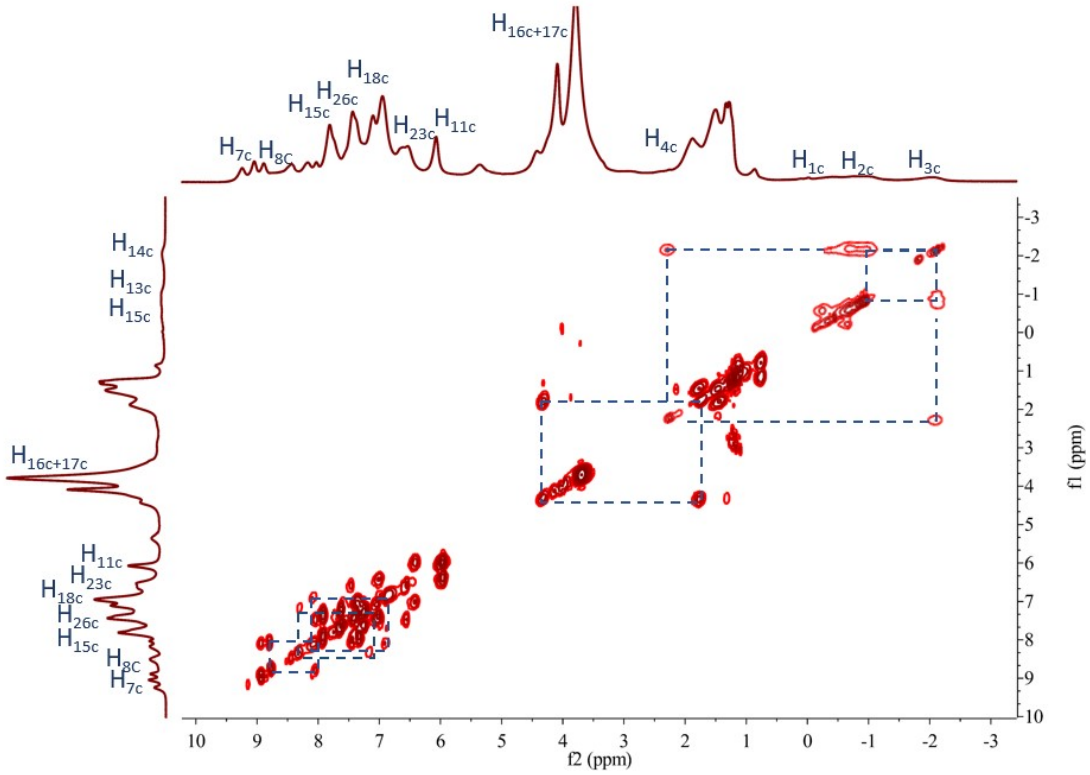


Fig. S4 The ^{1}H-^{1}H COSY spectrum of A3+B3+M1+Zn(OTf)$_2$ (400 MHz, $CDCl_3$-CD_3OD=3:1，v/v, 298 K), the peaks of the complexed protons were marked as c.

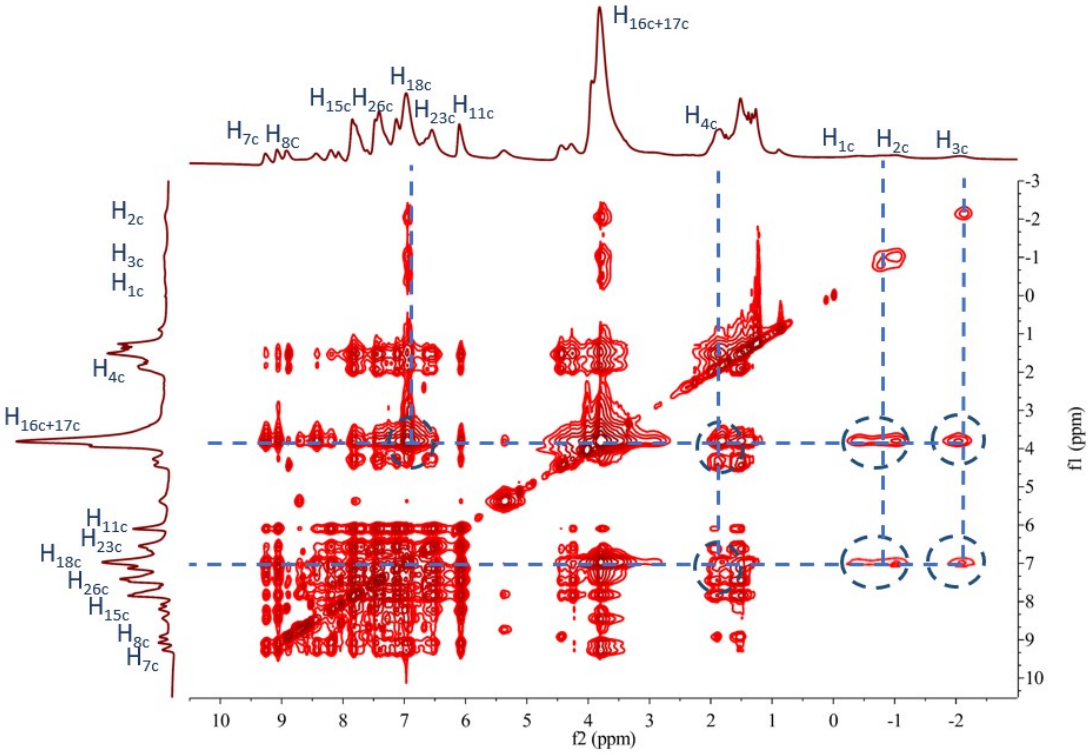


Fig. S5 The NOESY spectrum of A3+B3+M1+Zn(OTf)$_2$ (400 MHz, $CDCl_3$-CD_3OD=3:1，v/v,

298 K), the peaks of the complexed protons were marked as c.

3. Concentration-dependent ^{1}H NMR spectra

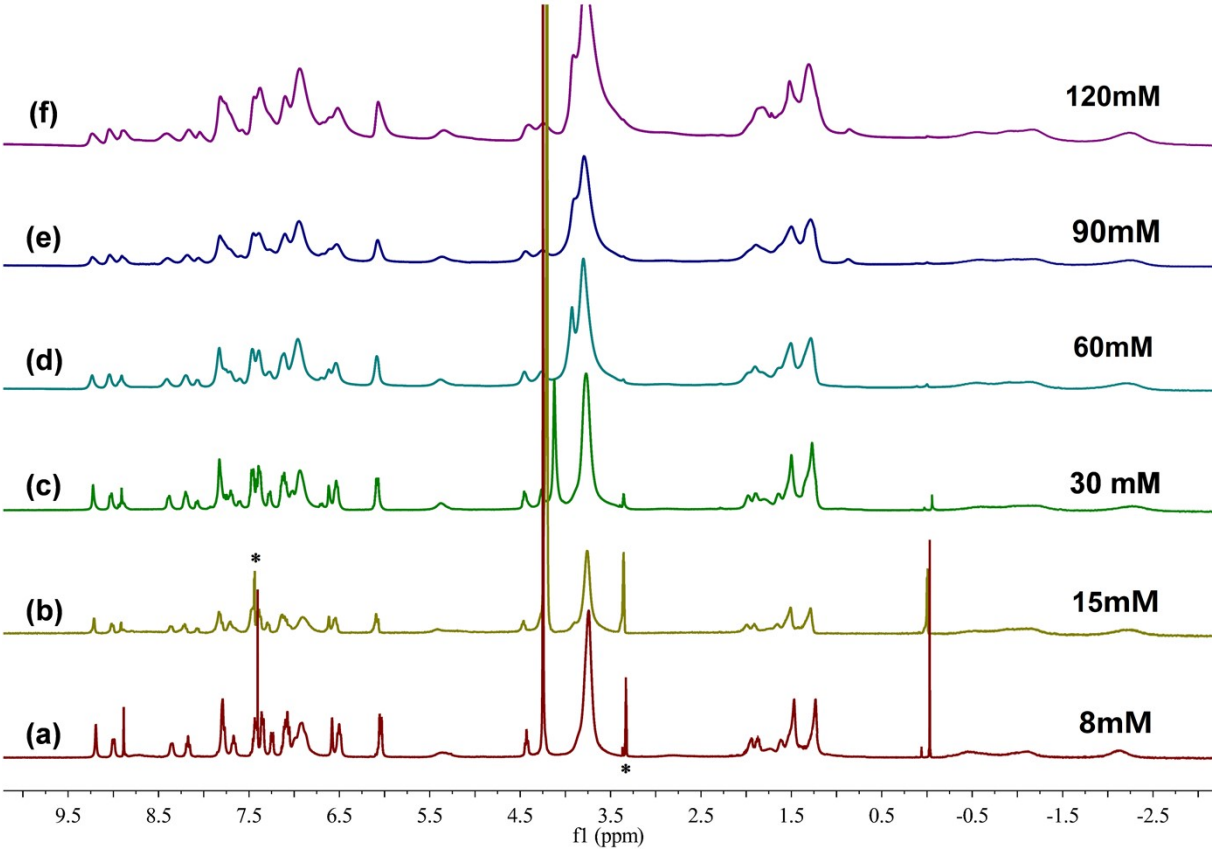


Fig.S6 ^{1}H NMR spectra (400 MHz, $CDCl_3$-CD_3OD= 3/1, v/v, 298 K) of A3+B3+M1+$Zn(OTf)_2$ at different concentrations (a) 8 mM, (b) 15 mM, (c) 30 mM, (d) 60 mM, (e) 90 mM, (f) 120 mM.

4. 2D DOSY NMR spectrum

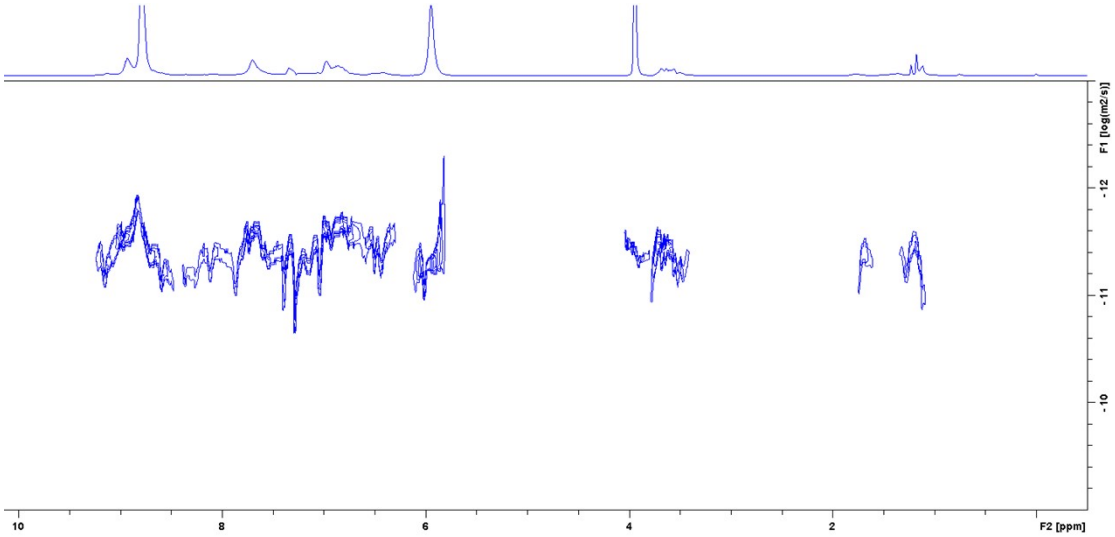


Fig. S7 Representative DOSY NMR spectrum (600 MHz, $CDCl_3$-CD_3OD = 3/1, v/v, 293 K) of A3+ B3+ M1+$Zn(OTf)_2$, the concentration of M1 is 110 mM.

5. Reduced viscosity of supramolecular polymer

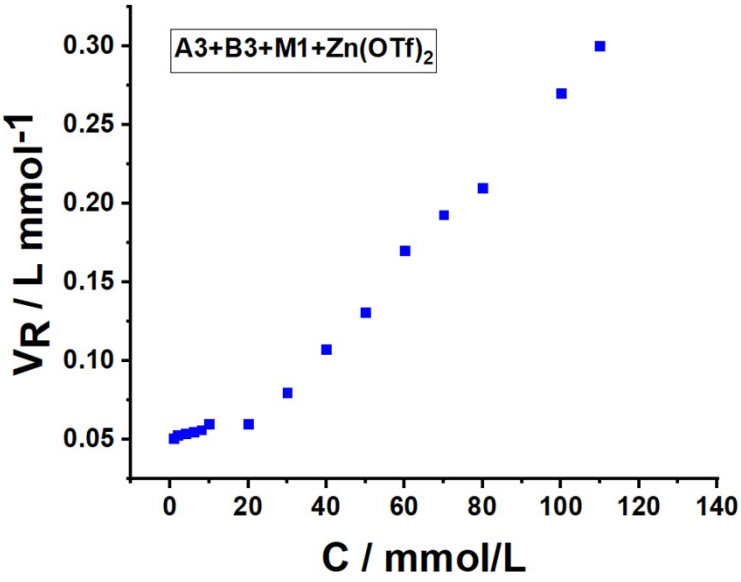


Fig. S8 Reduced viscosity of A3+B3+M1+$Zn(OTf)_2$ against the concentration of M1.

6. Stimuli-responsiveness study of SHP

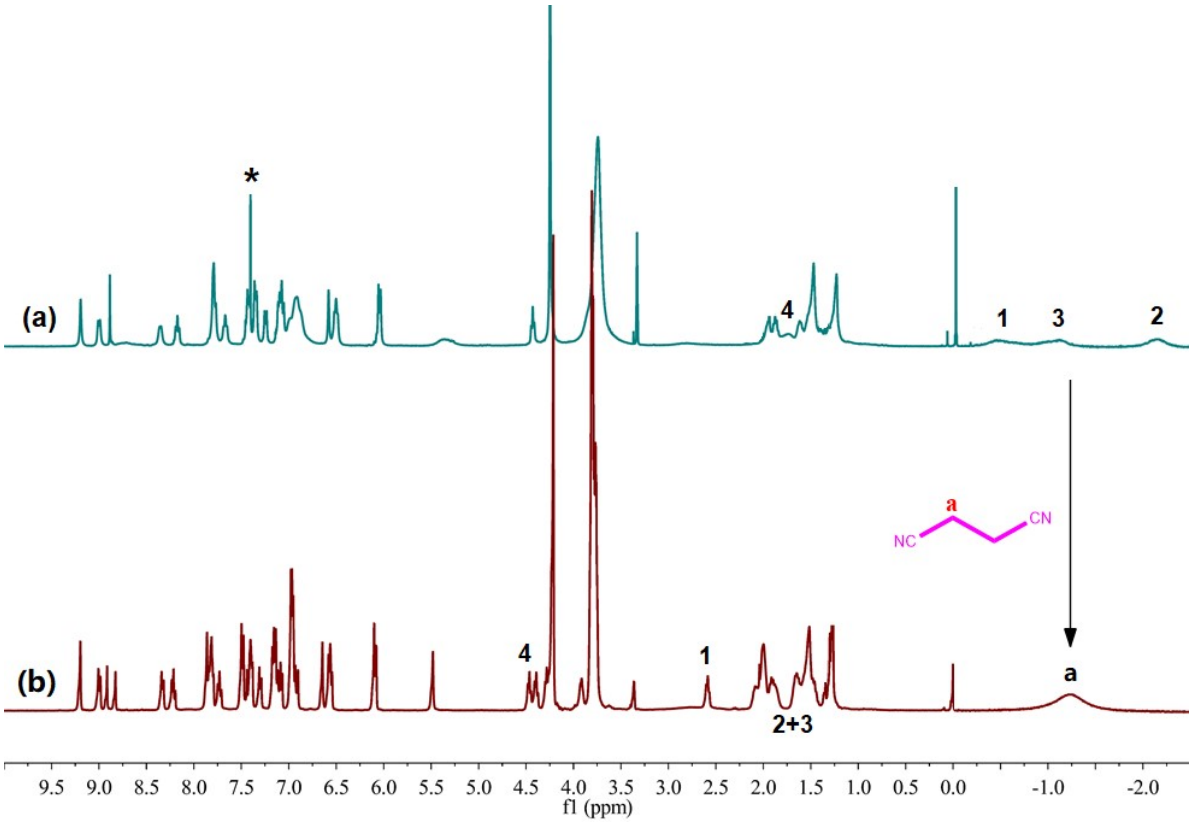


Fig. S9 ^{1}H NMR spectra (400 MHz, $CDCl_3$-CD_3OD = 3/1, v/v, 298 K, 30 mM) of (a) a solution of A3+B3+M1+$Zn(OTf)_2$, (b) after the addition of 3 equiv. butanedinitrile.

7. The discussion of binding constants

(1) tpy-Zn^{2+}-tay binding constant

To determine the association constant tpy-Zn^{2+}-tay, the UV/vis titration (Job plot method) was conducted on the basis of the reported method.[S1] Model compounds **M1** and **M2** were chosen as the ligands. The samples were prepared so that the total molar concentration of ligands ($\frac{[M1]+[M2]}{2}$) and zinc ion was 2×10^{-5}M in each sample: only the ratios of zinc ion to ligands changed. The absorbance intensity at 410 nm was plotted (Fig. S9) against the mole fraction of Zn^{2+}. The Job plot indicates a 1:1:1 binding among Zn^{2+}, M1 and M2.

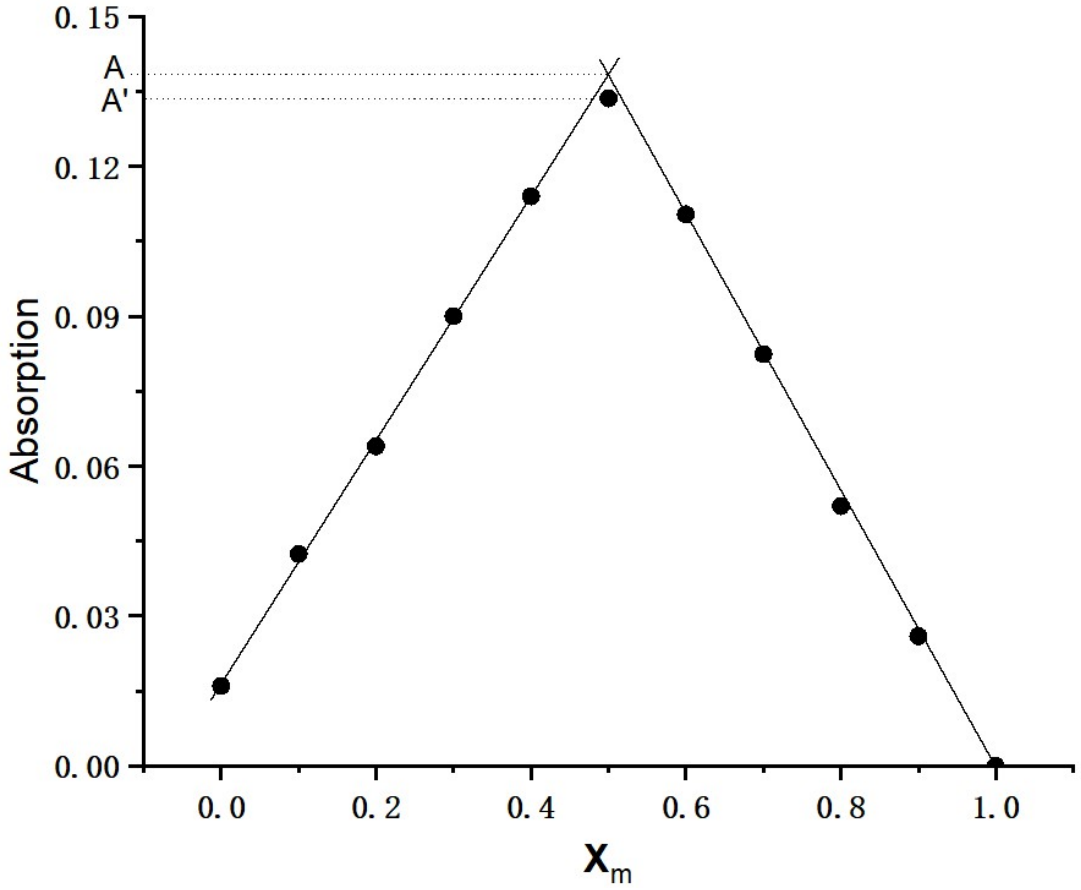


Fig. S10 Job plot of the complex formed among zinc ion, M1 (ligand) and M2 (ligand) showing a 1:1:1 stoichiometry by plotting the absorbance intensity at 410 nm against the mole fraction of zinc ion. Concentration: **[M1]**=**[M2]**, $\frac{[M1]+[M2]}{2}$ + [$Zn(OTf)_2$] = 20μM.

Furthermore, the data of job plot were divided into two groups around X_m= 0.5. When $X_m \leq 0.5$, the fitting equation is A = 0.2405Xm + 0.0160. When $X_m \geqslant 0.5$, the fitting equation is $A = -0.2719X_m + 0.2713$. The intersection of the two fitting curves is taken (X_m=0.4973, A=0.1373), and the experimental value is X_m=0.5, A'= 0.1321. The degree of dissociation of complex [ZnM1M2]$(OTf)_2$ was calculated from **Eq. 1**. According to the formula,[S1] the dissociation degree(α) of complex [ZnM1M2]$(OTf)_2$ was calculated to be 0.038.

$$\alpha = (A - A')/A, \textbf{ (Eq. 1)}$$

The binding constant *K* was then calculated to be 4.54×10^{13} M^{-1} based on **Eq. 2**.

$$\mathbf{[ZnM1M2](OTf)_2} \rightleftharpoons \mathbf{M1 + M2 + Zn(OTf)2}$$

total concentration	C	0	0	0
equilibrium concentration	C(1-α)	Cα	Cα	Cα

$$\boldsymbol{K} = \frac{[ZnM1M2](OTf)_2}{[M1]\,[M2]\,[Zn(OTf)_2]} = \frac{C(1-\alpha)}{[C\alpha]^3} \quad \textbf{(Eq.2)}$$

Where C is the total concentration of the complex [Zn**M1M2**](OTf)$_2$ and α is the degree of dissociation of complex [Zn**M1M2**](OTf)$_2$ when X_m value is 0.5, with the hypothesis that the ligands and zinc ion only form the complex [Zn**M1M2**](OTf)$_2$. The C is 1×10^{-5} M and the α is 0.038 when X_m is 0.5.

(2) P5-NAC binding constant

To estimate the *Ka* value of P5-NAC, we use monomer M1 and permethylated pillar[5]arene (P5) to determine the association constant *Ka*, fluorescence spectroscopy was performed with a constant concentration of monomer M1(0.01 mM) and the concentrations of permethylated pillar[5]arene ranged from 0 to 0.08 mM. By a non-linear curve-fitting method,[S3] the association constant (*K*a) of P5-NAC was estimated to be $(2.65\pm0.13)\times10^4$ M^{-1}.

The non-linear curve-fittings were based on the equation **Eq.3**:

$$\Delta F = (\Delta F\infty/[G]_0)\,(0.5[H]_0 + 0.5([G]_0+1/Ka) - (0.5\,([H]_0^2+(2[H]_0(1/Ka - [G]_0)) + (1/Ka + [G]_0)^2)^{0.5}))$$

Where ΔF is the fluorescence intensity change of emission band of guest M1 at 422 nm at $[H]_0$, $\Delta F\infty$ is the fluorescence intensity change of emission band **of** guest M1 at 422 nm when the guest M1 is completely complexed, $[G]_0$ is the fixed initial concentration of the guest M1 (0.01mM), and $[H]_0$ is the varying concentrations of host permethylated pillar[5]arene.

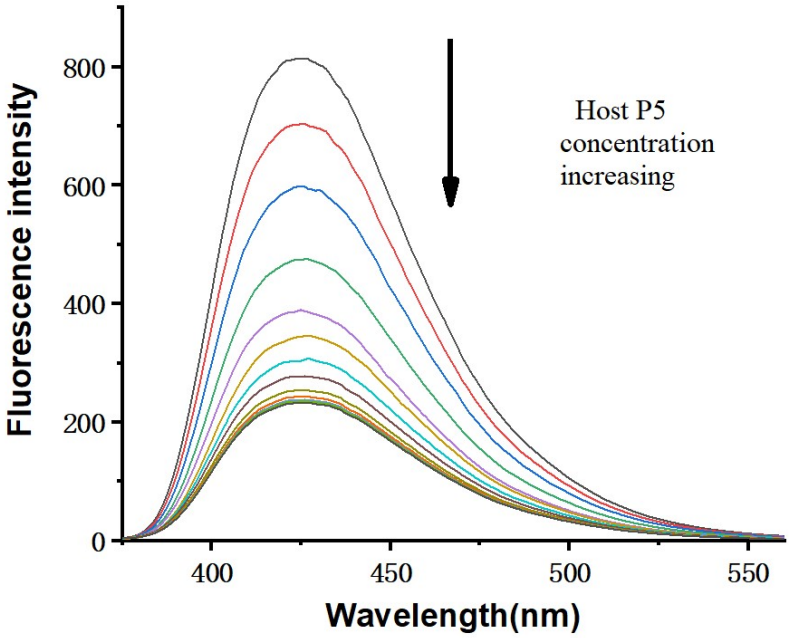


Fig. S11 Fluorescence spectra of solutions with different molar rate of **P5**/**M1**.

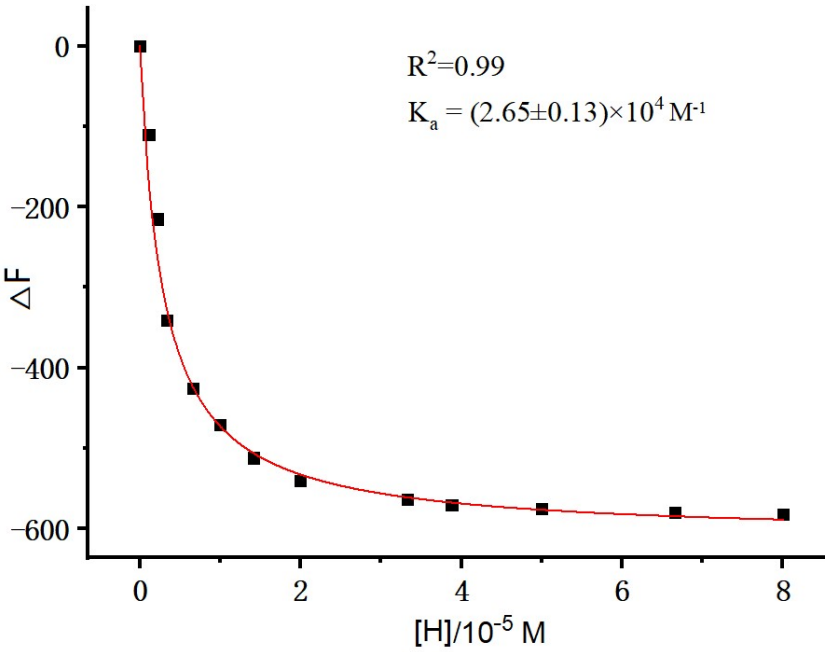
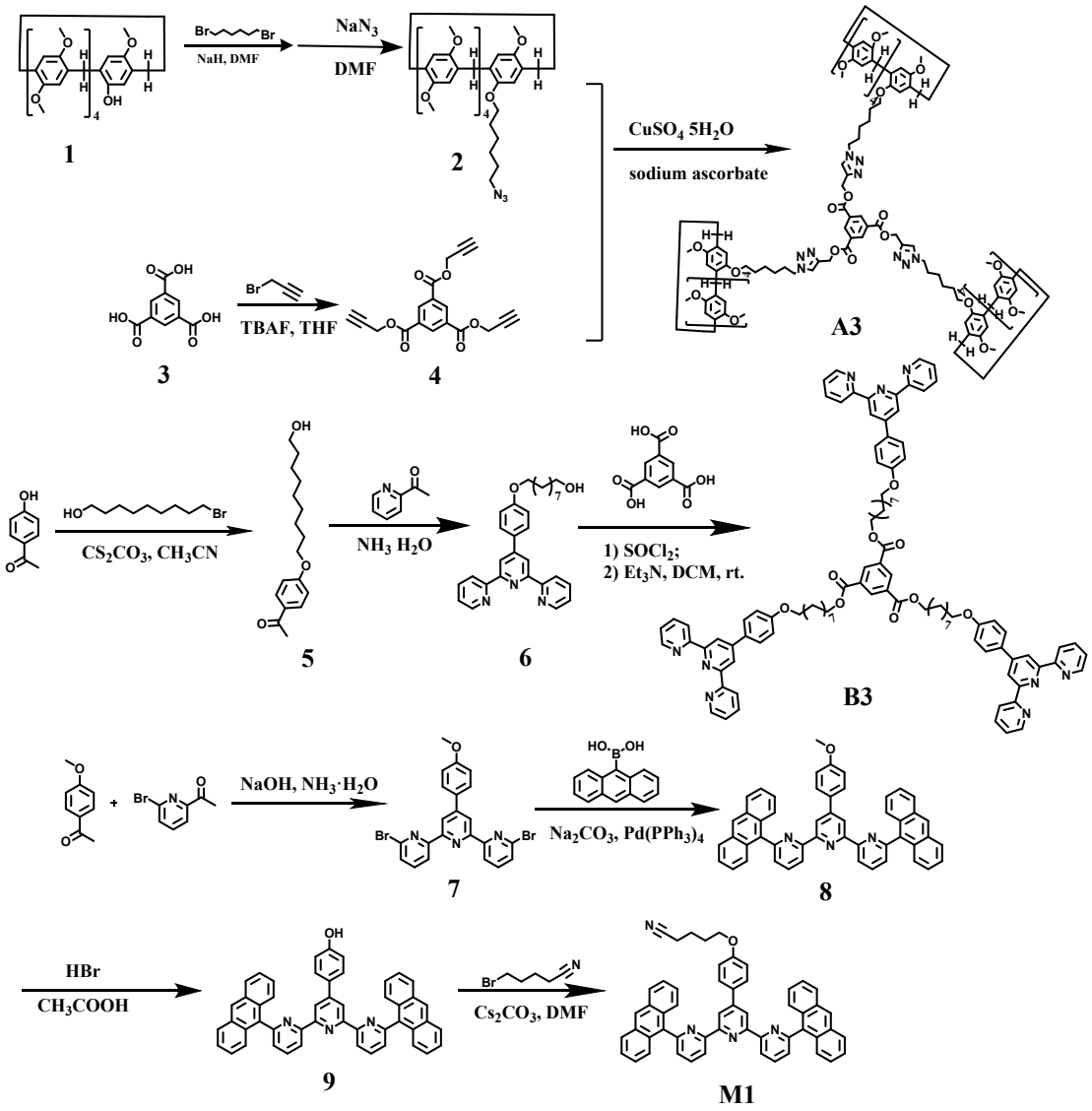


Fig. S12 The fluorescence intensity changes of **M1** upon addition of **P5**. The red solid line was obtained from the non-linear curve-fitting using eq. 3.

8. Synthesis of the monomers and intermediates



Scheme S1 The synthetic routes of the monomers **A3**，**B3**，**M1**.

Synthesis of the compound 4

A solution of benzene-1,3,5-tricarboxylic acid (0.50 g, 2.4 mmol), propargyl bromide (1.42 g, 10.8 mmol) and TBAF (14.3 mL, 18 mmol) in THF was stirred under inert atmosphere for 12 h at 30 °C. After the reaction mixture was cooled to ambient temperature, the solvent was evaporated under reduced pressure and the residue was partitioned between dichloromethane and water. The aqueous layer was further washed with dichloromethane. The organic phases were combined and dried over anhydrous Na_2SO_4. After the solvent was removed, the resulting residue was subjected to column chromatography (petroleum ether /ethyl acetate= 3:1), to give compound **4** (0.69 g, 90 %) as a white solid.^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ (ppm) = 8.92 (s, 1H), 4.99 (d, J = 2.5 Hz, 2H), 2.56 (t, J = 2.5 Hz, 1H). ^{13}C

NMR (100 MHz, $CDCl_3$): δ (ppm) = 163.99, 135.29, 130.79, 75.62, 53.14. ESI-MS ($C_{18}H_{12}O_6$): m/z calcd for $[M+H]^+$ = 325.0707, found = 325.0699, error = 2.46 ppm.

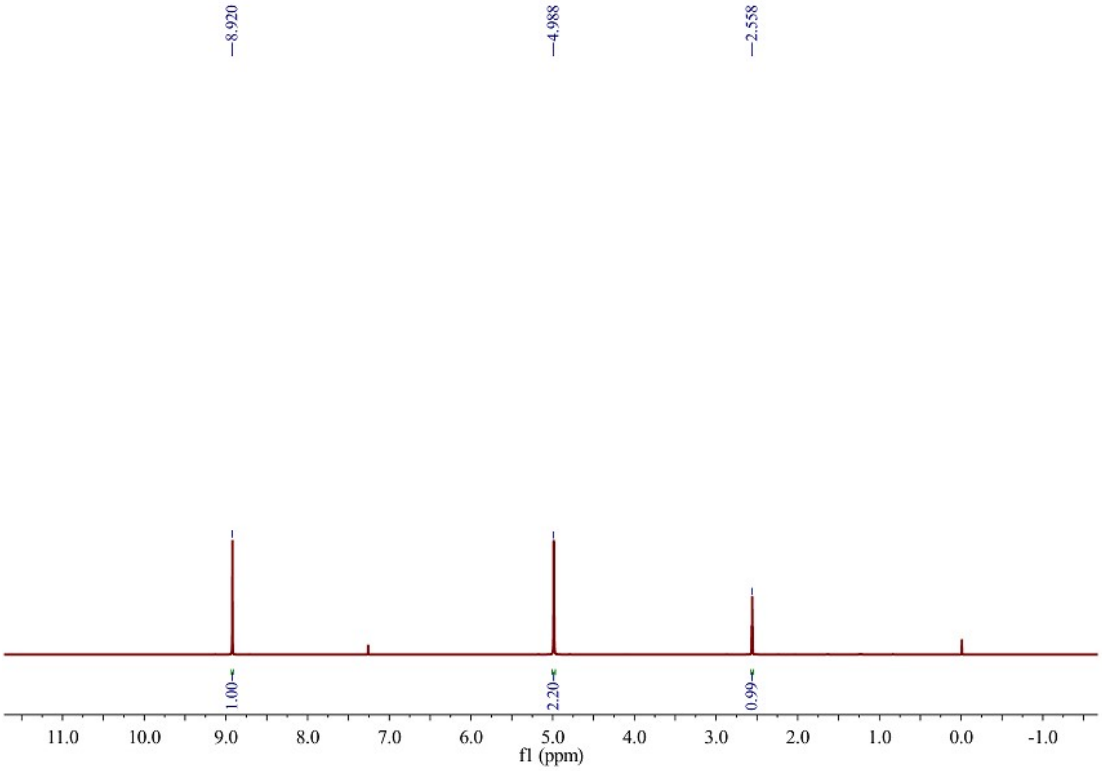


Fig. S13 The ^1H NMR of compound **4** (400 MHz, $CDCl_3$, 298K).

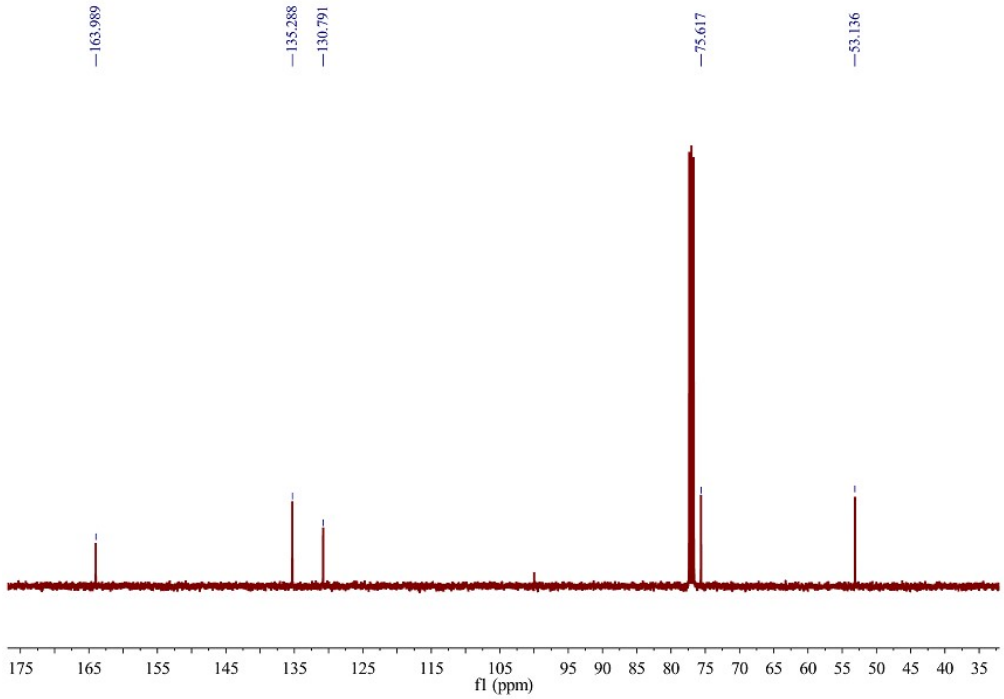


Fig. S14 The ^{13}C NMR of compound **4** (100 MHz, $CDCl_3$, 298K).

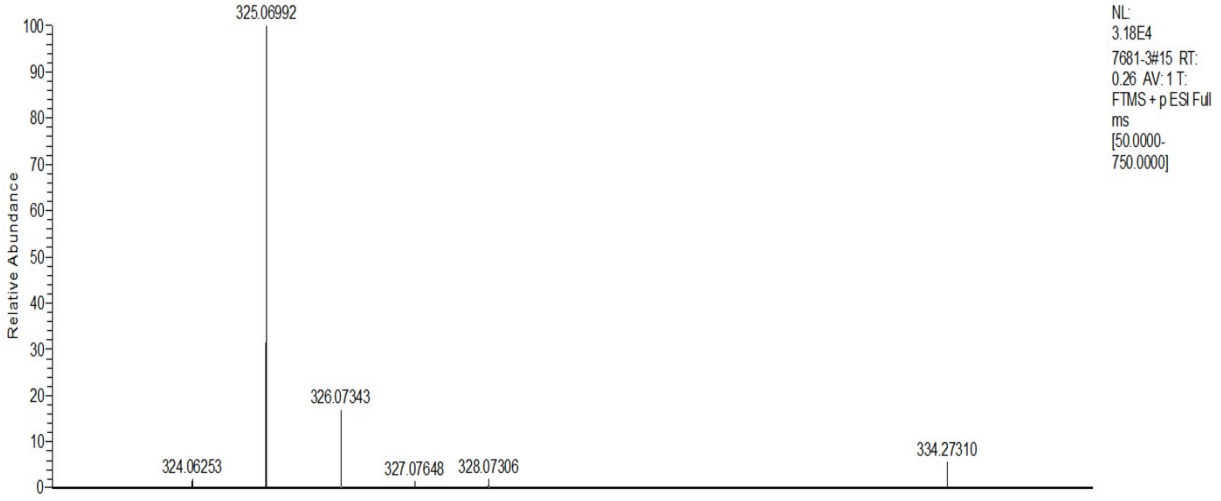


Fig.S15 The high-resolution ESI-MS of compound **4** ($CHCl_3$, 298K).

Synthesis of the compound A3

A solution of **2** (5.00 g, 5.4 mmol), **4** (0.50 g, 1.5 mmol), $CuSO_4 \cdot 5H_2O$ (0.60 g, 2.3 mmol) and sodium ascorbate (1.40 g, 6.9 mmol) in dry THF was stirred under inert atmosphere for 24 h at 65 °C. After the reaction mixture was cooled to ambient temperature, the solvent was evaporated under reduced pressure and the residue was partitioned between dichloromethane and water. The aqueous layer was further washed with dichloromethane. The organic phases were combined and dried over anhydrous Na_2SO_4. After the solvent was removed, the resulting residue was subjected to column chromatography (dichloromethane /acetonitrile = 10:1), to give compound **A3** (2.29 g, 51 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ (ppm) = 8.89 (s, 3H), 7.26 (s, 3H), 6.90-6.80 (m, 24H), 6.71 (d, J = 10.7 Hz, 6H), 5.48 (s, 6H), 3.93 (t, J = 6.0 Hz, 6H), 3.73 (m, 99H), 3.57 (d, J = 7.7 Hz, 18H), 1.71-1.62 (m, 6H), 1.24 (s, 6H), 0.87 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 164.67, 151.09, 150.99-150.37, 150.37-150.02, 149.87, 140.89, 134.87, 131.22, 129.07-128.61, 128.53-128.15, 127.85, 127.25, 123.81, 115.70, 114.87, 114.54-113.25, 67.22, 58.77, 56.61, 55.99-5.20, 55.08-54.89, 49.24, 29.77, 29.34, 28.97, 28.09, 25.51, 23.60. MALDI-TOF-MS ($C_{168}H_{189}N_9O_{36}$): m/z calcd for $[M]^+$ = 2909.3263, found = 2909.3379, error = 3.98 ppm.

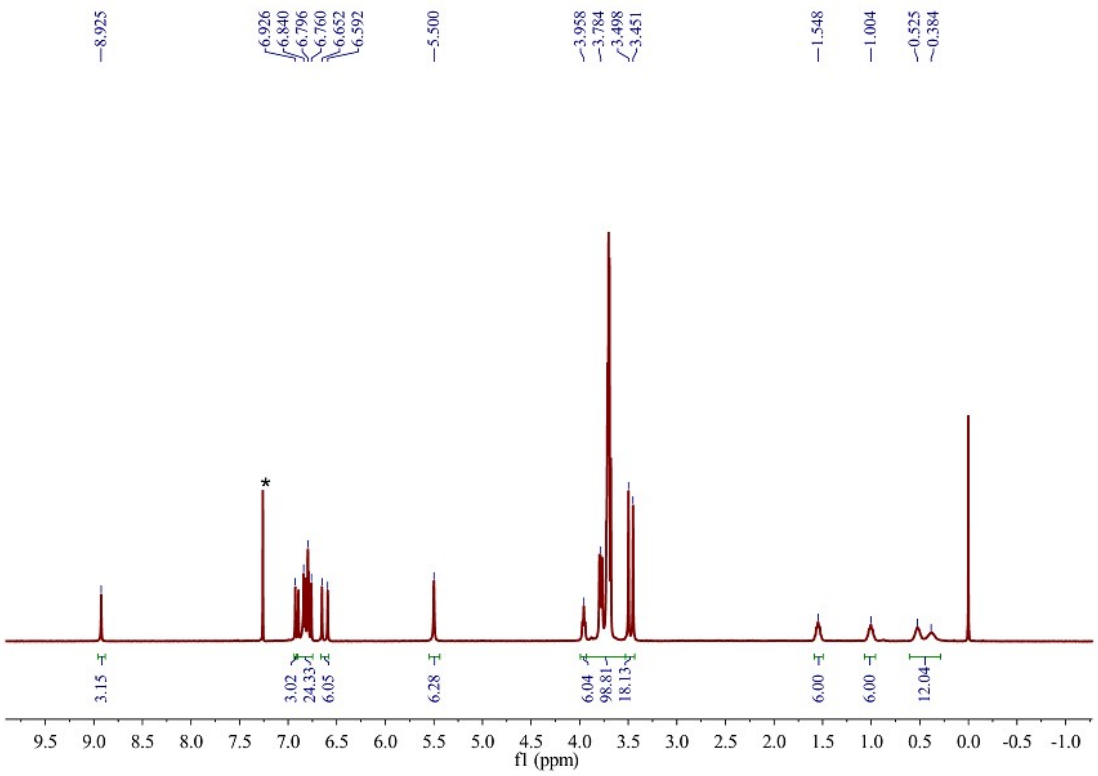


Fig. S16 The ^{1}H NMR of monomer **A3** (400 MHz, $CDCl_3$, 298 K).

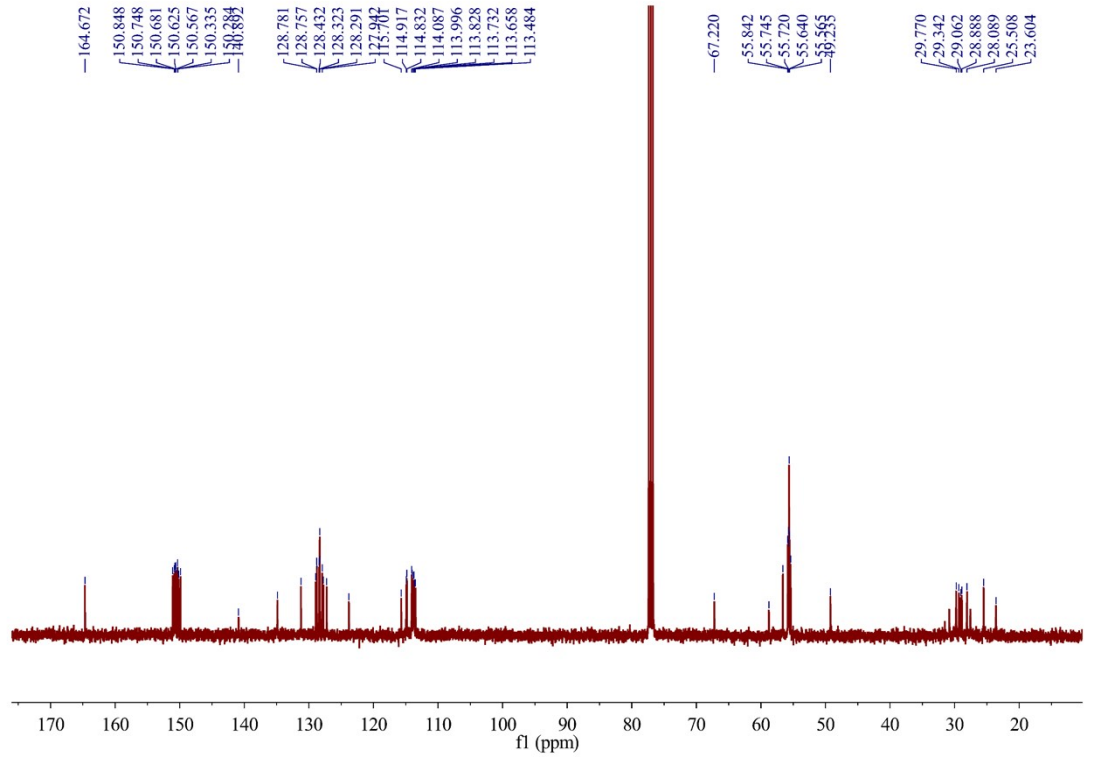


Fig. S17 The ^{13}C NMR of compound **A3** (100 MHz, $CDCl_3$, 298 K).

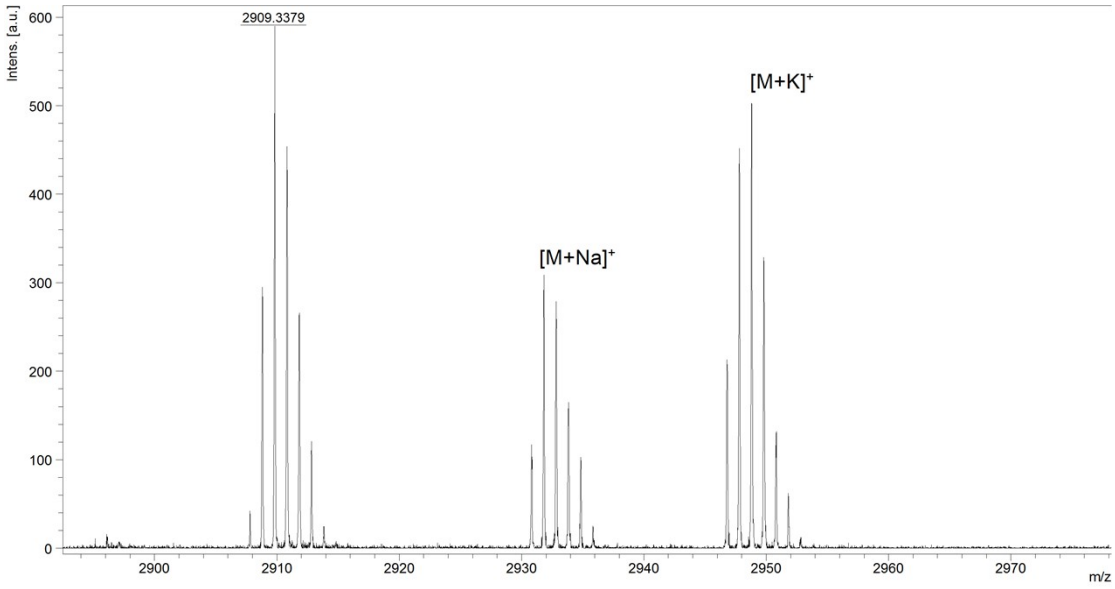


Fig. S18 The high-resolution MALDI-TOF-MS of monomer **A3**.

Synthesis of the compound 5

A solution of 9-bromo-1-nonanol (2.20 g, 9.8 mmol), 4-hydroxybenzaldehyde (1.00 g, 8.2 mmol) and Cs_2CO_3 (8.00 g, 24.57 mmol) in CH_3CN was stirred under inert atmosphere for 12 h at 85 °C. After the reaction mixture was cooled to ambient temperature, the solvent was evaporated under reduced pressure and the residue was partitioned between dichloromethane and water. The aqueous layer was further washed with dichloromethane. The organic phases were combined and dried over anhydrous Na_2SO_4. After the solvent was removed, the resulting residue was subjected to column chromatography (petroleum ether /ethyl acetate= 5:1), to give compound **5** (2.16 g, 90 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ (ppm) = 9.87 (s, 1H), 7.86-7.78 (m, 2H), 7.02-6.94 (m, 2H), 4.03 (t, *J* = 6.5 Hz, 2H), 3.64 (t, *J* = 6.6 Hz, 2H), 1.85-1.76 (m, 2H), 1.57 (m, 2H), 1.44 (d, *J* = 7.6 Hz, 2H), 1.34 (d, *J* = 15.6 Hz, 8H).

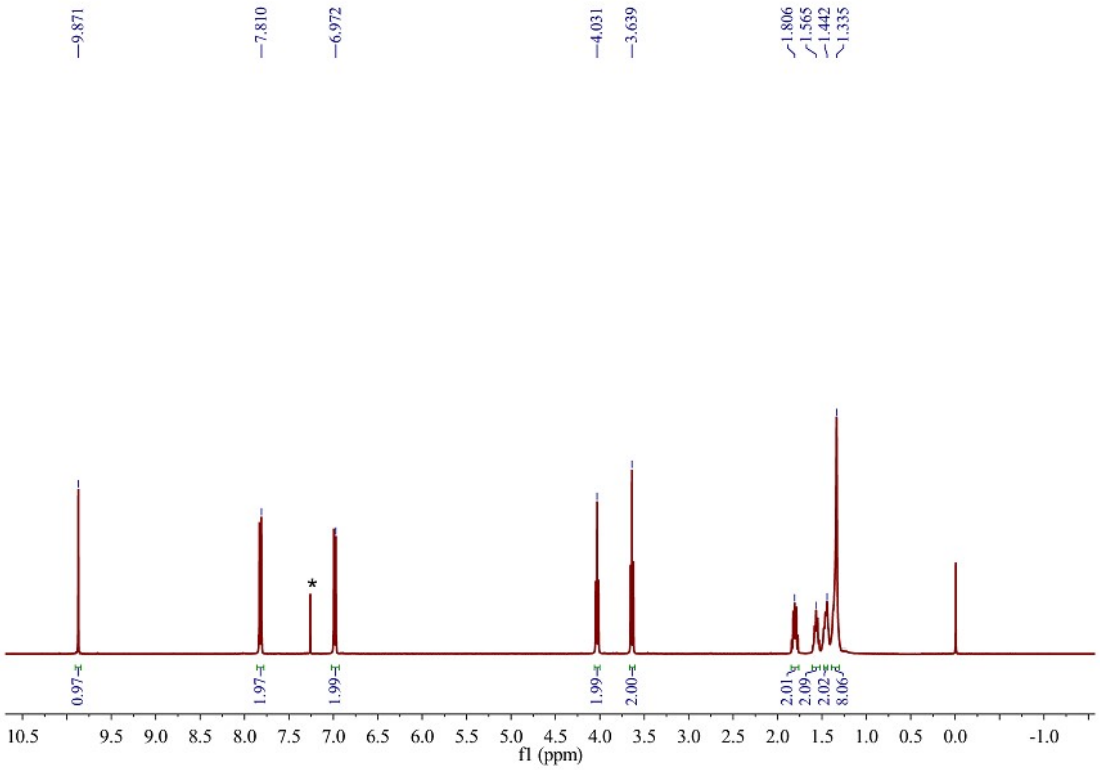


Fig. S19 The ^{1}H NMR of compound **5** (400 MHz, $CDCl_3$, 298 K).

Synthesis of the compound 6

A solution of **5** (1.45 g, 5.5 mmol), 2-acetyl-6-bromopyridine (1.46 g, 12.1 mmol) in ethanol was stirred, saturated aqueous NaOH (0.66 g, 16.5 mmol) solution was added. The above reaction was stirred for 2h under ambient temperature. Ammonium hydroxide was then added to the reaction solution and the temperature was raised to 55 °C and stirred overnight. After the reaction solution was cooled to room temperature, the crude product was obtained by filtration, and the crude product was recrystallized by ethanol to obtain compound **6** (1.92 g, 75 %) as a white solid.^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ (ppm) = 8.80-8.64 (m, 6H), 7.96-7.86 (m, 4H), 7.39 (m, 2H), 7.05 (d, J = 8.8 Hz, 2H), 4.06 (t, J = 6.5 Hz, 2H), 3.67 (t, J = 6.6 Hz, 2H), 1.91-1.77 (m, 3H), 1.60 (m, 2H), 1.51 (m, 2H), 1.37 (s, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 160.12, 156.33, 155.73, 149.03, 136.88, 130.35, 128.45, 123.77, 121.41, 118.19, 114.88, 68.07, 62.80, 32.79, 29.51, 29.37, 29.32, 29.22, 26.00, 25.79.

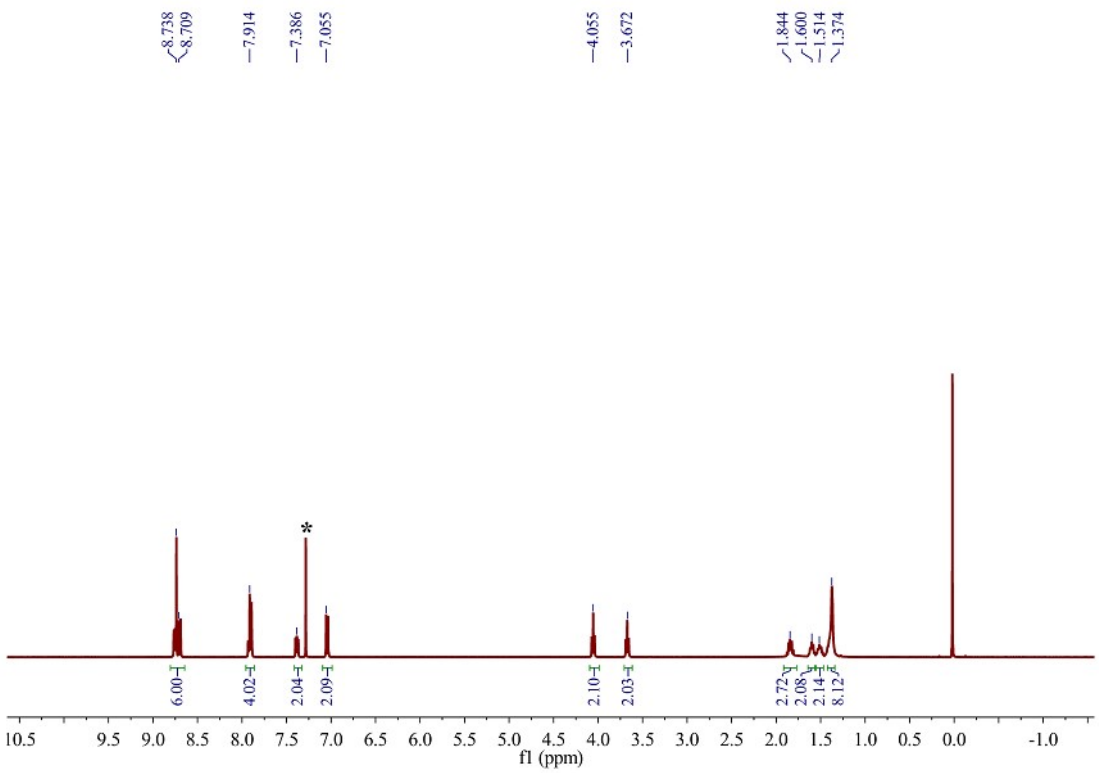


Fig. S20 The ^{1}H NMR of compound **6** (400 MHz, $CDCl_3$, 298 K).

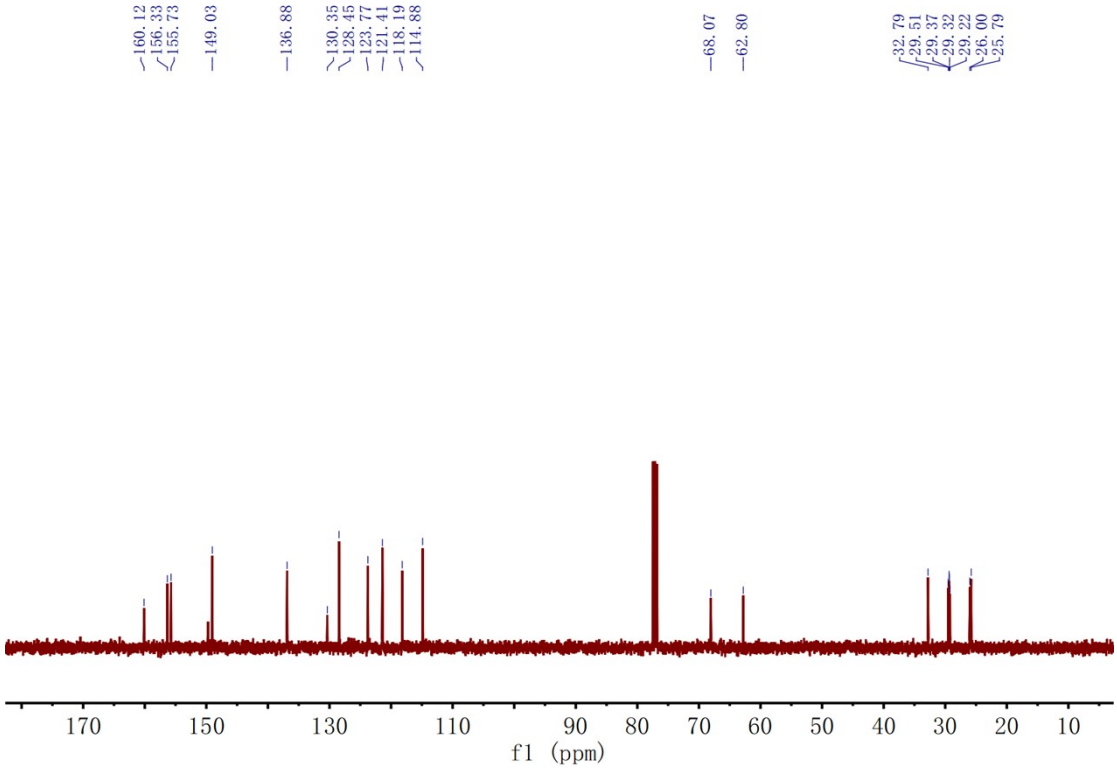


Fig. S21 The ^{13}C NMR of compound **6** (100 MHz, $CDCl_3$, 298 K).

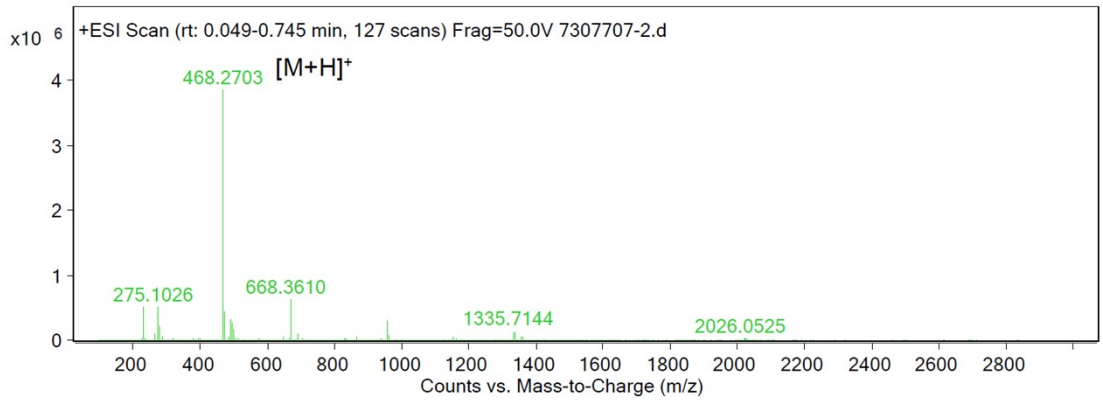


Fig. 22 The high-resolution ESI-MS of compound **6**.

Synthesis of the compound B3

In a 100 mL round–bottom flask, compound 6 (1.00 g, 0.6 mmol) and triethylamine were added. The reaction mixture was stirred for 0.5 h in dichloromethane at 0 °C, the 1,3,5-benzenetricarbonyl trichloride (0.16 g, 2.1 mmol) was then dropwise into the above solution. The reaction solution was stirred for another 12 h at ambient temperature. The solvent was evaporated under reduced pressure and the residue was partitioned between dichloromethane and water. The aqueous layer was further washed with dichloromethane. The organic phases were combined and dried over anhydrous Na_2SO_4. After the solvent was removed, the resulting residue was subjected to column chromatography (petroleum ether /ethyl acetate= 3:1), to give compound **B3** (0.46g, 50 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ (ppm) = 8.84 (s, 3H), 8.73 (d, *J* = 18.2 Hz, 18H), 7.97-7.86 (m, 12H), 7.39 (m, 6H), 7.00 (d, *J* = 8.8 Hz, 6H), 4.37 (t, *J* = 6.7 Hz, 6H), 4.00 (t, *J* = 6.5 Hz, 6H), 1.87-1.76 (m, 12H), 1.53-1.36 (m, 30H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 165.06, 160.05, 156.26, 155.65, 149.72, 148.94, 136.83, 134.36, 131.43, 130.34, 128.40, 123.68, 121.33, 118.19, 114.78, 68.00, 65.77, 29.24, 28.59, 25.93. MALDI-TOF-MS ($C_{99}H_{99}N_9O_9$): m/z calcd for $[M]^+$ = 1558.7599, found = 1558.7564, error = 2.2 ppm.

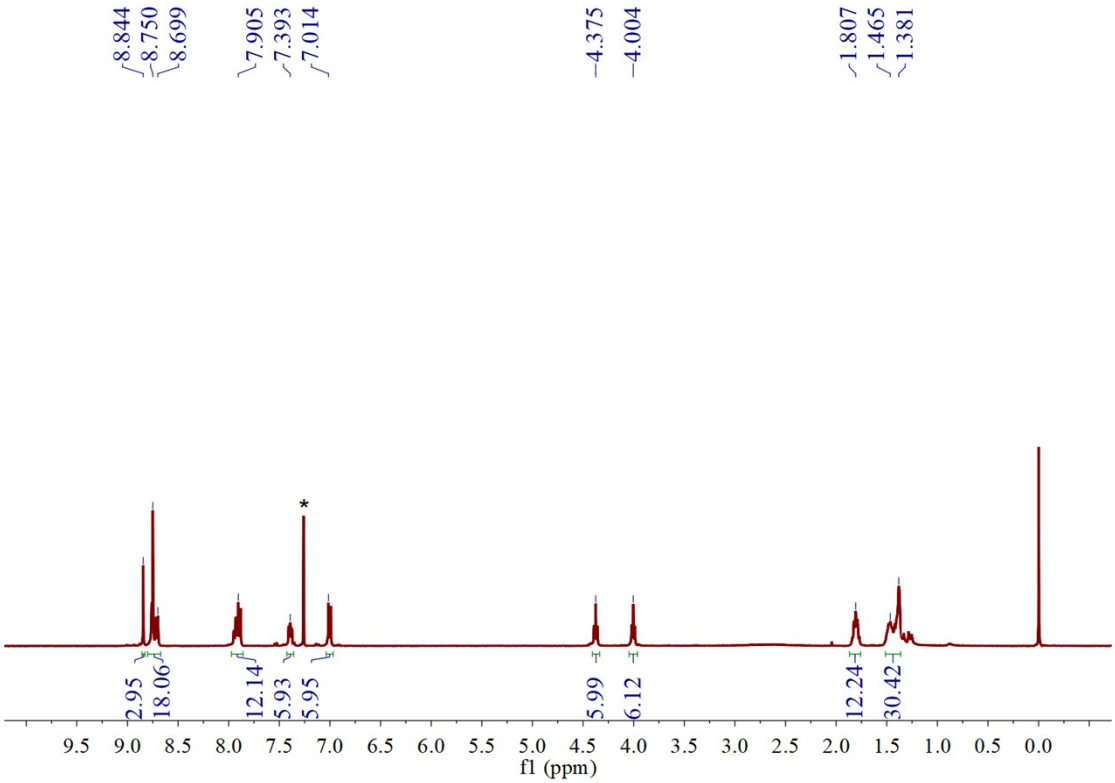


Fig. S23 The ^{1}H NMR of monomer **B3** (400 MHz, $CDCl_3$, 298 K)

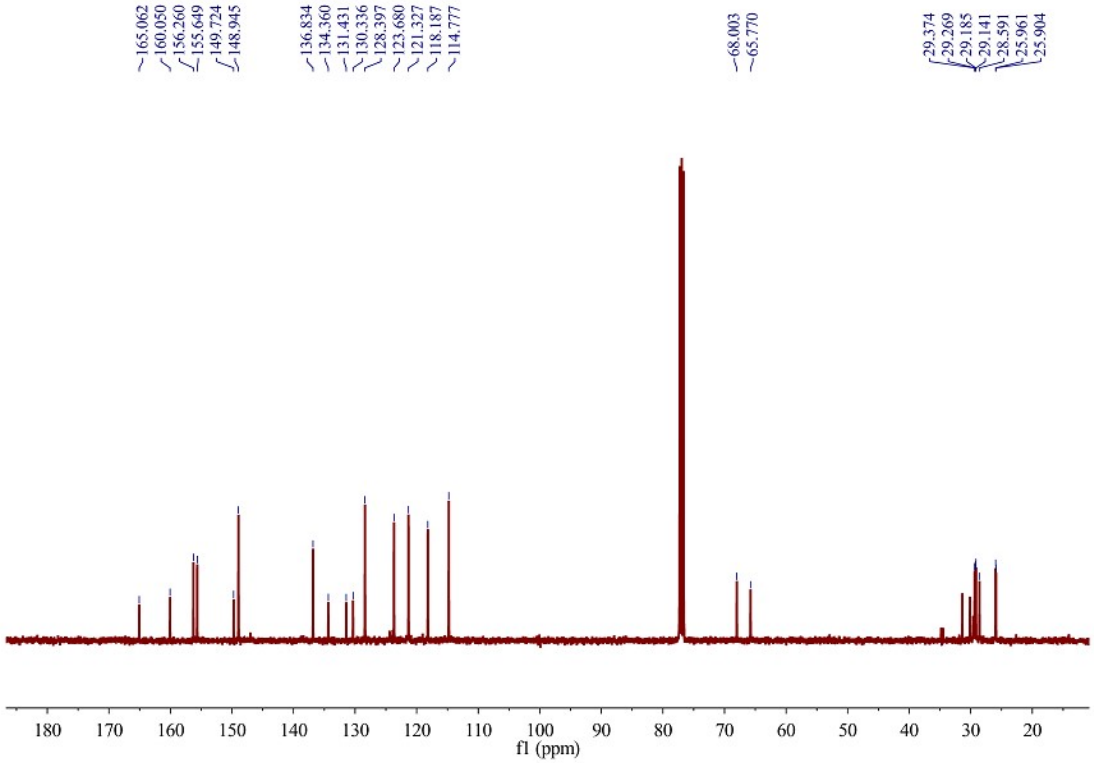


Fig. S24 The ^{13}C NMR of monomer **B3** (100 MHz, $CDCl_3$, 298 K)

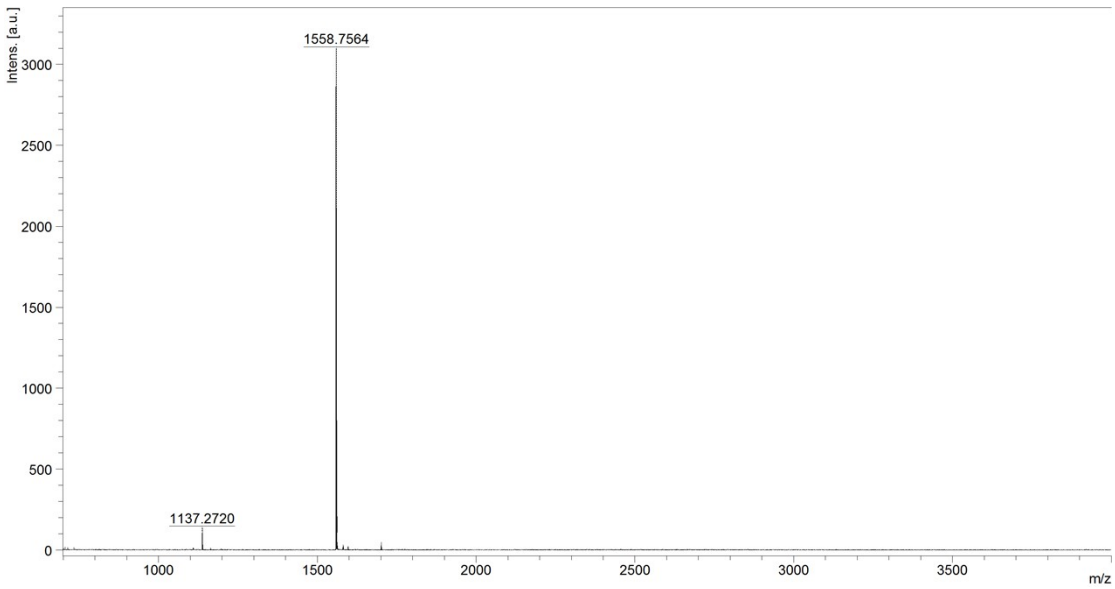


Fig. S25 The high-resolution MALDI-TOF-MS of monomer **B3**.

Synthesis of the compound M1

In a 100 mL round–bottom flask, compounds **9** (0.42 g, 0.6 mmol), 5-bromovaleronitrile (0.12 g, 0.7 mmol), Cs_2CO_3 (0.60 g, 1.2 mmol), and DMF (50ml) were added, the reaction mixture was stirred under inert atmosphere for 12 h at 80 °C. After the reaction mixture was cooled to ambient temperature, the solvent was evaporated under reduced pressure and the residue was partitioned between dichloromethane and water. The aqueous layer was further washed with dichloromethane. The organic phases were combined and dried over anhydrous Na_2SO_4. After the solvent was removed, the resulting residue was subjected to column chromatography (petroleum ether /dichloromethane= 3:1), to give compound **M1** (0.36g, 75 %) as a white solid.^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ (ppm) = 8.94 (d, *J* = 7.8 Hz, 2H), 8.68 (s, 2H), 8.58 (s, 2H), 8.16 (t, *J* = 7.7 Hz, 2H), 8.08 (d, *J* = 8.5 Hz, 4H), 7.74 (d, *J* = 8.3 Hz, 4H), 7.59 (m, 4H), 7.51-7.44 (m, 4H), 7.41-7.34 (m, 4H), 6.73 (d, *J* = 8.4 Hz, 2H), 3.88 (t, *J* = 5.6 Hz, 2H), 2.35 (t, *J* = 6.8 Hz, 2H), 1.81 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, 298K): δ (ppm) = 159.45, 157.60, 156.32, 155.63, 150.03, 137.20, 135.40, 131.45, 130.18, 128.57, 127.56, 127.12, 126.30, 125.83, 125.19, 120.19, 114.59, 66.56, 28.03, 22.34, 16.91. HR-ESI-MS ($C_{54}H_{38}N_4O$): m/z calcd for $[M+H]^+$ = 759.3006, found = 759.2984, error = 2.9 ppm.

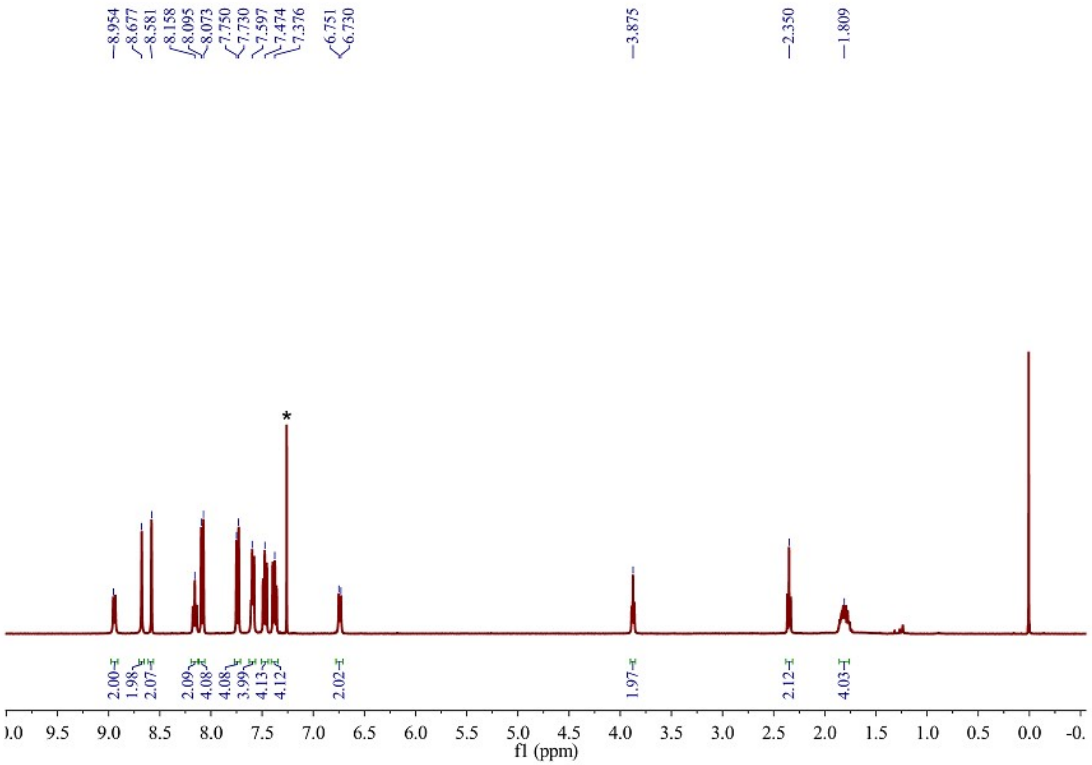


Fig. S26 The ^{1}H NMR of monomer **M1** (400 MHz, $CDCl_3$, 298 K).

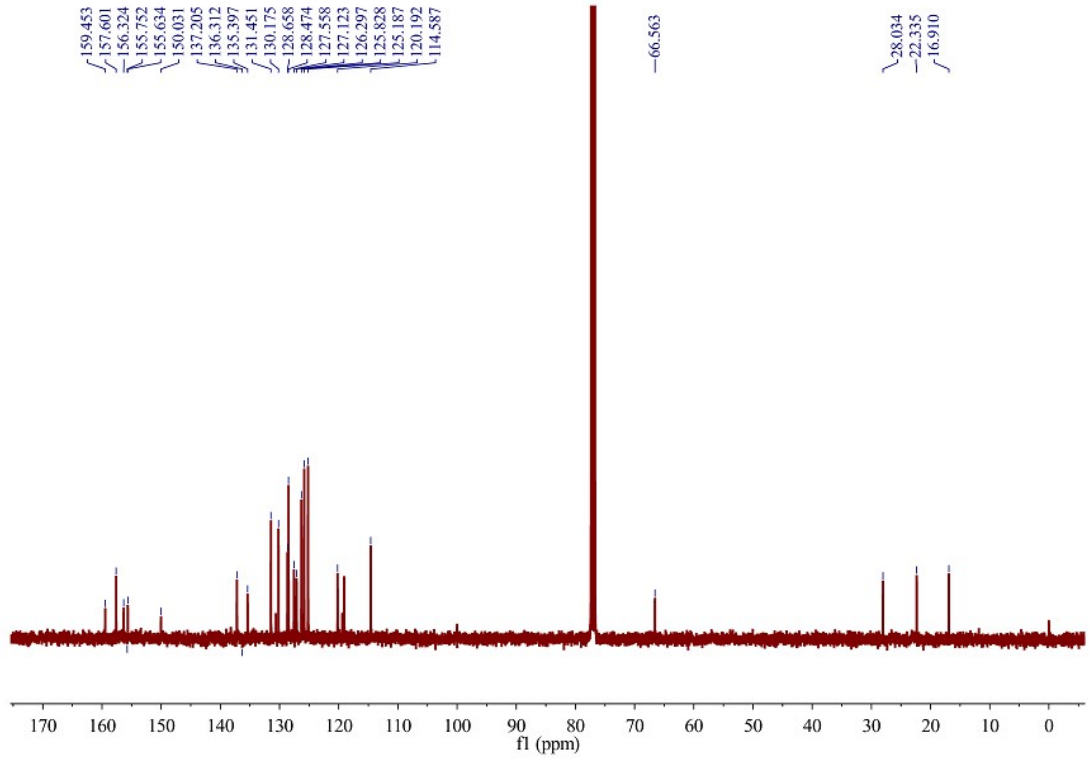


Fig. S27 The ^{13}C NMR of monomer **M1** (100 MHz, $CDCl_3$, 298 K).

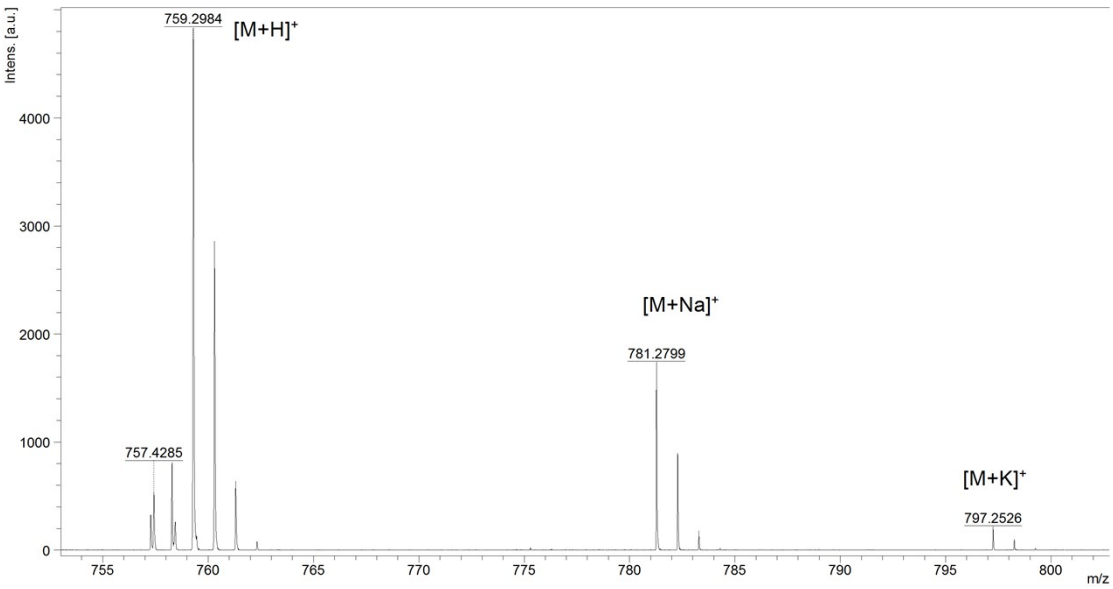


Fig. S28 The high-resolution MALDI-TOF-MS of monomer **M1** ($CHCl_3$, 298K).

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