A fluorescent controllable supramolecular crosslinked polymer constructed by complementary metal coordination interaction

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Supporting information

1. 2D ^1H-^1H COSY NMR spectrum

Fig. S1 Partial ^1H-^1H COSY NMR spectrum of M1+M2+Zn(OTf)$_2$ (400 MHz, CDCl$_3$-CD$_3$CN = 2/1, v/v, 298 K, 21mM), the peaks of the complexed protons were marked as c.

2. 2D NOESY NMR spectrum

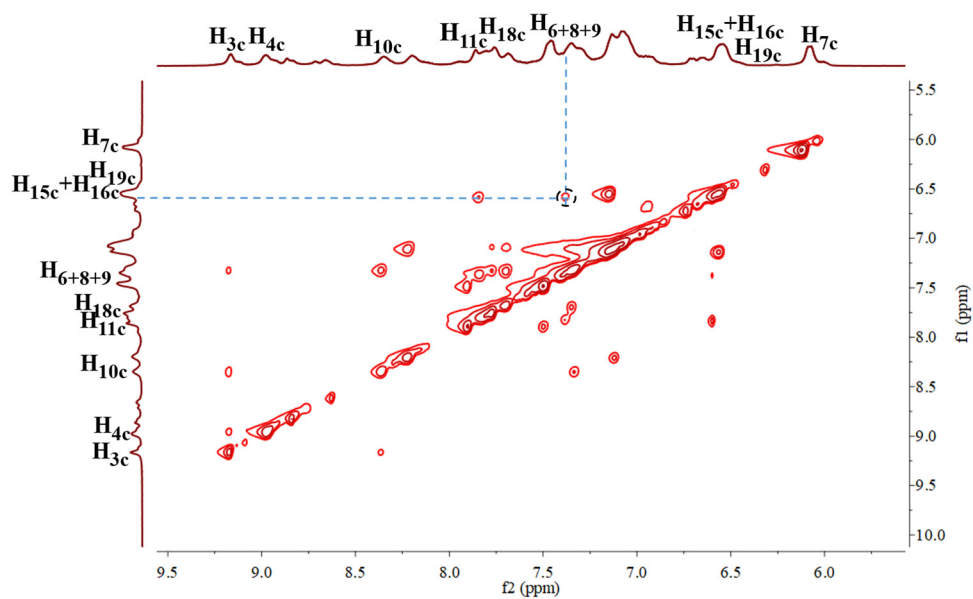**Fig. S2** Partial 2D NOESY NMR spectrum of M1+M2+Zn(OTf)$_2$ (400 MHz, CDCl$_3$-CD$_3$CN = 2/1, v/v, 298 K, 21mM), the peaks of the complexed protons were marked as c
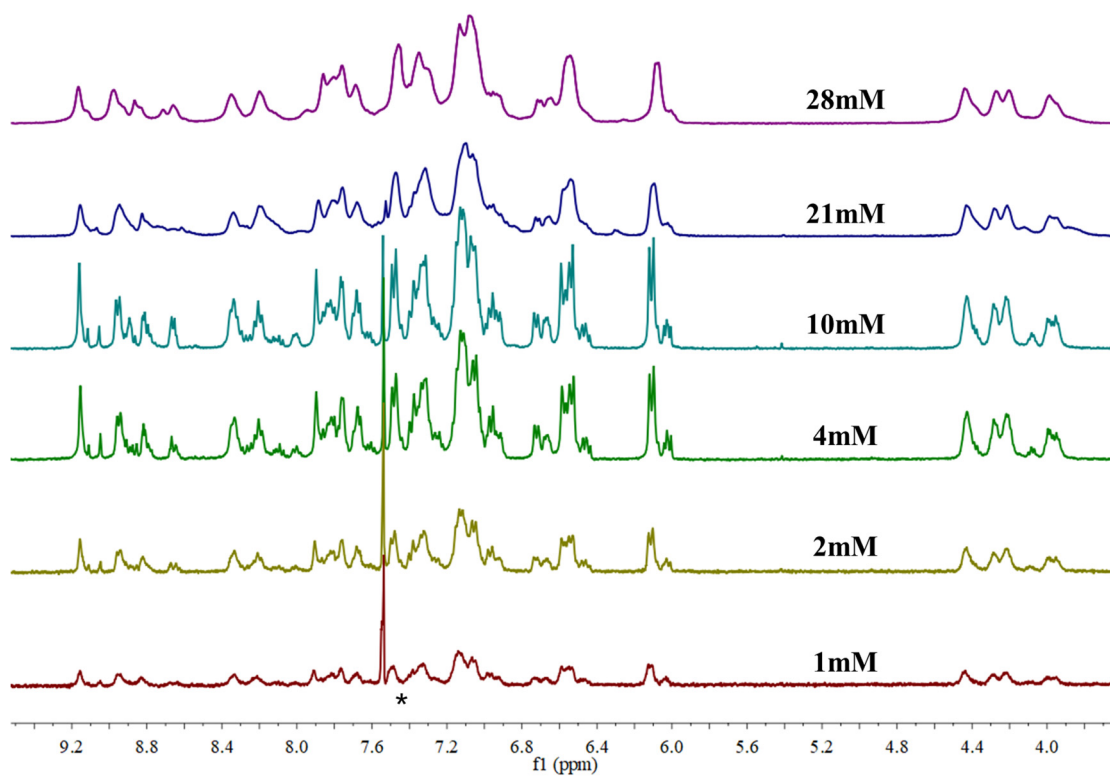
3. Concentration-dependent ^{1}H NMR spectrum

Fig. S3 ^{1}H NMR spectra (400 MHz, CDCl$_3$-CD$_3$CN = 2/1, v/v, 298 K) of M1+M2 +Zn(OTf)$_2$ at different concentrations (a) 1 mM, (b) 2 mM, (c) 4 mM, (d) 10 mM, (e) 21 mM, (f) 28mM.
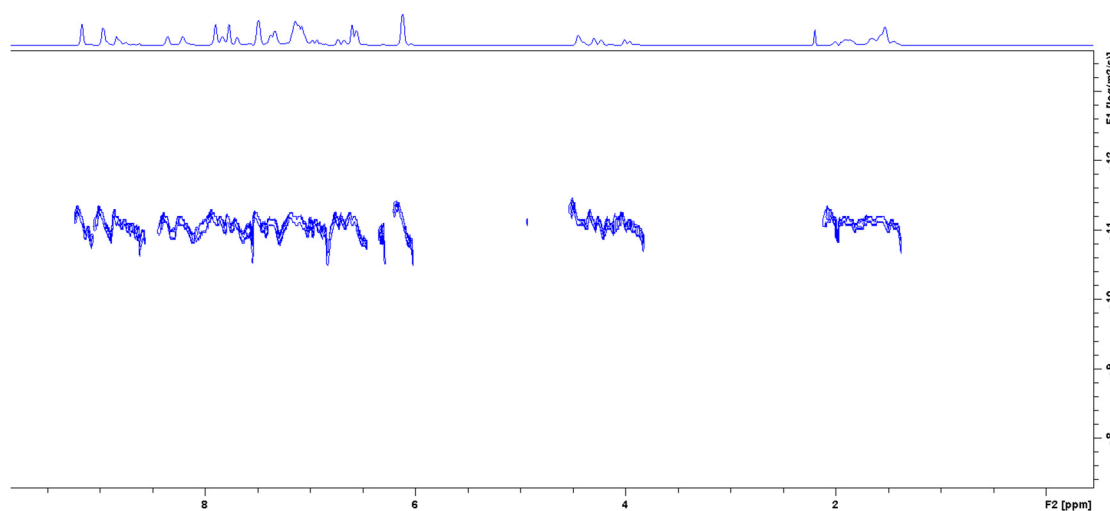
4. 2D DOSY NMR spectrum

Fig. S4 Representative DOSY NMR spectrum (600 MHz, CDCl$_3$-CD$_3$CN = 2/1, v/v, 298 K) of M1+M2+Zn(OTf)$_2$, the concentration of M1 is 21 mM.

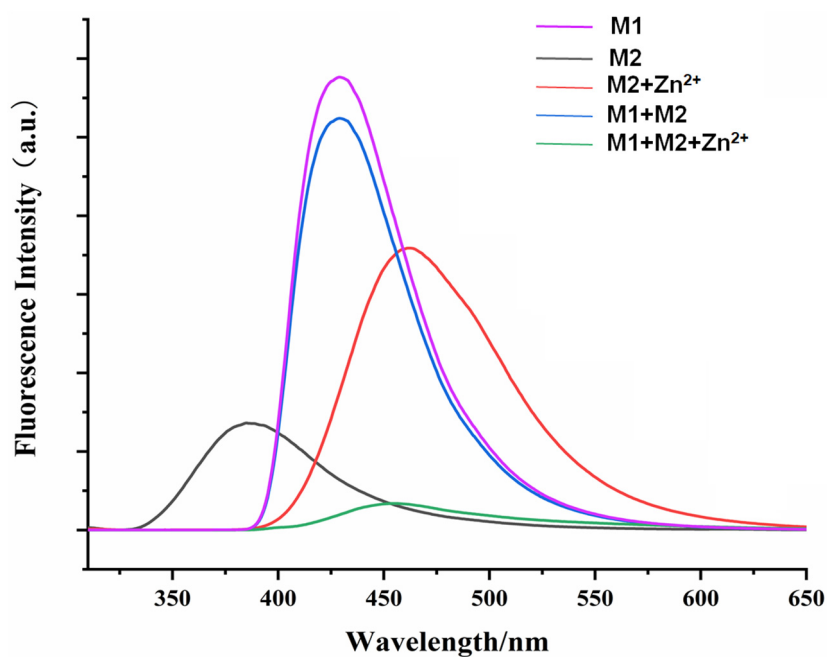# 5. Fluorescence Emission spectra

Fig. S5 Fluorescence emission spectra of 0.02mM M1, M2, M1+M2, M2+Zn(OTf)$_2$ and M1+M2+Zn(OTf)$_2$ in CDCl$_3$-CD$_3$CN (2:1, v/v).
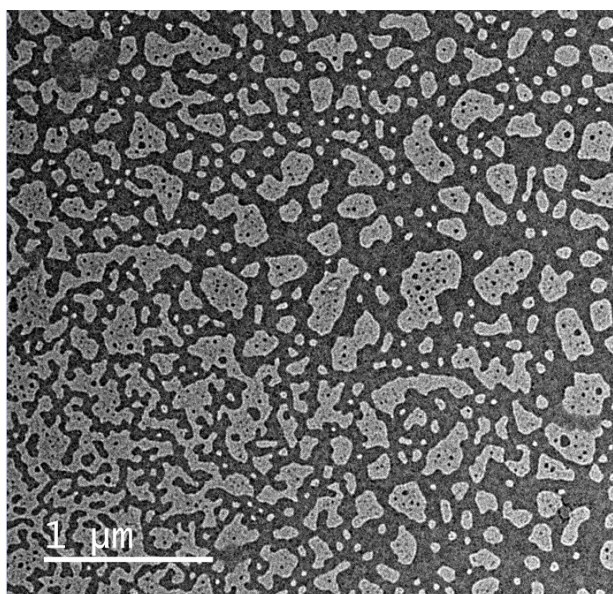
6. TEM photograph of SCP

Fig. S6 The representative TEM image of SCP prepared at a 21 mM concentration.

7. The discussion of tpy-Zn^{2+}-tey binding constant

To determine the association constant of tpy-Zn^{2+}-tey, the UV-Vis experiment (Job plot method) was conducted according to the literature method [S1]. Model compounds 1 and 2 were chosen as the ligands. A series of samples were prepared and the total molar concentration of ligands ([1]+[2])/2) and zinc ion was maintained at 2×10^{-5}M in each sample and only the ratios of zinc ion and ligands were altered. The job plot was conducted by varying the mole fractions of the ligands ([1]+[2])/2) and zinc ion. The concentration: [1]+[2])/2 + [Zn(OTf)$_2$] = 2×10^{-5}M. The absorbance intensity at 412 nm was plotted (Fig. S7) against the mole fraction of Zn(OTf)$_2$. The Job plot (Fig. S7) indicated a 1:1:1 binding among Zn^{2+}, 1, and 2.
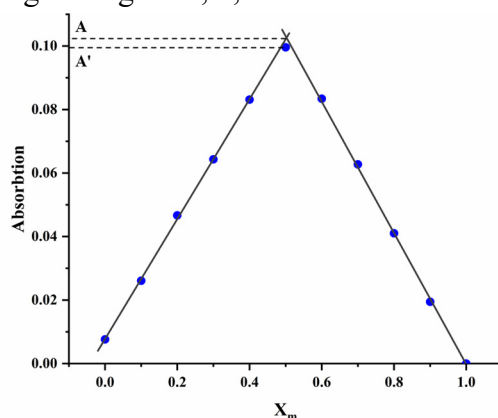

Fig. S7 Job plot of the complex formed among zinc ion, 1 (ligand) and 2 (ligand) showing a 1:1:1 stoichiometry by plotting the absorbance intensity at 412 nm against the mole fraction of zinc ion. Concentration: [1]=[2], [1]+[2])/2 + [Zn(OTf)$_2$] = 2×10^{-5}M. (chloroform versus acetonitrile=2:1, v/v, 298K).

Furthermore, the data of job plot was divided into two groups around X_m = 0.5. When $Xm \leq 0.5$, the fitting equation is A = 0.18878 X_m + 0.00778. When $X_m \geq 0.5$, the fitting equation is A = -0.20672X_m + 0.20648. The intersection point of the two fitting curves is taken (X_m = 0.5024, A = 0.1031), and the experimental value is X_m = 0.5000, A' = 0.0996. The dissociation degree of complex [Zn12](OTf)$_2$ was calculated from Eq. 1. According to the formula, the dissociation degree(α) of complex [Zn12](OTf)$_2$ was calculated to be 0.034.

α= (A - A') /A, **(Eq. 1)**

The binding constant K was then calculated to be 8.35×10^7 M^{-1} based on Eq. 2.

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

$$\mathbf{1} + [Zn2](OTf)_2 \rightleftharpoons [Zn\mathbf{12}](OTf)_2$$
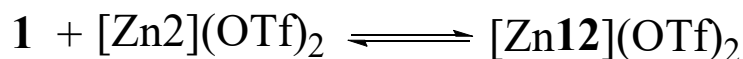
$$K = \frac{[\text{Zn}\mathbf{12}](\text{OTf})_2}{[\mathbf{1}]\,[\text{Zn2}](\text{OTf})_2)} = \frac{1-\alpha}{C\alpha^2} \quad \textbf{(Eq.2)}$$

Where C is the total concentration of the complex [Zn12](OTf)$_2$ and α is the degree of dissociation of complex [Zn12](OTf)$_2$ when X_m value is 0.5, with the hypothesis that the ligands and zinc ion only form the complex [Zn12](OTf)$_2$. The C is 1×10^{-5} M and the α is 0.034 when Xm is 0.5.

8. Synthesis of the intermediates and monomers
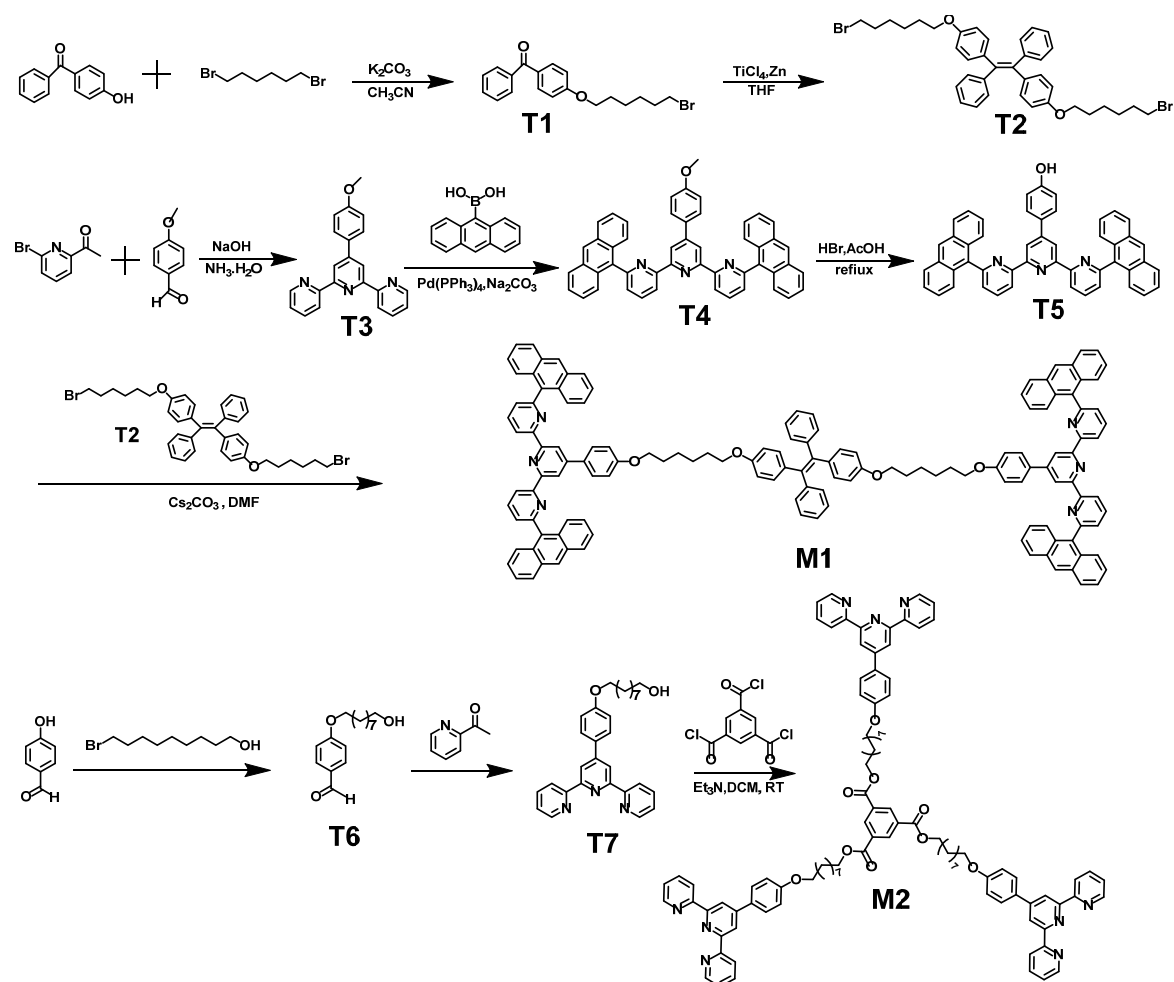
Scheme S1. Synthetic route of monomers M1 and M2.

Synthesis of Compound T1

A solution of compound 4-hydroxybenzophenone (1.50 g, 7.57 mmol), 1.6-dibromohexane (3.69 g, 15.17 mmol), K$_2$CO$_3$(3.14 g, 22.70 mmol) in CH$_3$CN (180 mL) was stirred for 14 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 (200 mL) and water (100 mL). The aqueous layer was further washed with dichloromethane (2 × 30 mL). 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 (PE/CH_2Cl_2 = 1:1, v/v), to give compound 1 (1.94 g, 80.00 %) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.84-7.80 (m, 2H), 7.77-7.74 (m, 2H), 7.59-7.54 (m, 1H), 7.49-7.45 (m, 2H), 4.05 (t, J = 6.4 Hz, 2H), 3.43 (t, J = 6.8 Hz, 2H), 1.94-1.80 (m, 4H), 1.55-1.51 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 195.43, 162.77, 138.33, 132.56, 131.87, 129.96, 129.71, 128.20, 114.03, 68.01, 33.81, 32.65, 28.95, 27.89, 25.25. HR-ESI-MS ($C_{19}H_{21}BrO_2$): m/z calcd for [M+H]$^+$ = 361.0803, found = 361.0812, error = 2.49 ppm.
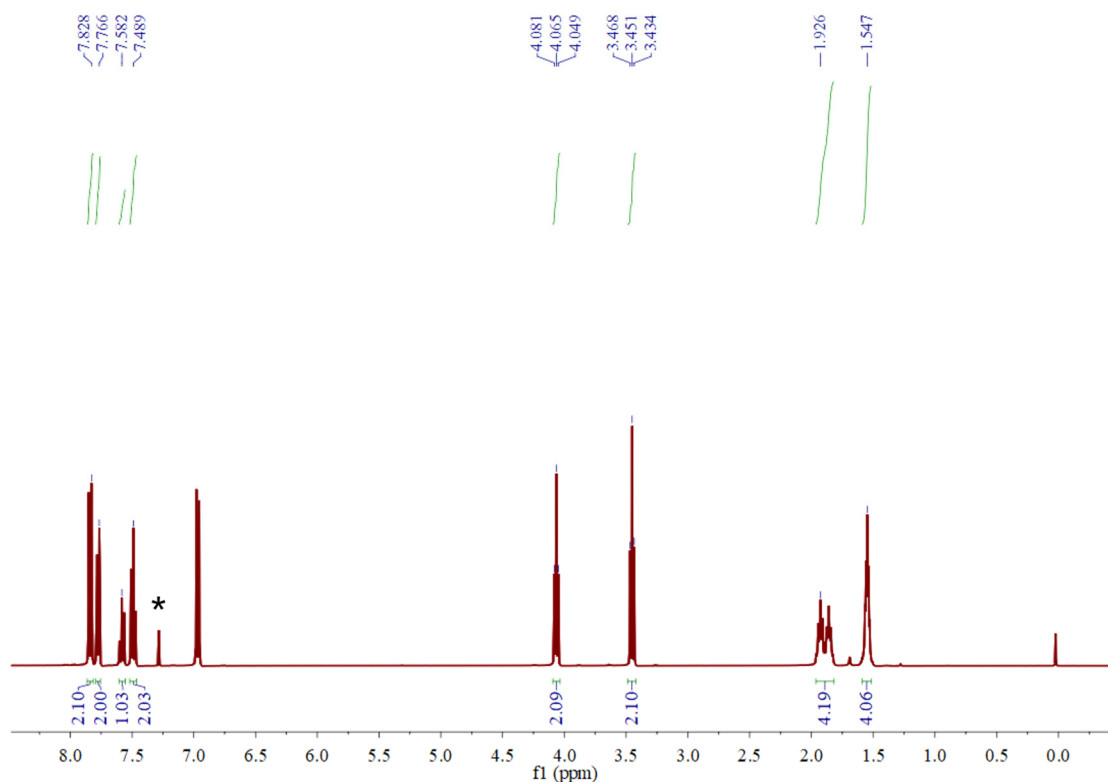

Fig. S8 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of compound **T1**
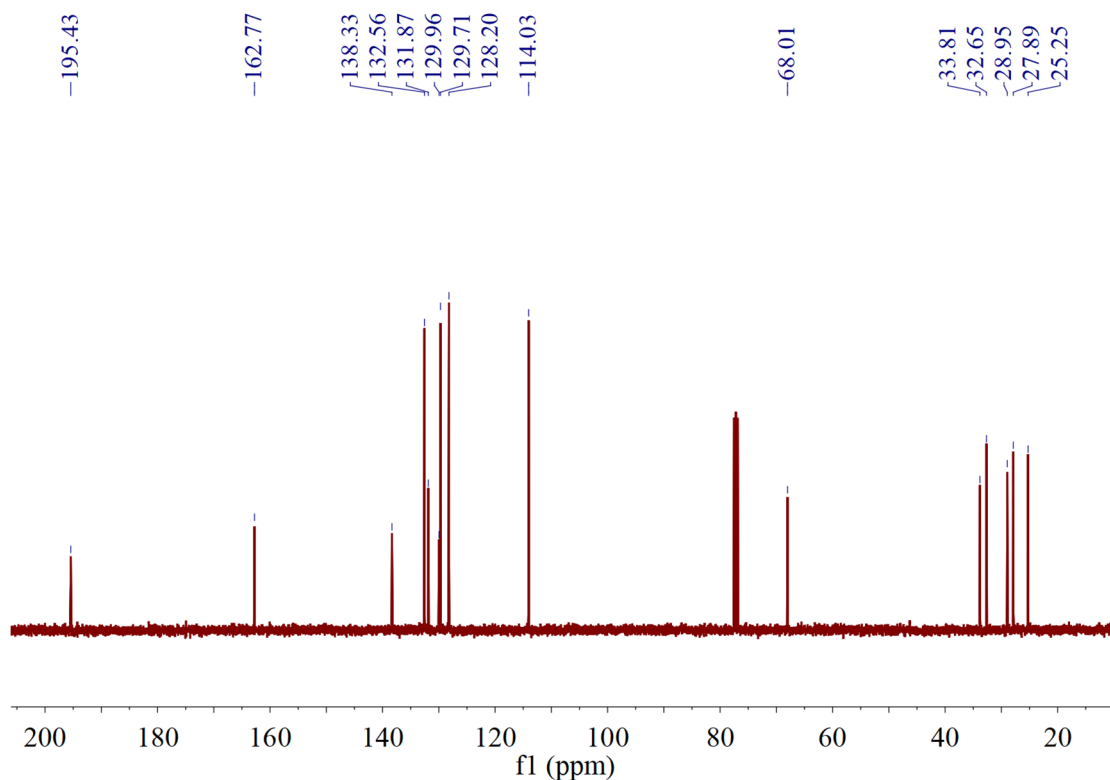
Fig. S9 ^{13}C NMR spectrum (100 MHz, CDCl$_3$, room temperature) of compound **T1**
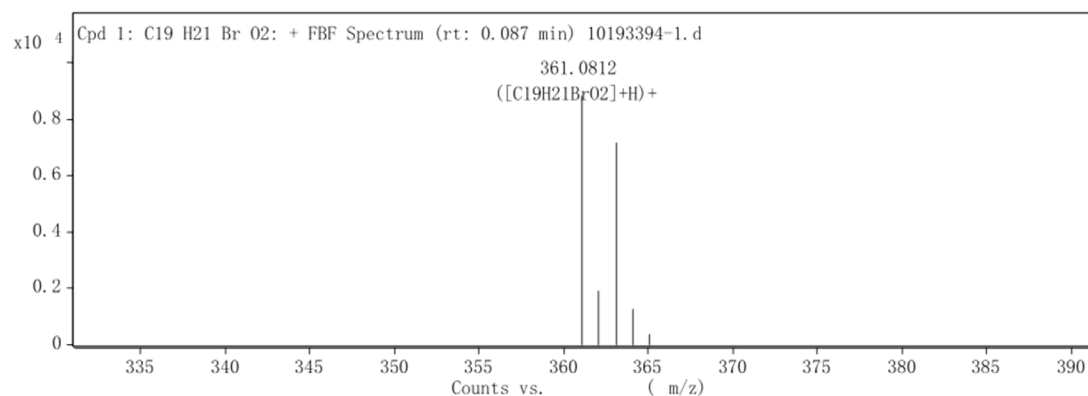

Fig. S10 Electrospray ionization mass spectrum of compound **T1**

Synthesis of Compound T2

To a solution of compound T1 (2.00 g, 5.54 mmol) and zinc powder (2.17 g, 33.22 mmol) in THF (120 mL) was added dropwise TiCl$_4$ (3.15 g, 16.61 mmol). After the reaction mixture was refluxed for 12 h, the reaction mixture was cooled to room temperature and filtered. The solvent was evaporated under vacuum and the crude product was purified by column chromatography using dichloromethane/petroleum ether (v/v = 5:1) as the eluent. Finally, compound T2 was obtained as a white solid (2.48g, 65.05%). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.17-7.03 (m, 10H), 6.99-6.91 (m, 4H), 6.70-6.61 (m, 4H), 3.94-3.89 (m, 4H), 3.47-3.43 (m, 4H), 1.98-1.86 (m, 4H), 1.84-1.74 (m,

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4H), 1.56-1.46 (m, 8H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 157.49, 144.36, 139.69, 136.35, 132.59, 131.45, 127.66, 126.21, 113.64, 67.54, 33.87, 32.74, 29.18, 28.00, 25.38. HR-ESI-MS (C$_{38}$H$_{42}$Br$_2$O$_2$): m/z calcd for [M+H]$^+$ =691.56800, found = 691.15859, error = 5.92 ppm.
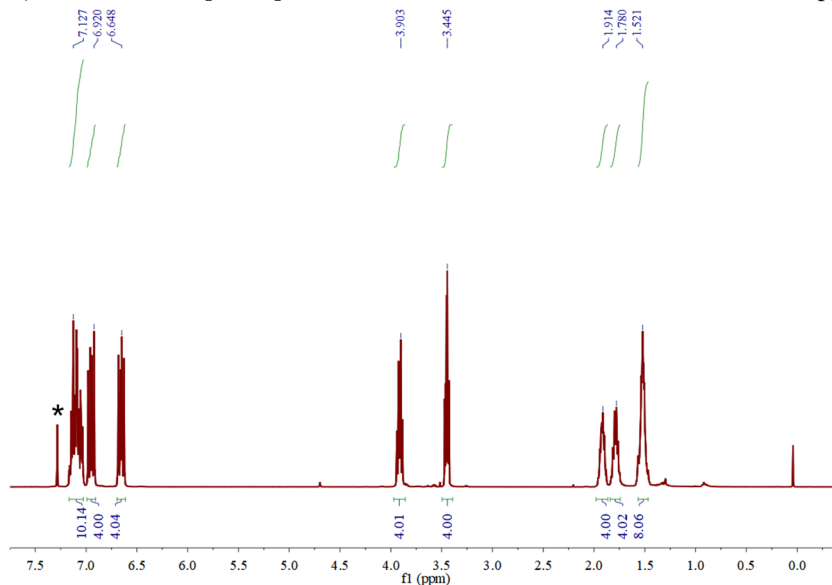

Fig. S11 ^{1}H NMR spectrum (400 MHz, CDCl$_3$, room temperature) of compound **T2**
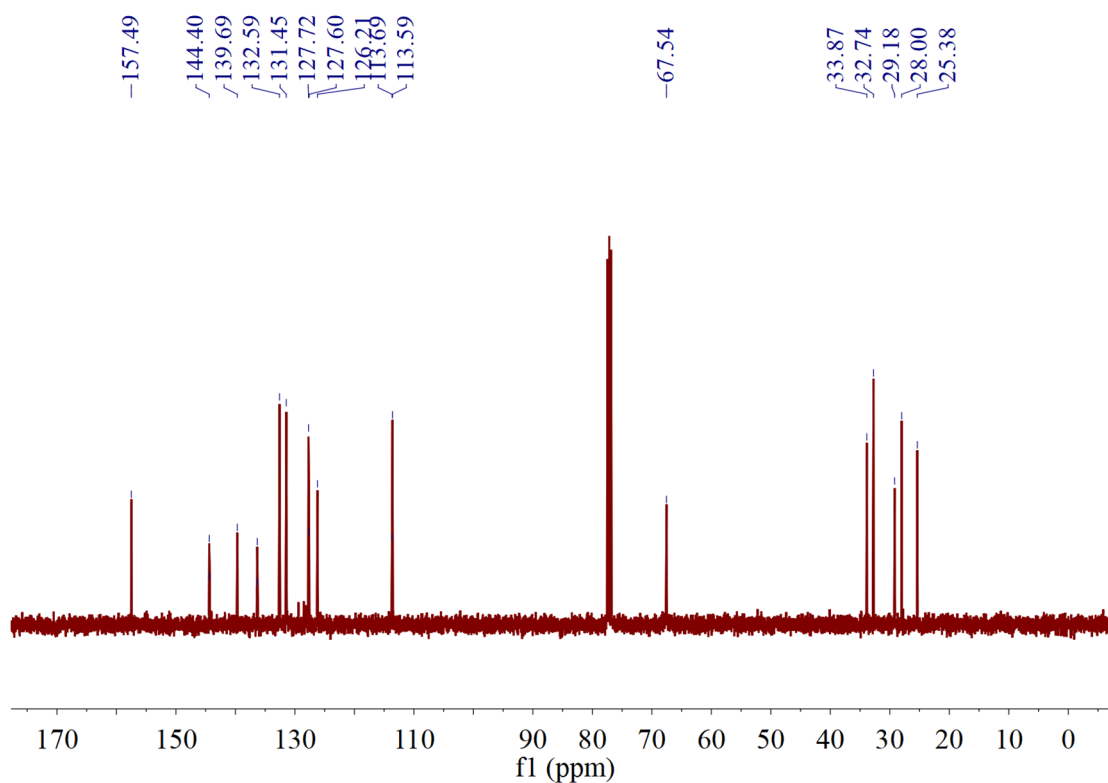

Fig. S12 ^{13}C NMR spectrum (100 MHz, CDCl$_3$, room temperature) of compound **T2**
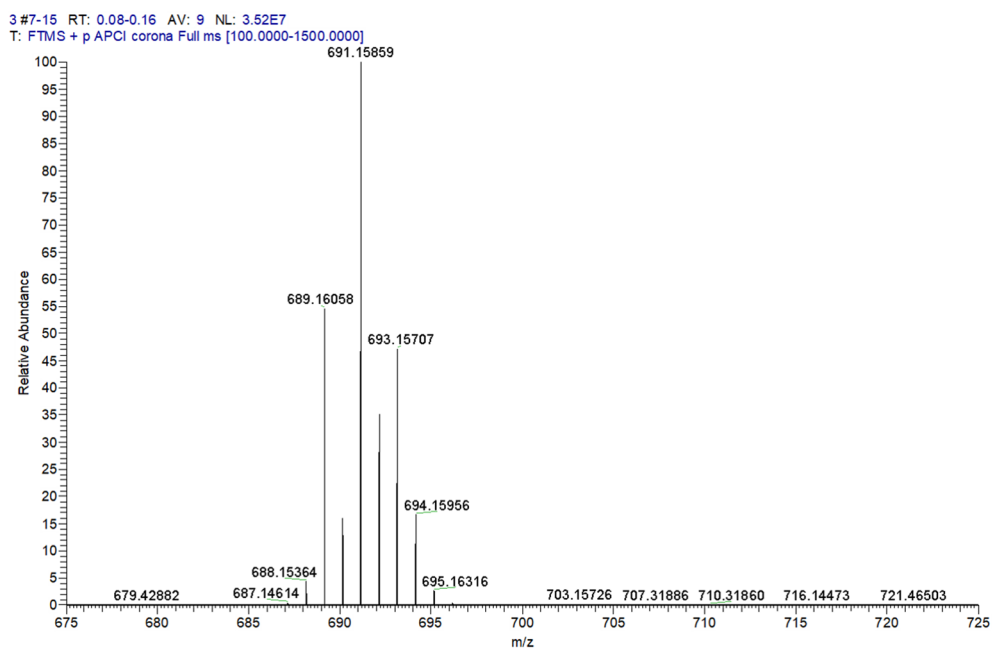
Fig. S13 Electrospray ionization mass spectrum of compound **T2**

Synthesis of Compound M1

A solution of T2 (0.85 g, 1.23 mmol), T5 (2.00 g, 2.95 mmol), and NaH with mineral oil (0.30 g, 12.51 mmol) in DMF (55 mL) was stirred for 24 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 (200 mL) and water (100 mL). The aqueous layer was further washed with dichloromethane (3 × 40 mL). 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 / petroleum ether = 4:1), to give M1 (0.95g, 41.02 %) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.93 (t, J = 8.7 Hz, 4H), 8.67 (d, J = 6.9 Hz, 4H), 8.56 (d, J = 14.4 Hz, 4H), 8.17-8.03 (m, 12H), 7.74 (t, J = 9.4 Hz, 8H), 7.62-7.51 (m, 8H), 7.50-7.41 (m, 8H), 7.41-7.32 (m, 8H), 7.09-7.00 (m, 10H), 6.76-6.67 (m , 4H), 6.75-6.69 (m, 4H), 6.58-6.55 (m, 4H), 3.85-3.73 (m, 8H), 1.73-1.58 (m, 8H), 1.46-1.31 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): 159.85, 157.68,157.59, 156.88, 156.06, 149.82, 144.49, 139.75, 137.16, 136.31,135.73, 132.64, 131.56, 130.30, 128.59,128.47,128.42, 127.79, 127.68, 127.61, 127.02, 126.46, 126.28, 125.82 , 125.30, 120.11, 118.94 , 114.68, 113.66, 67.75, 29.26,29.19,29.11,29.06, 25.89,25.84,25.77. HR-ESI-MS ($C_{136}H_{102}N_6O_4$): m/z calcd for $[M+H]^+$ = 1885.8137, found = 1885.8110, error = 1.43 ppm.
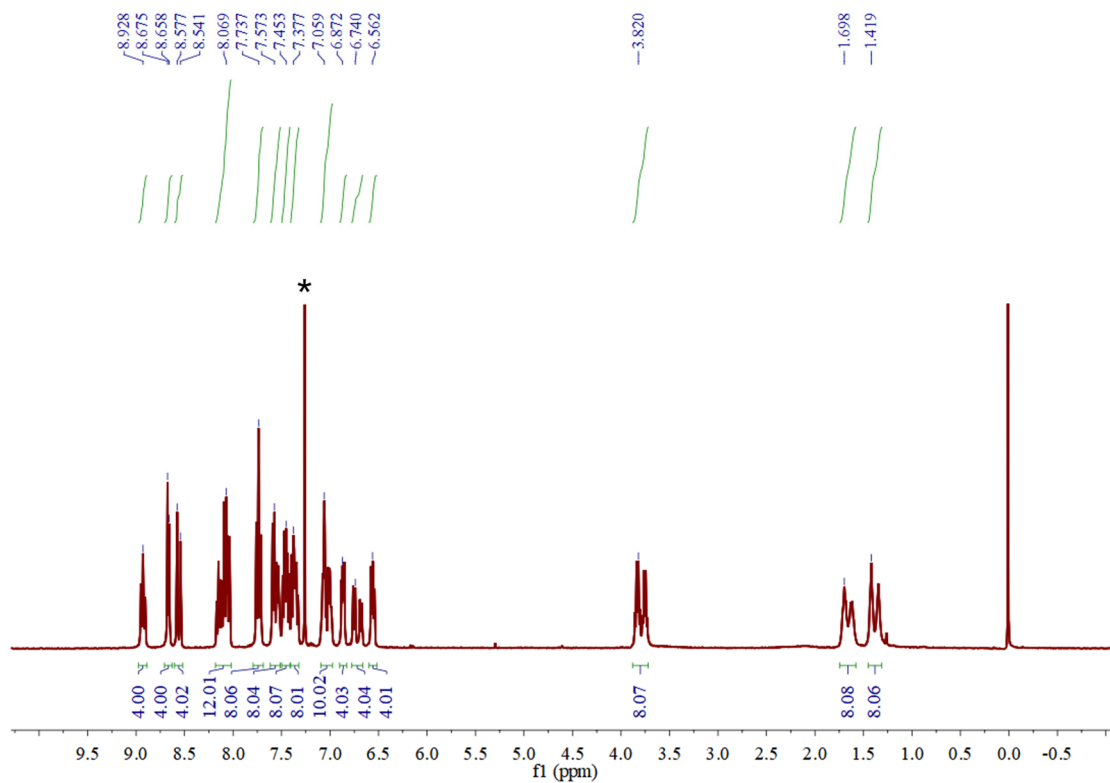
Fig. S14 ^{1}H NMR spectrum (400 MHz, CDCl$_3$, room temperature) of compound **M1**
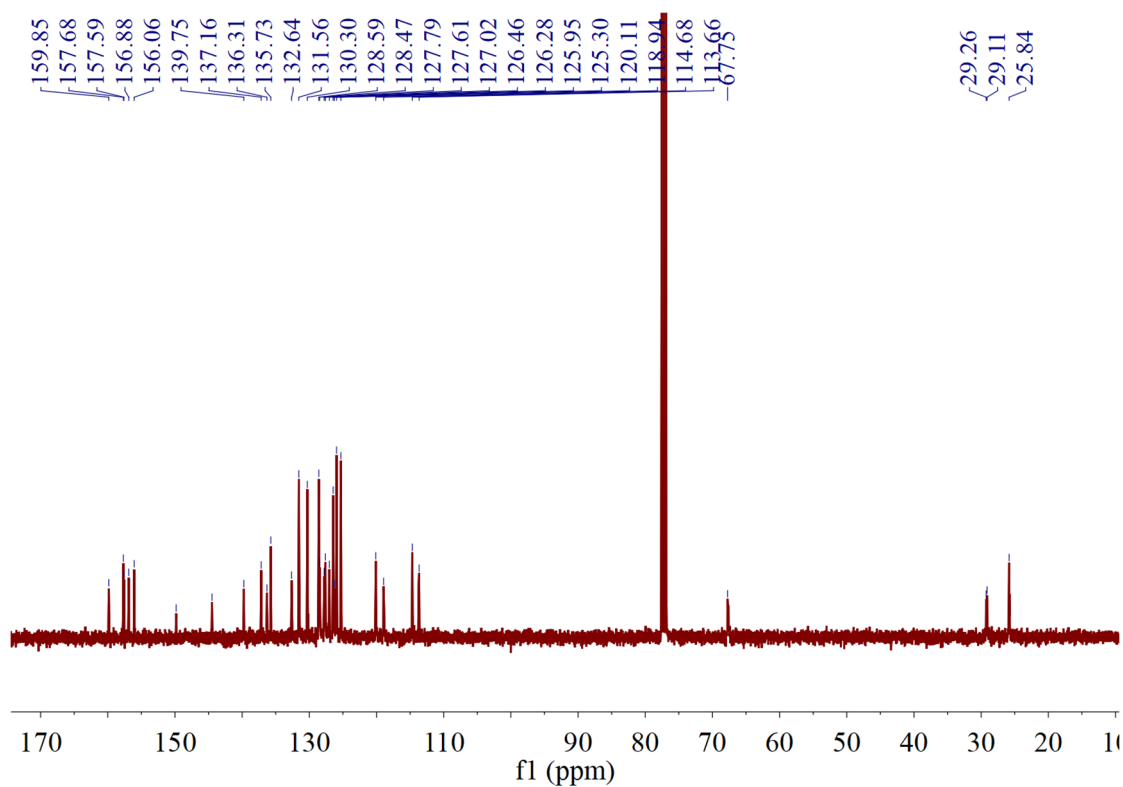

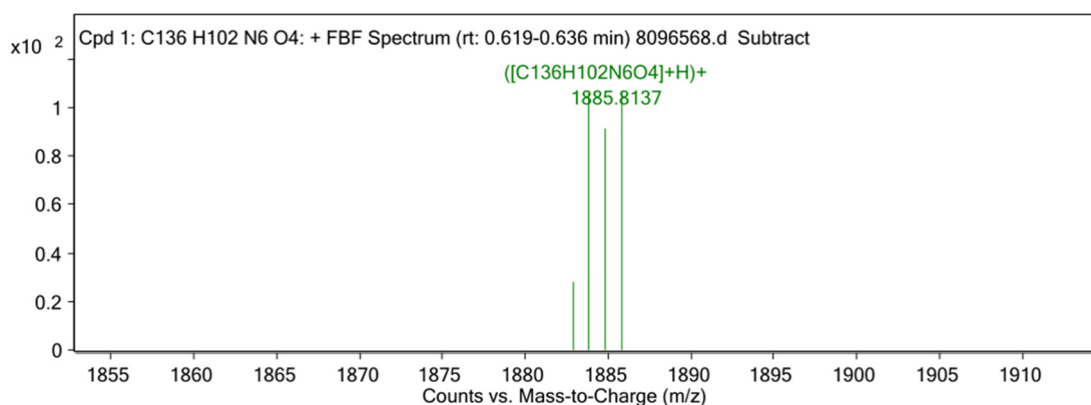**Fig. S15** ^{13}C NMR spectrum (100 MHz, CDCl$_3$, room temperature) of compound **M1**

Fig. S16 Electrospray ionization mass spectrum of compound **M1**

Synthesis of monomer M2

Compound T7 (2.00 g, 1.20 mmol), triethylamine (0.37 g, 3.65 mmol) and 50ml dichloromethane were added into a 150 mL round–bottom flask. The solution was stirred for 0.5 h at 0 °C, the 1,3,5-benzenetricarbonyl trichloride (0.32 g, 4.20 mmol) was then added dropwise into the above solution. The reaction mixture was stirred for another 12 h at ambient temperature. After the solvent was evaporated under reduced pressure, the residue was partitioned between dichloromethane and water. The aqueous layer was further washed with dichloromethane. The organic phase was combined and dried using anhydrous Na_2SO_4. After the solvent was removed, the resulting residue was subjected to column chromatography (petroleum ether /ethyl acetate= 3:1), to afford compound **M2** (0.98g, 51 %) as a white solid. ^1H NMR (400 MHz, CDCl$_3$, 298K): δ (ppm) = 8.87 (s, 3H), 8.75 (d, J = 4.0 Hz, 6H), 8.72 (s, 6H), 8.68 (d, 8.0Hz, 6H), 7.97-7.84 (m, 12H), 7.36 (m, 6H), 7.03 (d, J = 8.8 Hz, 6H), 4.39 (t, J = 6.7 Hz, 6H), 4.02 (t, J = 6.5 Hz, 6H), 1.87-1.78 (m, 12H), 1.53-1.36 (m, 30H). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) = 165.52, 160.51, 156.71, 156.10, 150.18, 149.40, 137.29, 134.81, 131.88, 130.79, 128.85, 124.13, 121.78, 118.64, 115.23, 68.46, 66.22, 29.83, 29.72, 29.64, 29.59, 29.04, 26.41, 26.36. ESI-MS (C$_{99}$H$_{99}$N$_9$O$_9$): m/z calcd for $[M]^+$ = 1558.7599, found = 1558.7623, error = 1.6 ppm.
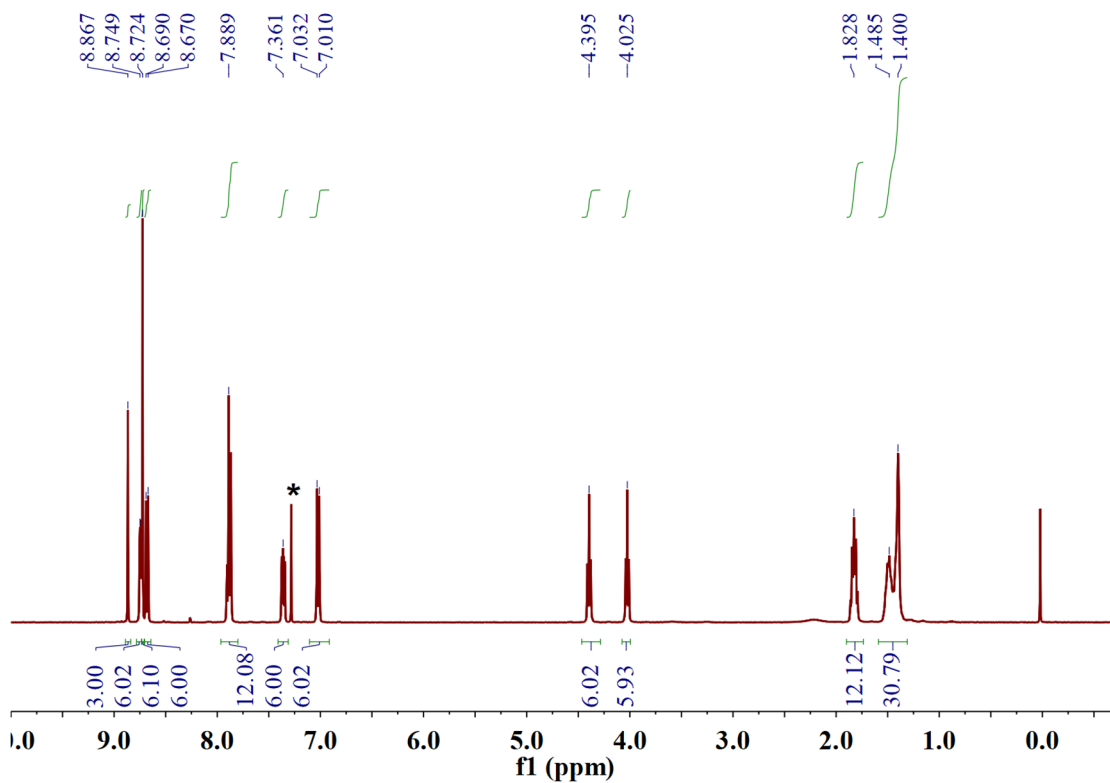
Fig. S17 The ^{1}H NMR of monomer **M2** (400 MHz, CDCl$_3$, 298 K)
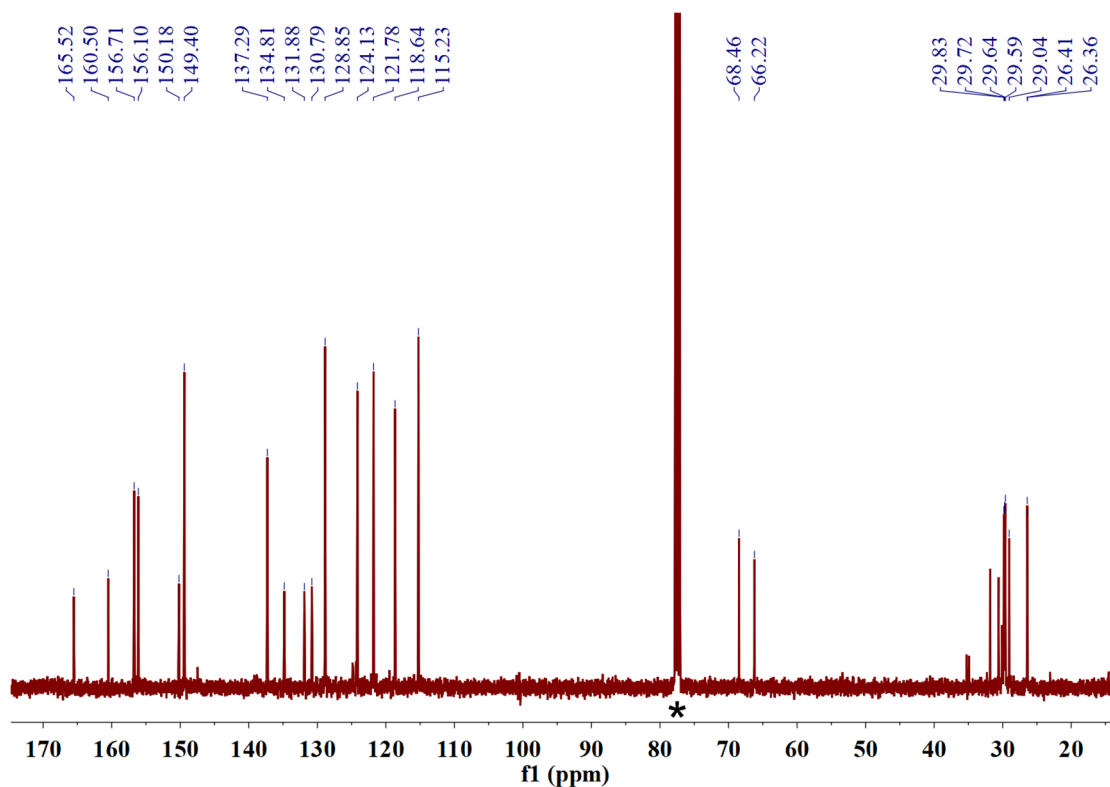

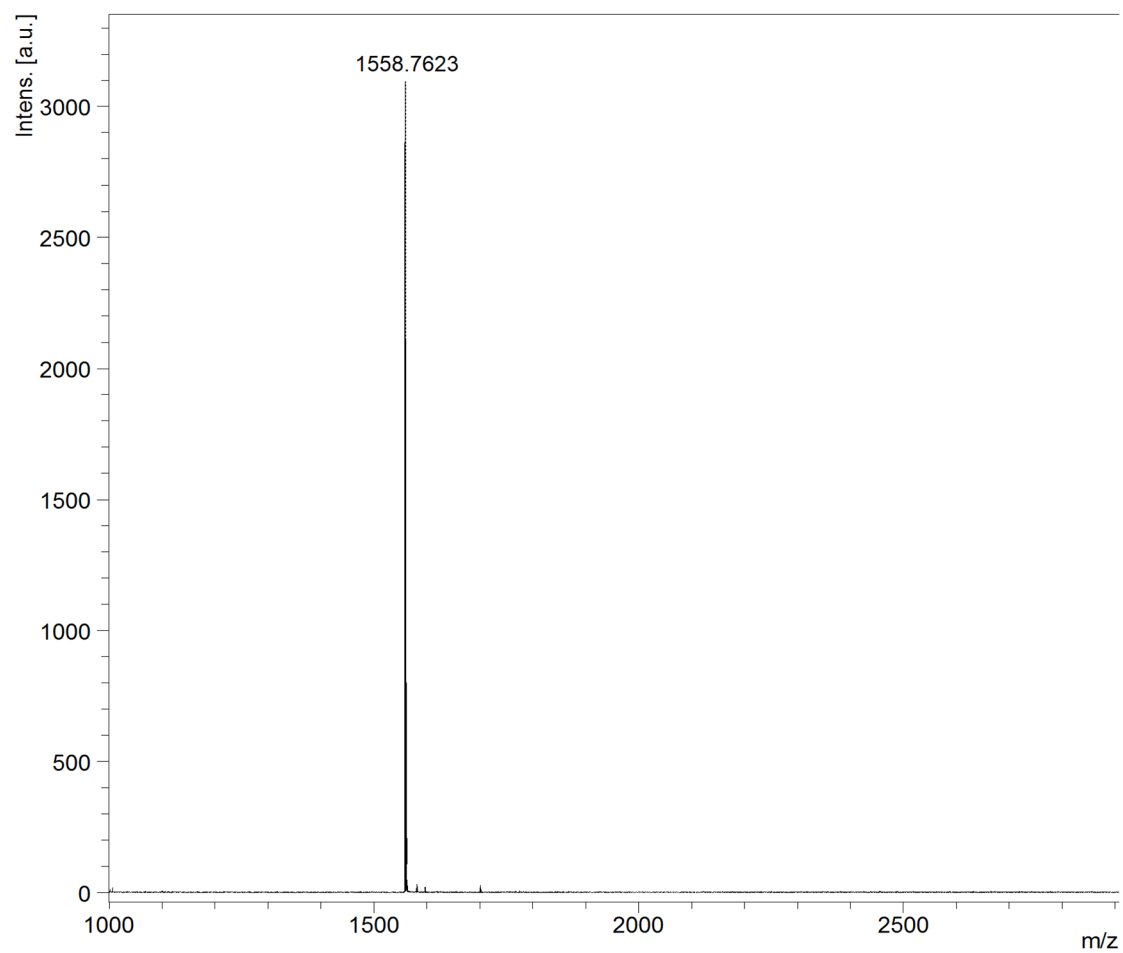**Fig. S18** The ^{13}C NMR of monomer **M2** (100 MHz, CDCl$_3$, 298 K)

Fig. S19 The high-resolution ESI-MS of monomer **M2**.

Reference:

S1. W. Likussar, D. F. Boltz. *Anal. Chem.* **1971**, 43, 10, 1265-1272.