Hierarchical Supramolecular Assembly based on Metal Coordination of Asymmetric Ligand Pairs and Host-Guest Recognition

Hui Li,*[a] Yan Dong, [a] RiQiang Li,[a] Yan Zhang,[a] Shengyong Liu,[a] and Wei Tian*[b]

[a] Jiangxi Province Key Laboratory of Functional Crystalline Materials Chemistry, School of Chemistry and Chemical Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, Jiangxi Province, P.R. China.

[b] Shaanxi Key Laboratory of Macromolecular Science and Technology, School of Science, Northwestern Polytechnical University, Xi'an 710072, P. R. China.

* E-mail: lh@jxust.edu.cn (H. Li.)

* E-mail: happytw_3000@nwpu.edu.cn (W. Tian)

Supporting information

1. Materials and methods

The reagents and solvents were either used as purchased or synthesized using laboratory methods. Column chromatography was performed on silica gel (200-300 mesh). All reactions were carried out in atmosphere unless noted. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer. DOSY NMR experiments were performed on a Bruker AVANCE III 500 MHz spectrometer. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were obtained on a Bruker Esquire 3000 plus mass spectrometer equipped with an ESI interface and ion trap analyzer. Viscosity measurements were carried out with Ubbelohde micro viscometers (0.40 mm inner diameter) at 298 K in chloroform/acetonitrile (2/1, v/v). The UV/vis absorption experiment was conducted on a PerkinElmer L950 device. Fluorescence spectroscopy was performed on a HZTACHZ F-2500 spectrometer. Fluorescence lifetime measurements were performed using an Edinburgh Instruments FLS1000 photoluminescence spectrometer, equipped with several Pulsed Lasers - EPL Series. Fluorescence Quantum Yield measurements were performed using an Edinburgh FLS1000 photoluminescence spectrometer, equipped with an integrating sphere. The measurements were conducted at room temperature.

Self-assembly of Monomers. For the preparation of SLP1: CD2 and $Zn(OTf)_2$ were mixed in a 1:1 molar ratio and dissolved in $CDCl_3/CD_3CN$ (2:1, v/v). The whole reaction mixture was heated to 50 °C and then cooled to room temperature to obtain supramolecular polymer SLP1. The preparation method for SLP2 is similar to that of SLP1. CD2, E2, and $Zn(OTf)_2$ were mixed in a 1:1:2 molar ratio and dissolved in $CDCl_3/CD_3CN$ (2:1, v/v), the whole reaction mixture was heated to 50 °C and then cooled to room temperature to obtain supramolecular polymer SLP2. For the preparation of SCP3: CD2, E2, F2, and $Zn(OTf)_2$ were mixed in a 2:2:1:4 molar ratio and dissolved in $CDCl_3/CD_3CN$ (2:1, v/v), the whole reaction mixture was heated to 50 °C and then cooled to room temperature to obtain supramolecular polymer SCP3, the concentration of the monomer CD2 is below 115mM, as the SCP3 will transform into a gel when the concentration of CD2 exceeds 115mM.

The preparation of SCP3 gel. The gel samples used for the rheological testing and SEM observation were prepared at a concentration of 150 mM. CD2, E2, F2, and $Zn(OTf)_2$ were mixed in a 2:2:1:4 molar ratio and dissolved in $CHCl_3/CH_3CN$ (2:1, v/v), the whole reaction mixture was heated to 55 °C, the mixture was then cooled to room temperature and stand for several hours to obtain a gel.

TEM and SEM observation: The TEM observation of SLP1, SLP2, and SCP3: A drop of sample solution (chloroform/ acetonitrile = 2/1, v/v) was placed on a carbon-coated copper grid. After the solvent was removed in a short time, TEM images were taken on a FE-SEM S-4800 instrument. The SEM observation of SCP3 xerogel: A sample of SCP3 gel was prepared at a concentration of 150mM, the gel was then instantaneously cooled in liquid nitrogen followed by freeze-drying to obtain the xerogel, the morphology of the xerogel was then examined by a JEOL 6390LV scanning electron microscopy (SEM) instrument.

Rheological experiments were performed on a Kinexus rheogoniometer (diameter: 25 mm; gap: 200 μm). Frequency sweep experiment was conducted from 0.1 to 100 rad/s with a 1% strain at 25 °C. The dynamic strain sweep experiment was performed at a frequency of 10 rad/s. Cyclic strain scan experiment was conducted by alternately changing 1% and 300% strains at a frequency of 10 rad/s.

TGA experiment was performed on a TA Q500 device with a heating rate of 10 °C/min from 30 to 1000 °C. Before testing, the solvent of the gel was removed to form a xerogel.

2. The study of noncovalent interactions using model compounds

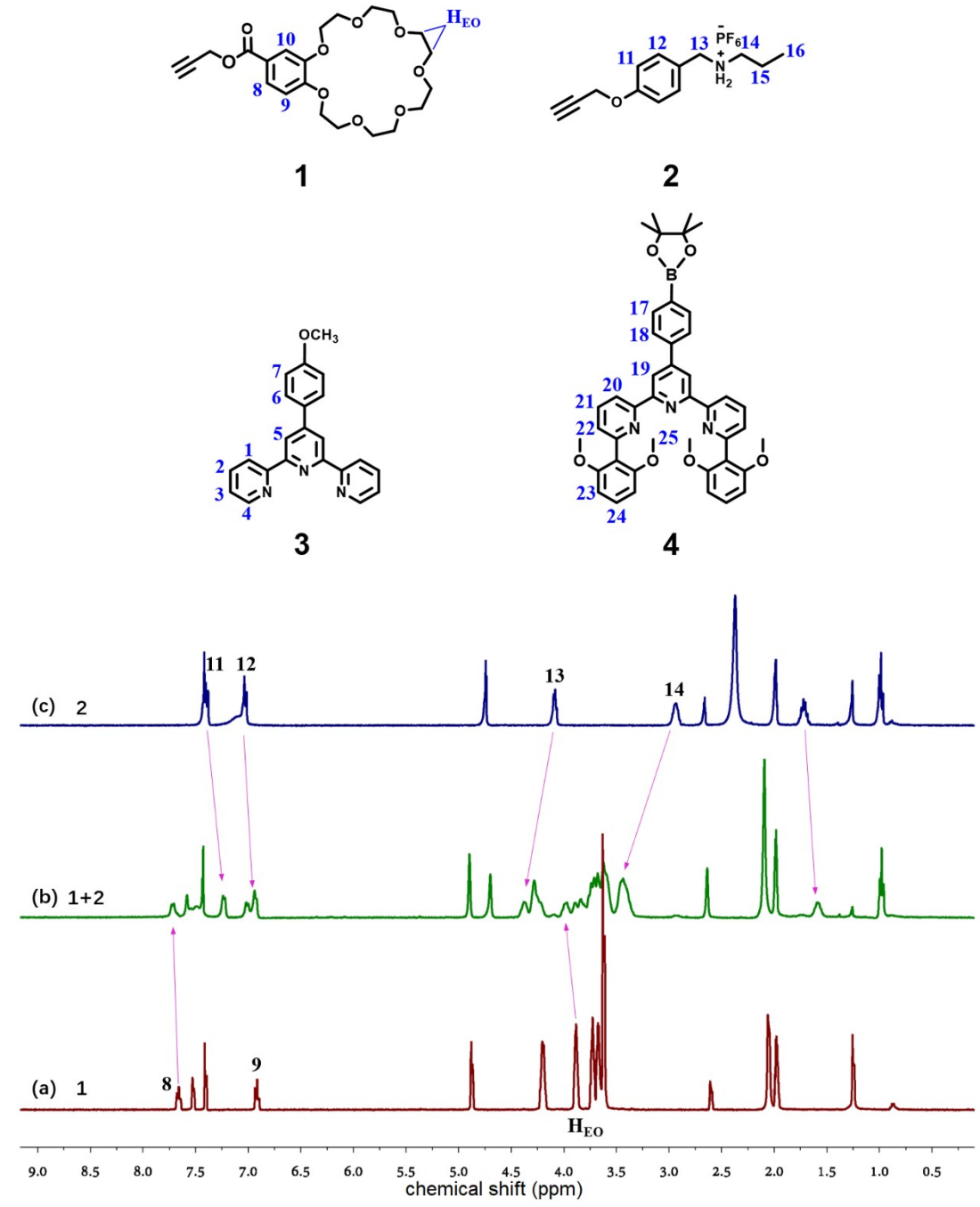


Fig. S1 ^{1}H NMR spectra (400 MHz, $CDCl_3$-CD_3CN (2/1, v/v), 293K) of (a) **1**, (b) an equimolar solution of **1** and **2**, (c) **2.**

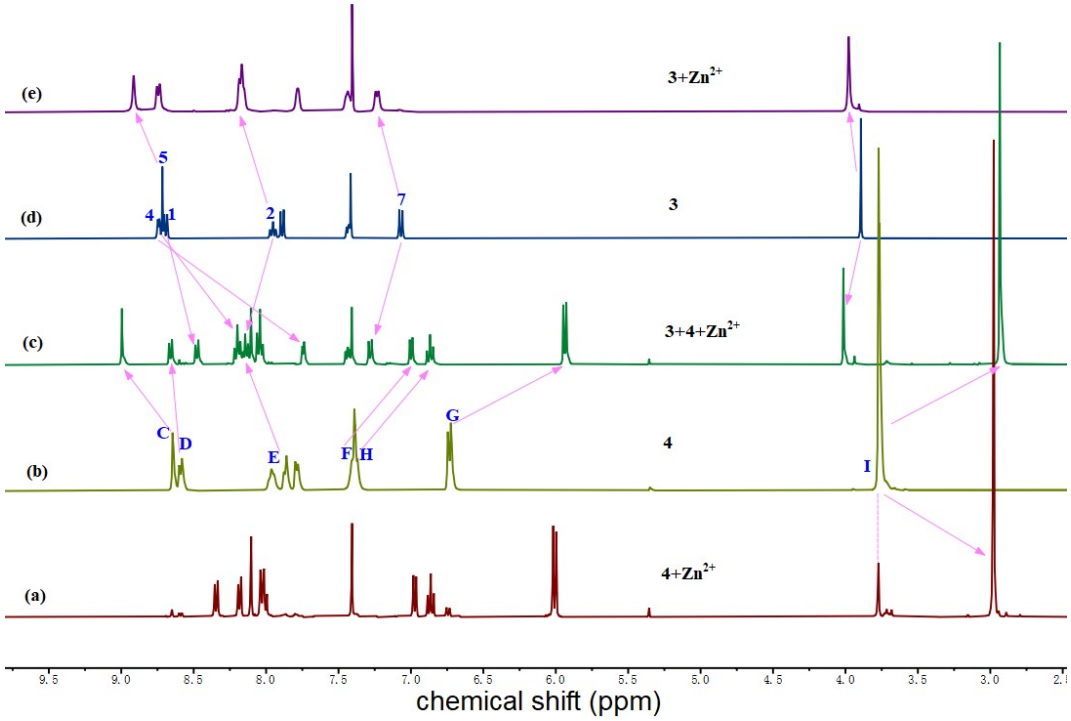


Fig. S2 ^{1}H NMR spectra (400 MHz, $CDCl_3$-CD_3CN (2/1, v/v), 293K) of (a) 4+$Zn(OTf)_2$, (b) 4, (c) 3+4+$Zn(OTf)_2$, (d) 3, (e) 3+$Zn(OTf)_2$.

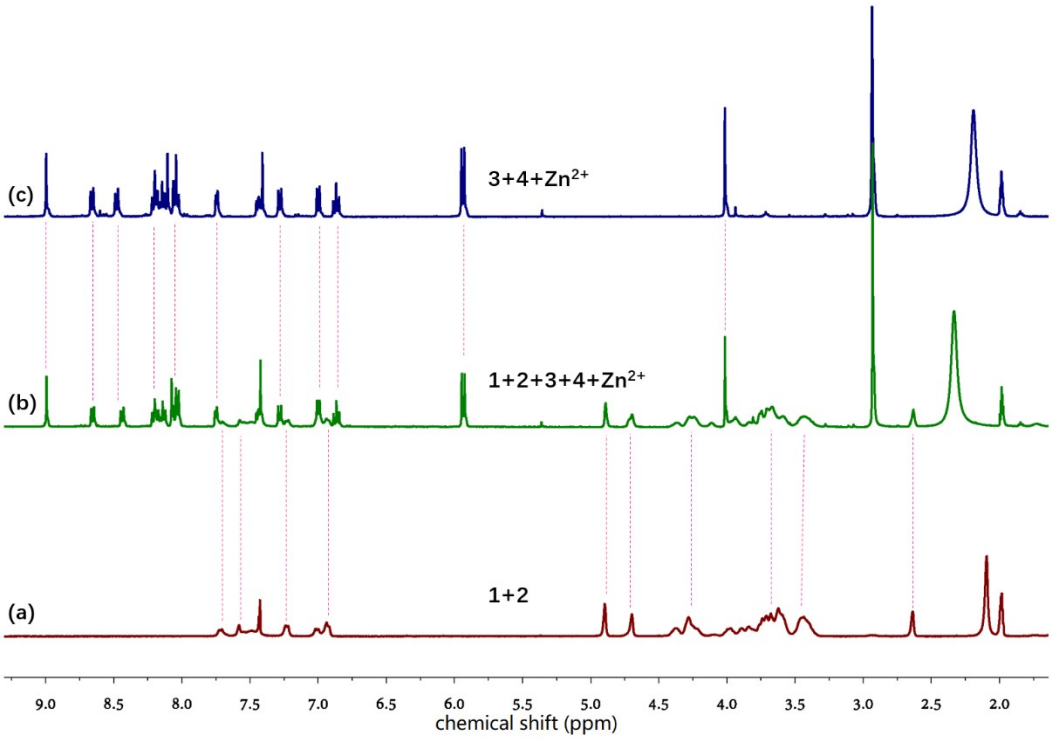


Fig. S3 ^{1}H NMR spectra (400 MHz, $CDCl_3$-CD_3CN (2/1, v/v), 293K) of (a) 1+2, (b) 1+2+3+4+$Zn(OTf)_2$, (c) 3+4+$Zn(OTf)_2$.

3. ^{1}H-^{1}H COSY NMR

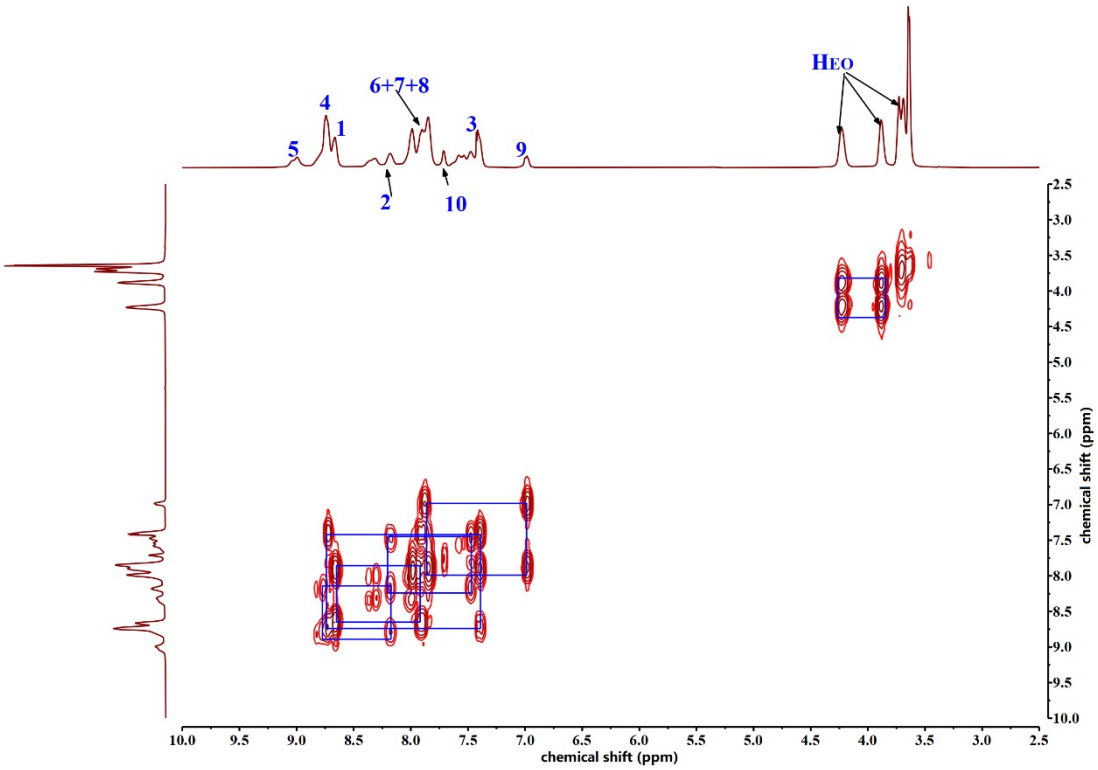


Fig S4 ^{1}H-^{1}H COSY NMR of CD2+Zn(OTf)$_2$ (400 MHz, $CDCl_3$-CD_3CN (2/1, v/v), 293 K).

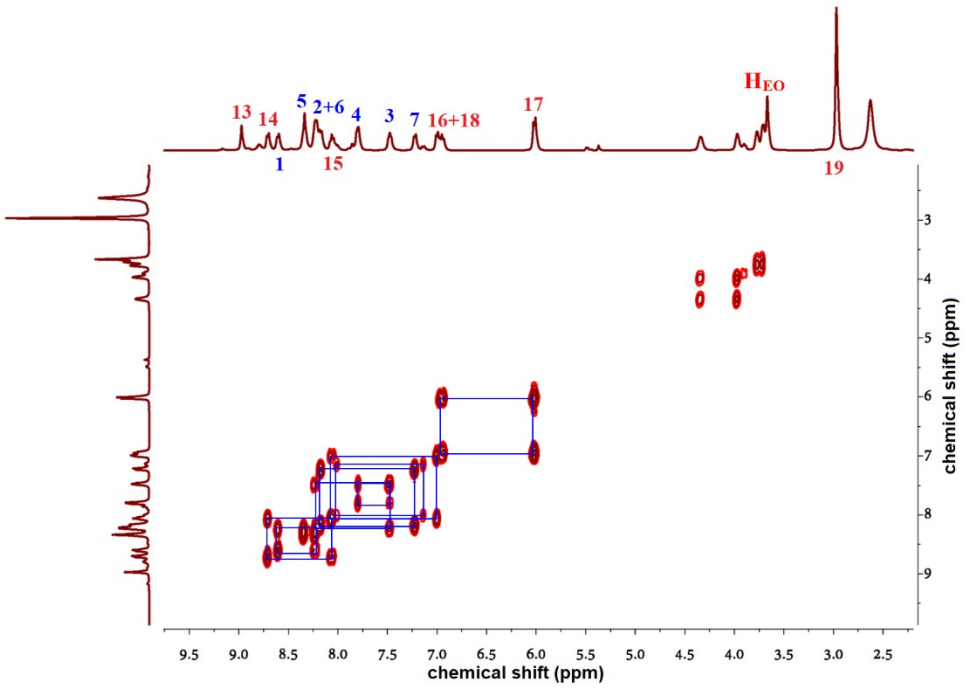


Fig S5 ^{1}H-^{1}H COSY NMR of CD2+E2+Zn(OTf)$_2$ (400 MHz, $CDCl_3$-CD_3CN (2/1, v/v), 293 K).

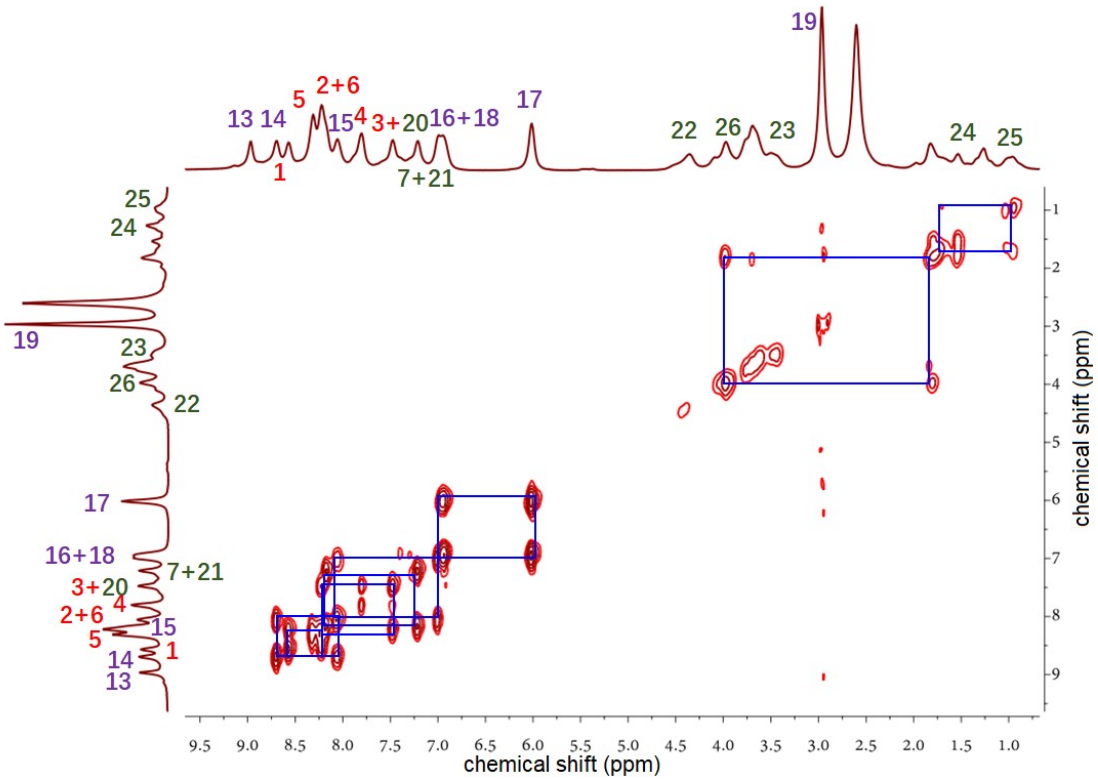


Fig. S6 ^{1}H-^{1}H COSY NMR of CD2+E2+F2+Zn(OTf)$_2$ (400 MHz, $CDCl_3$-CD_3CN (2/1, v/v), 293 K).

4. 2D NOESY NMR spectra

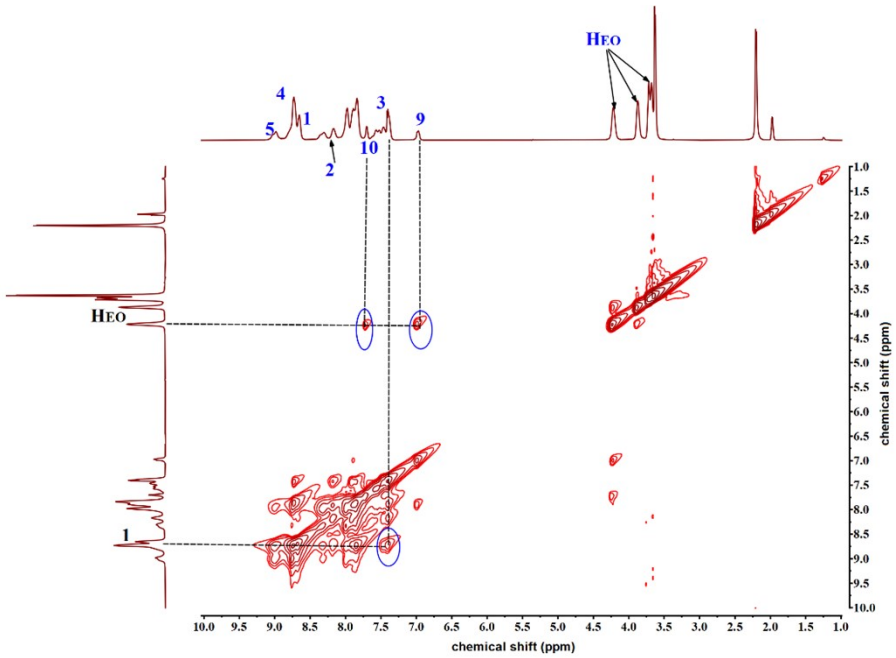


Fig. S7 2D NOESY NMR spectrum of CD2+Zn(OTf)$_2$ (400 MHz, $CDCl_3$-CD_3CN = 2/1, v/v, 298 K).

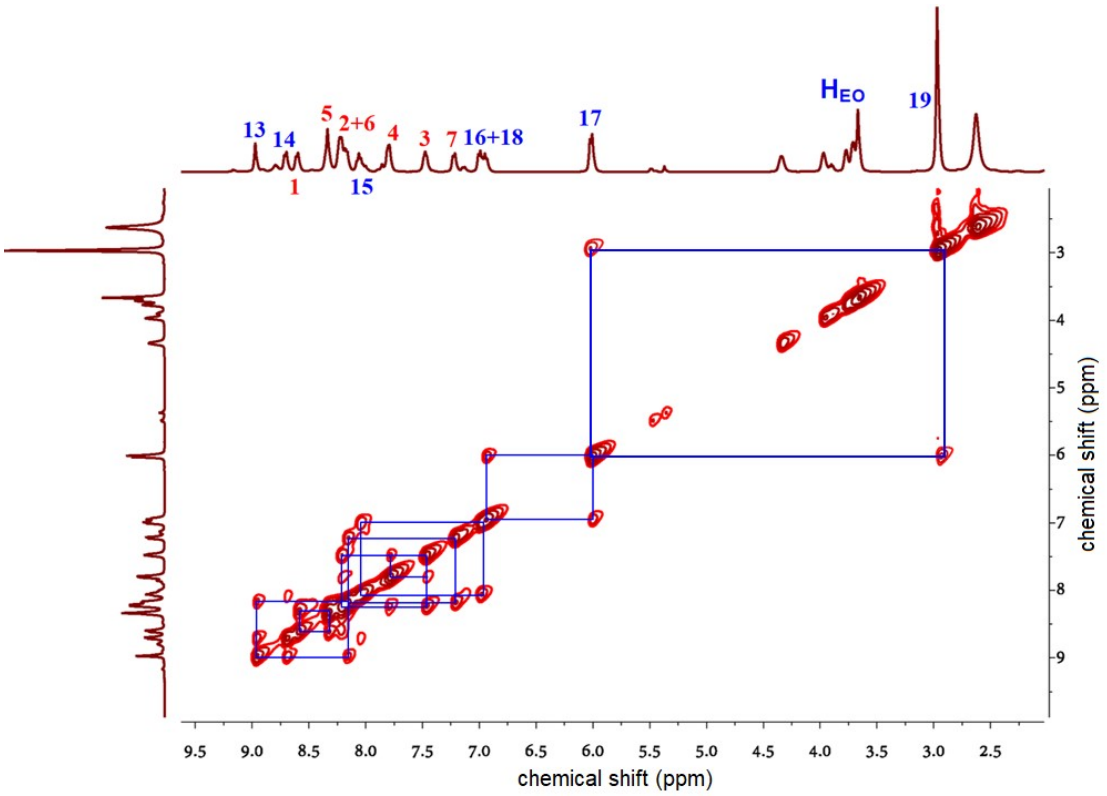


Fig. S8 2D NOESY NMR spectrum of CD2+E2+Zn(OTf)$_2$ (400 MHz, $CDCl_3$-CD_3CN = 2/1, v/v, 298 K).

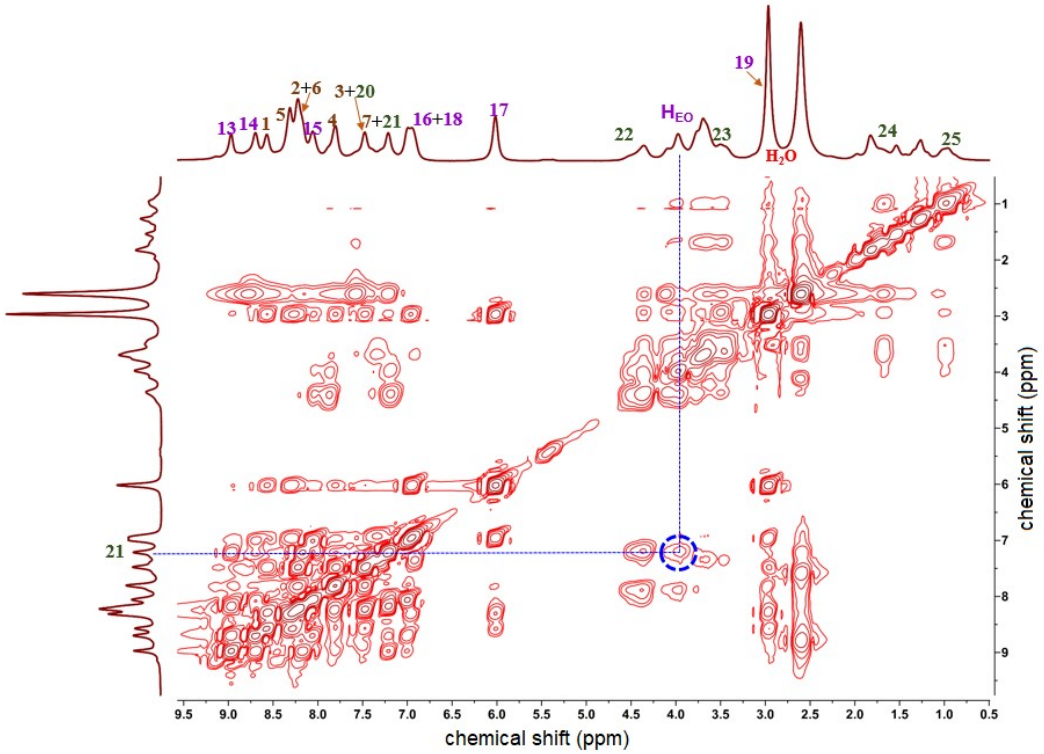


Fig. S9 2D NOESY NMR spectrum of CD2+E2+F2+Zn(OTf)$_2$ (400 MHz, $CDCl_3$-CD_3CN = 2/1, v/v, 298 K).

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

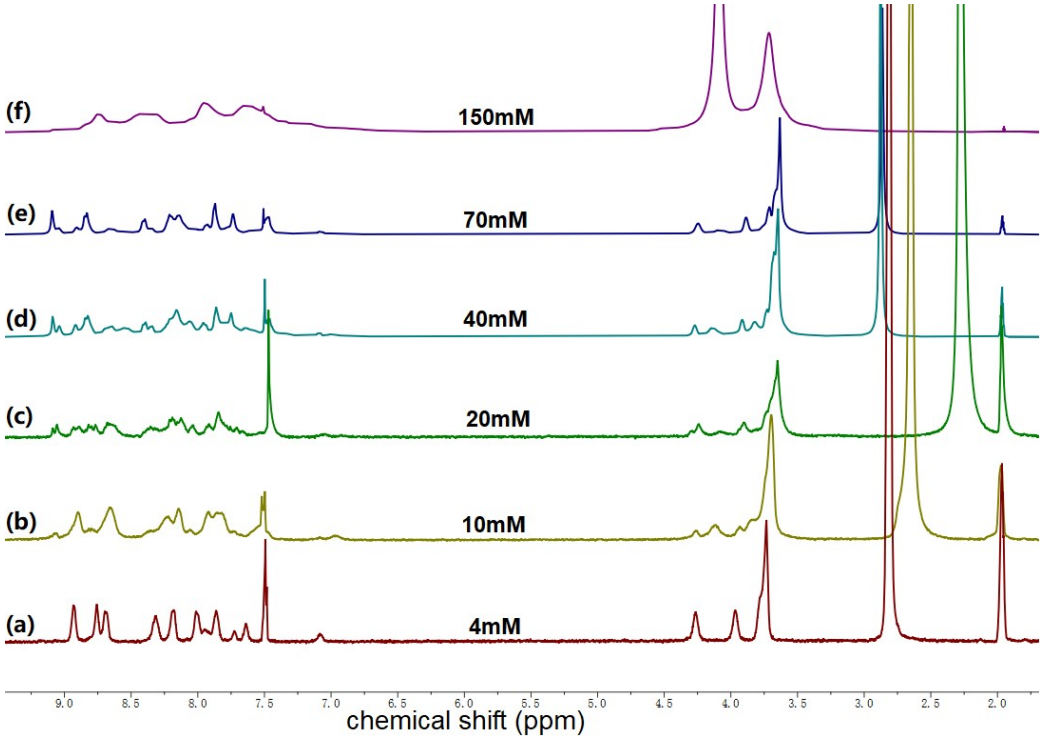


Fig. S10 ^{1}H NMR spectra (400 MHz, $CDCl_3$-CD_3CN = 2/1, v/v, 298 K) of CD2+$Zn(OTf)_2$ at different concentrations (a) 4 mM, (b) 10 mM, (c) 20 mM, (d) 40 mM, (e) 70 mM, (f) 150 mM.

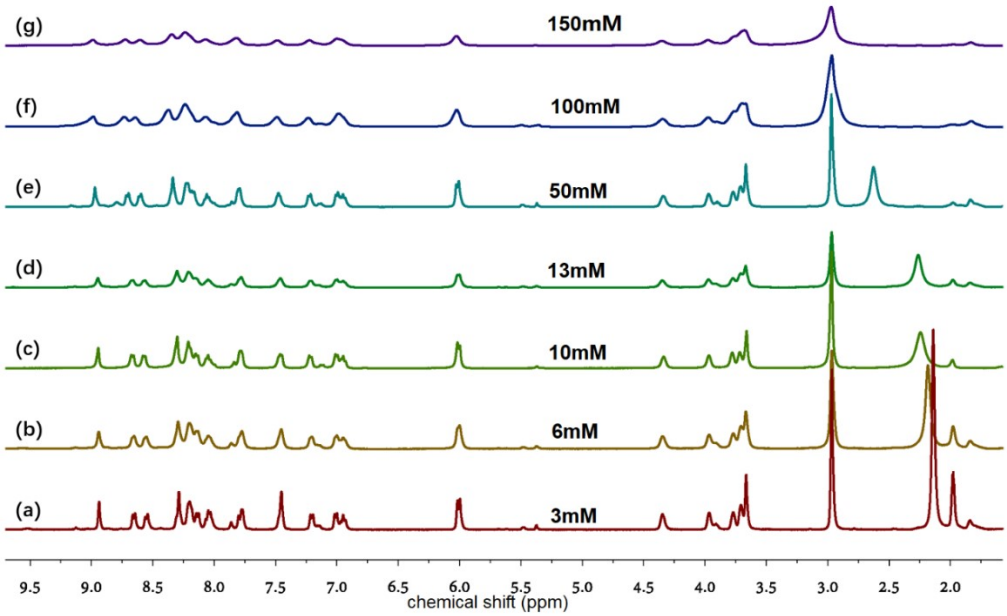


Fig. S11 ^{1}H NMR spectra (400 MHz, $CDCl_3$-CD_3CN = 2/1, v/v, 298 K) of CD2+E2+$Zn(OTf)_2$ at different concentrations (a) 3 mM, (b) 6 mM, (c) 10 mM, (d) 13 mM, (e) 50 mM, (f) 100 mM, (g)150Mm.

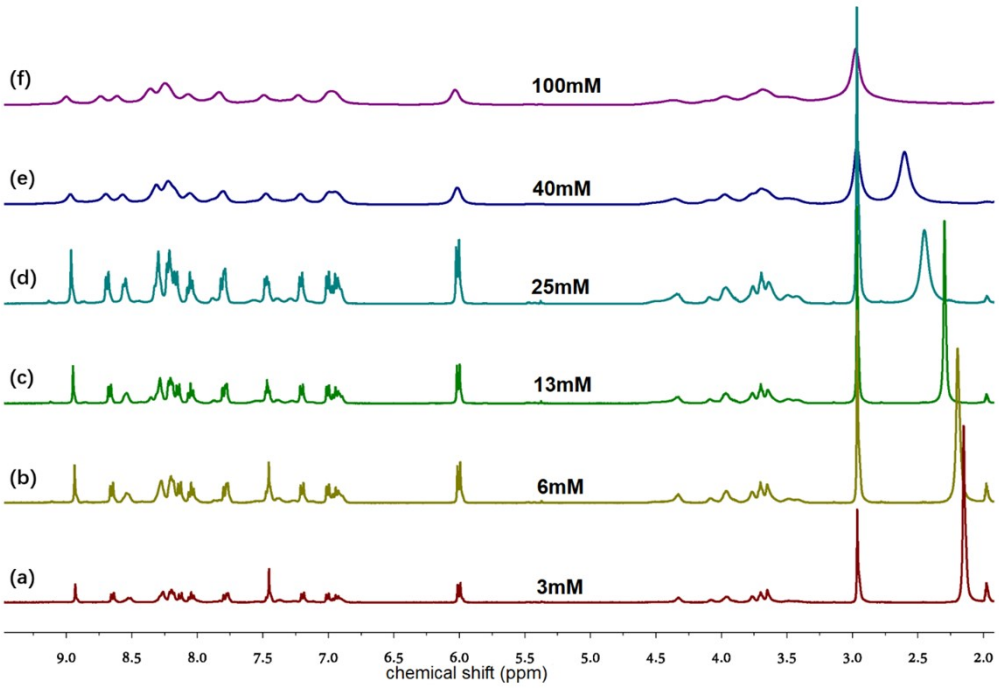


Fig. S12 ^{1}H NMR spectra (400 MHz, $CDCl_3$-CD_3CN = 2/1, v/v, 298 K) of CD2+E2+F2+$Zn(OTf)_2$ at different concentrations (a) 3 mM, (b) 6 mM, (c) 13 mM, (d) 25 mM, (e) 40 mM, (f) 100 Mm.

6. 2D DOSY NMR

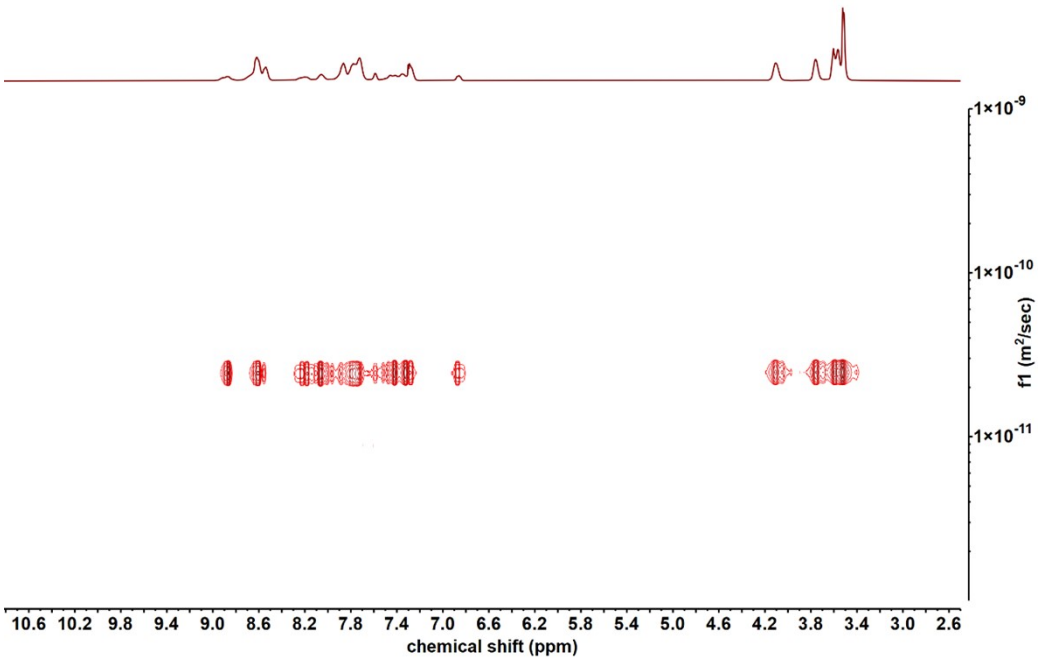


Fig. S13 DOSY NMR spectrum (500 MHz, $CDCl_3$-CD_3CN = 2/1, v/v, 298 K) of CD2+ $Zn(OTf)_2$,

the concentration of CD2 is 80 mM.

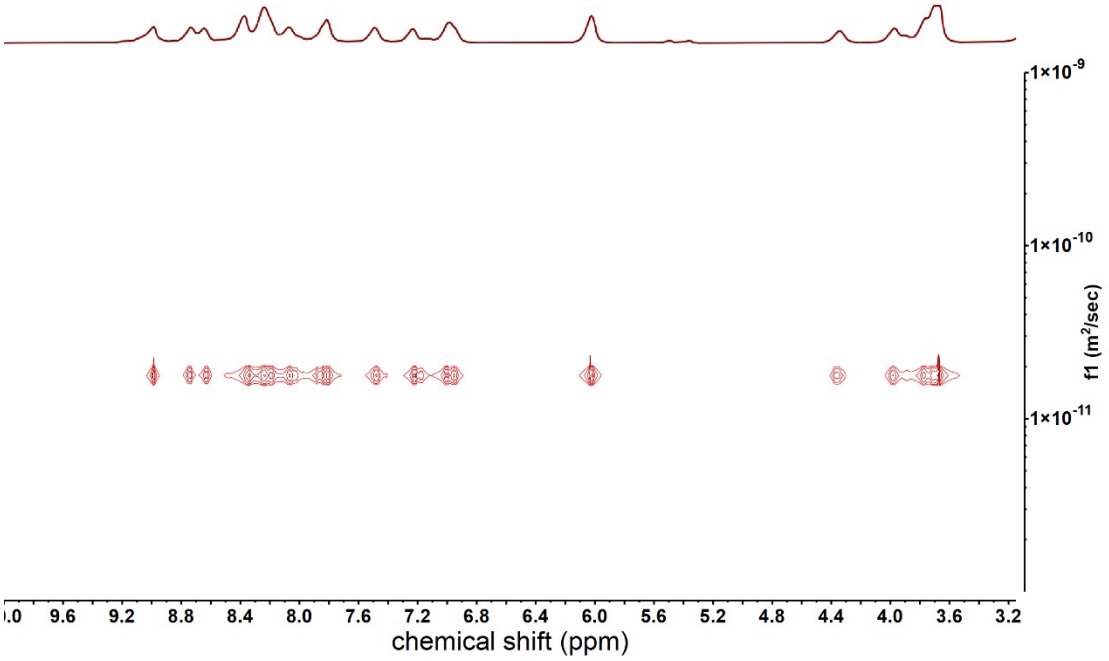


Fig. S14 Representative DOSY NMR spectrum (500 MHz, $CDCl_3$-CD_3CN = 2/1, v/v, 298 K) of CD2+E2+$Zn(OTf)_2$, the concentration of CD2 is 80 mM.

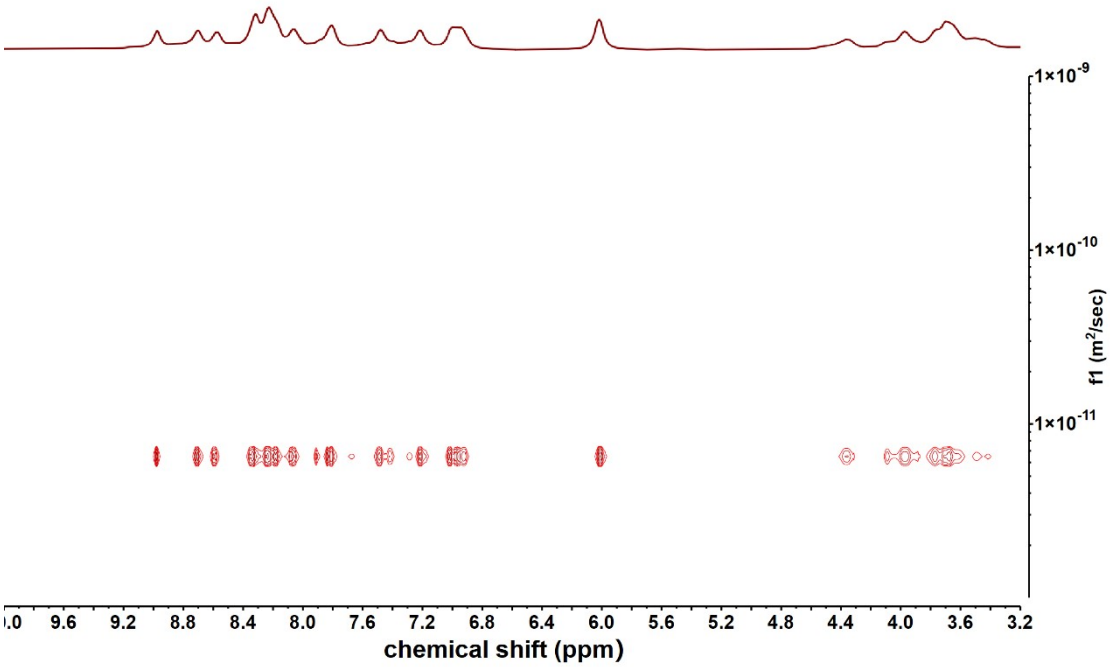


Fig. S15 Representative DOSY NMR spectrum (500 MHz, $CDCl_3$-CD_3CN = 2/1, v/v, 298 K) of CD2+E2+F2+$Zn(OTf)_2$, the concentration of CD2 is 80 mM.

7. The discuss of binding constants

1. tpy-Zn^{2+}-tpy binding constant

To determine the association constant of tpy-Zn^{2+}-tpy, the UV-Vis experiment (Job plot method) was conducted according to the literature method.[S1] Model compound 3 was chosen as the ligand. A series of samples were prepared and the total molar concentration of ligand 3 and zinc ion was maintained at 2×10^{-5}M in each sample and only the ratios of zinc ion to ligand were altered. The job plot was conducted by varying the mole fractions of the ligand 3 and zinc ion. The concentration: 3+ [$Zn(OTf)_2$] = 2×10^{-5}M. The absorbance intensity at 342 nm was plotted (Fig. S16) against the mole fraction of $Zn(OTf)_2$. The Job plot indicates a 1:2 binding ratio between Zn^{2+} and 3.

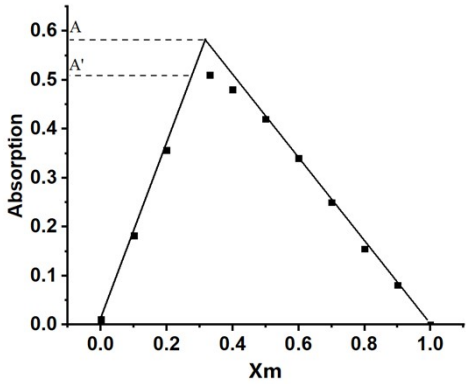


Fig. S16 Job plot of the complex formed between zinc ion, 3 (ligand) showed a 1:2 stoichiometry by plotting the absorbance intensity at 342 nm against the mole fraction of zinc ion. Concentration: [**3**] + [$Zn(OTf)_2$] = 2×10^{-5}M. (chloroform versus acetonitrile=2:1, v/v, 298K).

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 $A = 1.54515X_m + 0.02074$. When $X_m \geq 0.5$, the fitting equation is $A = -0.80938X_m + 0.806$. The intersection point of the two fitting curves is taken (X_m=0.331, A=0.587), and the experimental value is X_m=0.333, A'=0.511. The dissociation degree of complex [Zn$\mathbf{3_2}$]$(OTf)_2$ was calculated from **Eq. 1**. According to the formula,[S1] the dissociation degree(α) of complex [Zn$\mathbf{3_2}$]$(OTf)_2$ was calculated to be 0.129.

$\alpha = (A - A')/A$, **(Eq. 1)**

The binding constant K was calculated to be 5.23×10^6 M^{-1} based on **Eq. 2**.

$$\mathbf{3} + Zn(OTf)_2 \rightleftharpoons [Zn\mathbf{3}](OTf)_2$$

$$\mathbf{3} + [Zn\mathbf{3}](OTf)_2 \rightleftharpoons [Zn\mathbf{3_2}](OTf)_2$$

$$K = \frac{[Zn3_2](OTf)_2}{[3]\,[Zn3](OTf)_2)} = \frac{1-\alpha}{C\alpha^2} \quad \text{(Eq.2)}$$

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

To determine the association constant of tpy-Zn^{2+}-tmy, the UV-Vis experiment (Job plot method) was conducted according to the literature method.[S1] Model compounds 3 and 4 were chosen as the ligands. A series of samples were prepared and the total molar concentration of ligands ($\frac{[3]+[4]}{2}$) and zinc ion was maintained at 2×10^{-5}M in each sample and only the ratios of zinc ion to ligands were altered. The job plot was conducted by varying the mole fractions of the ligands ($\frac{[3]+[4]}{2}$) and zinc ion. The concentration: $\frac{[3]+[4]}{2}$ + $[Zn(OTf)_2]$ = 2×10^{-5}M. The absorbance intensity at 342 nm was plotted (Fig. S17) against the mole fraction of $Zn(OTf)_2$. The Job plot indicates a 1:1:1 binding among Zn^{2+}, 3 and 4.

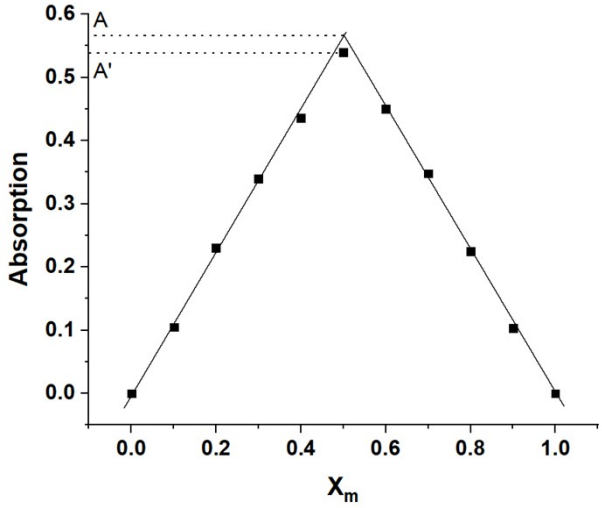


Fig. S17 Job plot of the complex formed among zinc ion, 3 (ligand) and 4 (ligand) showing a 1:1:1 stoichiometry by plotting the absorbance intensity at 342 nm against the mole fraction of zinc ion. Concentration: [**3**]=[**4**], $\frac{[3]+[4]}{2}$ + $[Zn(OTf)_2]$ = 2×10^{-5}M. (chloroform versus acetonitrile=2:1, v/v, 298K).

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 $A = 1.095X_m + 0.0019$. When $X_m \geq 0.5$, the fitting equation is $A = -1.103X_m + 1.104$. The intersection point of the two fitting curves is taken (X_m=0.5062, A=0.567), and the experimental value is X_m=0.5000, A'= 0.535. The dissociation degree of complex [Zn**34**](OTf)$_2$ was calculated from **Eq. 3**. According to the formula,[S1] the dissociation degree(*α)* of complex [Zn**34**](OTf)$_2$ was calculated to be 0.056.

α= (A - A')/A, **(Eq. 3)**

The binding constant *K* was then calculated to be 2.96×10^7 M^{-1} based on **Eq. 4**.

$$\mathbf{3} + Zn(OTf)_2 \rightleftharpoons [Zn\mathbf{3}](OTf)_2$$

$$\mathbf{4} + [Zn3](OTf)_2 \rightleftharpoons [Zn\mathbf{34}](OTf)_2$$

$$\boldsymbol{K} = \frac{[Zn34](OTf)_2}{[4]\,[Zn3](OTf)_2)} = \frac{1-\alpha}{C\alpha^2} \quad (\textbf{Eq.4})$$

Where C is the total concentration of the complex [Zn**34**](OTf)$_2$ and α is the degree of dissociation of complex [Zn**34**](OTf)$_2$ when X_m value is 0.5, with the hypothesis that the ligands and zinc ion only form the complex [Zn**34**](OTf)$_2$. The C is 1×10^{-5} M and the α is 0.056 when X_m is 0.5.

(3) B21C7-DAS binding constant

We use model compound 1 and 2 to determine the association constant K_a of the B21C7-DAS according to the reference method.[S2] The K_a value of B21C7-DAS complex, slow-exchange system, could be calculated from integrations of complexed and uncomplexed peaks in ^{1}H NMR spectrum. The *K*a value was determined at 10.00 mM 1 and 2 in $CDCl_3/CD_3CN$(2/1,v/v)solution. Using the reference method, *K*a value was calculated as below: $[(2.19/3.19) \times 10 \times 10^{-3}]/[(1-2.19/3.19) \times 10 \times 10^{-3}]^2 = 698\ M^{-1}$ in $CDCl_3/CD_3CN$ solution(2/1, v/v), the experiment was repeated for two times and the average *K*a was determined to be $698 \pm 55 M^{-1}$.

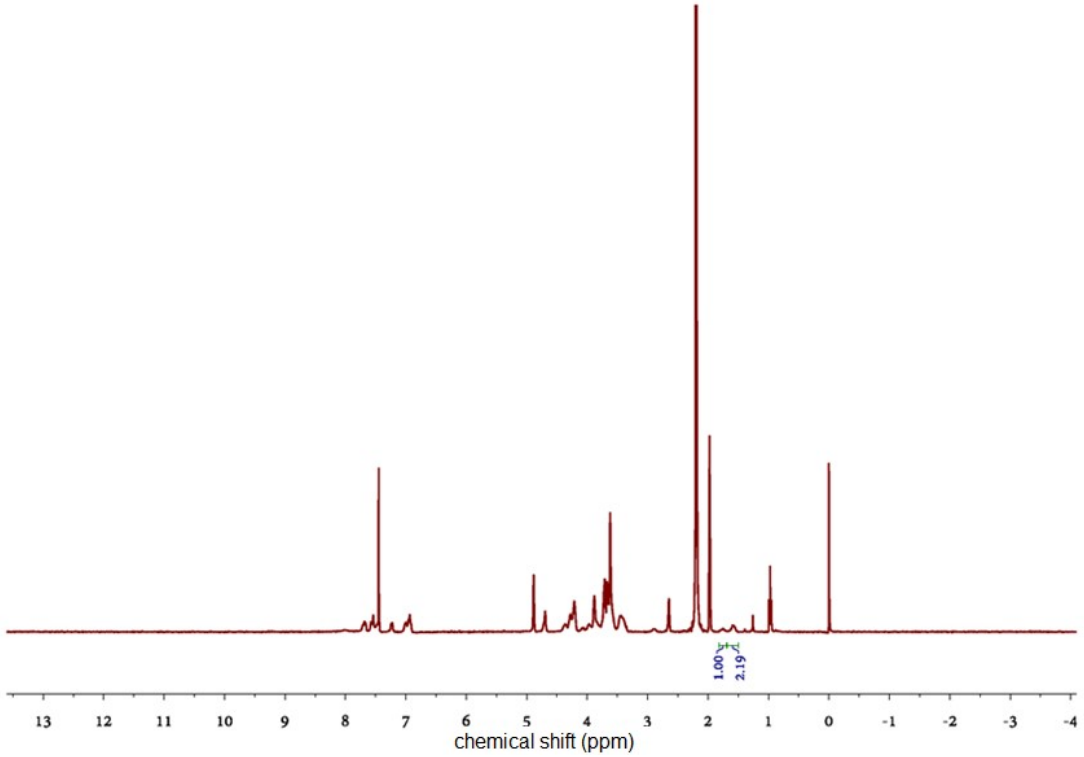


Fig.S18 ^{1}H NMR spectrum (400 MHz, $CDCl_3$-CD_3CN = 2/1, v/v, 298 K) of model compounds 1+2 at a concentration of 10mM.

8. Photophysical properties of supramolecular polymers

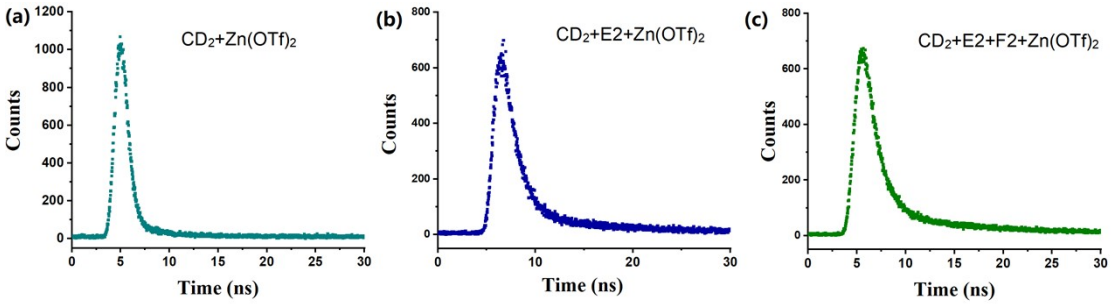


Fig. S19 Fluorescence decays (emission wavelength 450 nm) of (a) CD2+Zn(OTf)$_2$, (b) CD2+E2+Zn(OTf)$_2$, and (c) CD2+E2+F2+Zn(OTf)$_2$ in $CHCl_3/CH_3CN$ solution (2:1 v/v, [CD2]=0.02 mM). The excitation wavelength was 335 nm. The fluorescence lifetime is 1.56 ns for CD2+Zn(OTf)$_2$, 6.16 ns for CD2+E2+Zn(OTf)$_2$, and 6.27 ns for CD2+E2+F2+Zn(OTf)$_2$.

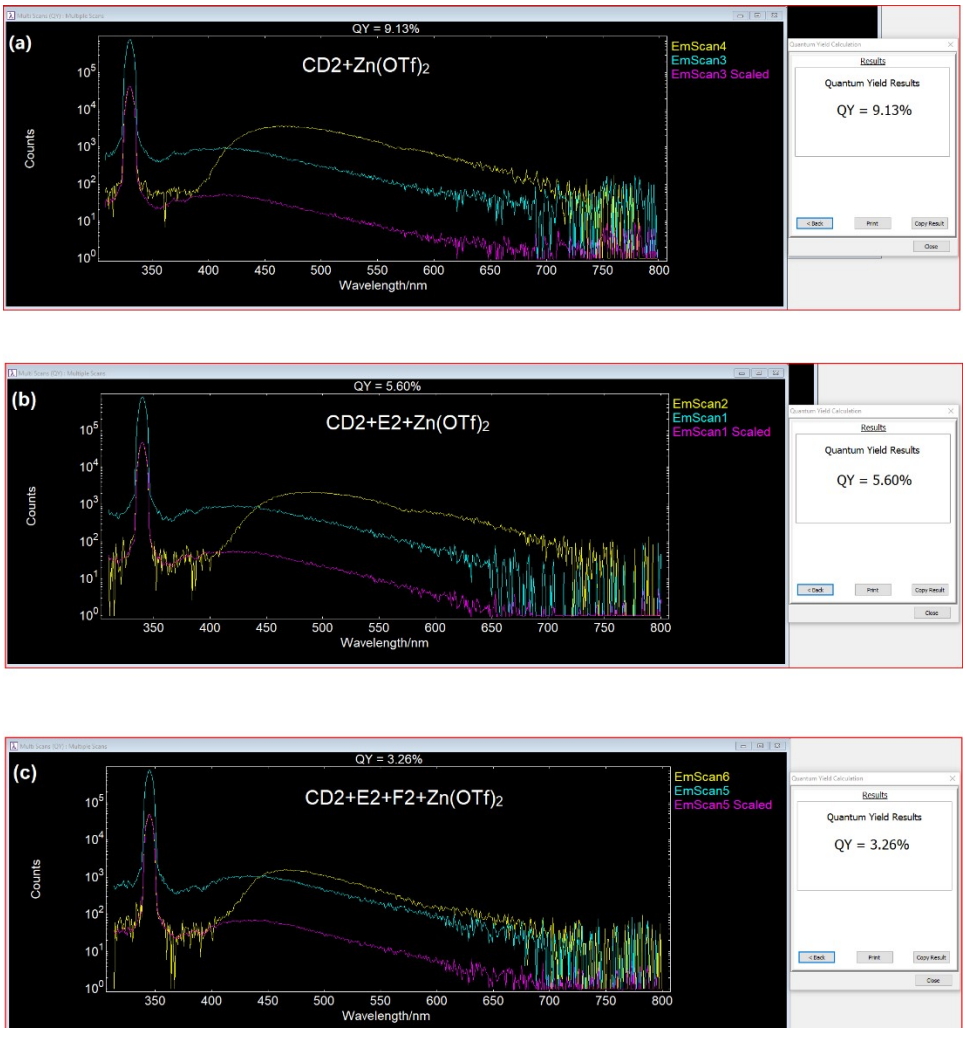


Fig. S20 Fluorescence quantum yield measurements of CD2+Zn(OTf)$_2$, CD2+E2+Zn(OTf)$_2$, and CD2+E2+F2+Zn(OTf)$_2$ in $CHCl_3/CH_3CN$ (v/v=2/1, [CD2]=0.02 mM). The excitation wavelength

was 335 nm.

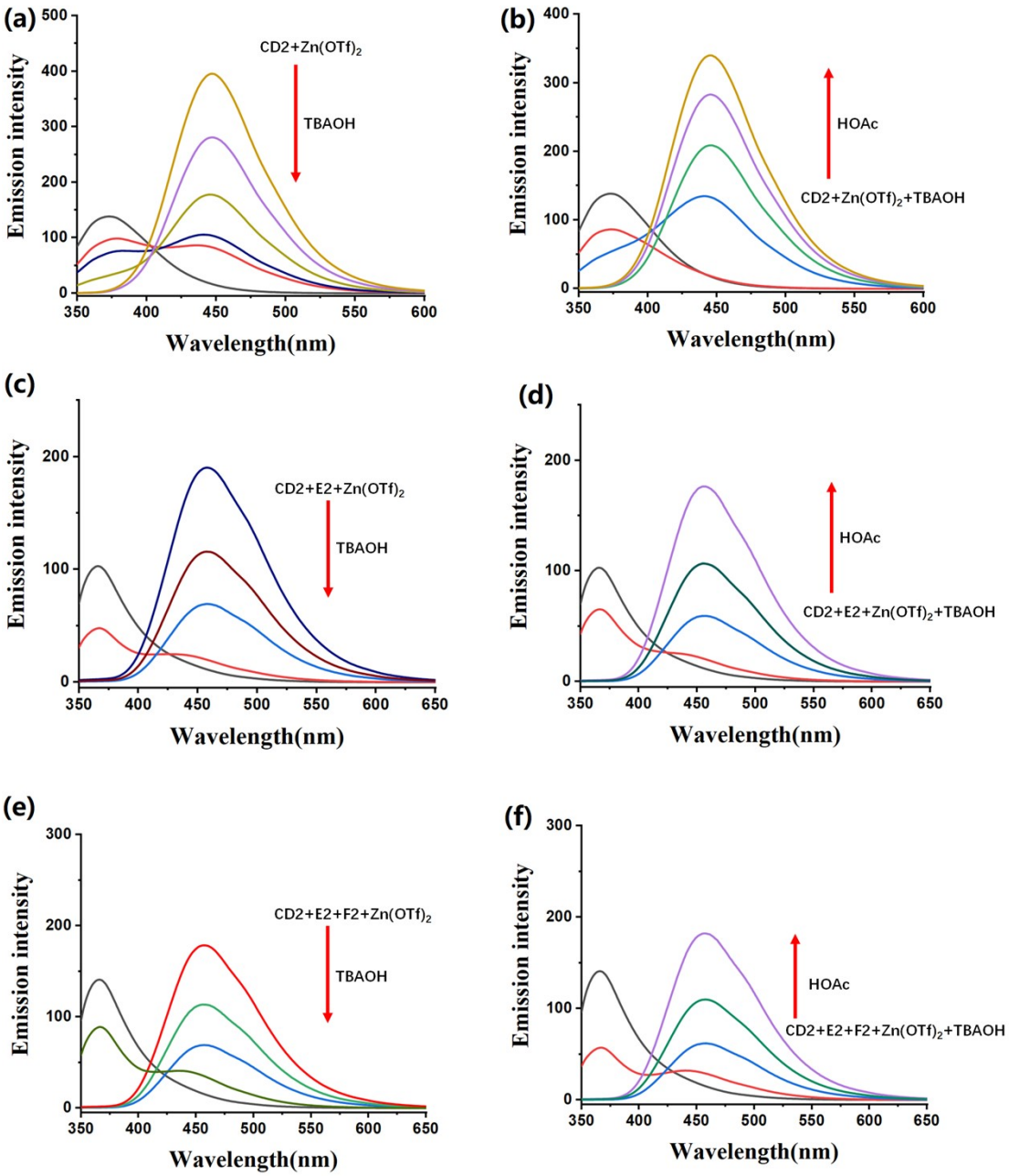


Fig.S21 The fluorescence changes of (a-b) CD_2+$Zn(OTf)_2$ by adding TBAOH/HOAc, (c-d) CD_2+E2+$Zn(OTf)_2$ by adding TBAOH/HOAc, (e-f) CD_2+E2+F2+$Zn(OTf)_2$ by adding TBAOH/HOAc. ([CD2]=0.01mM) in $CHCl_3$/CH_3CN solution (2:1 v/v). The excitation wavelength was 335 nm.

9. The self-healing behavior of SCP3 gel

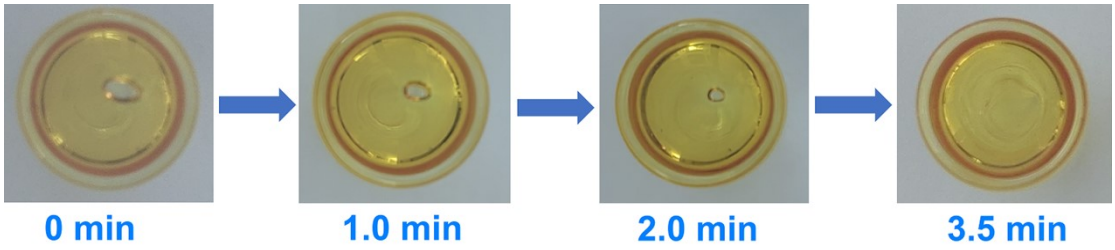
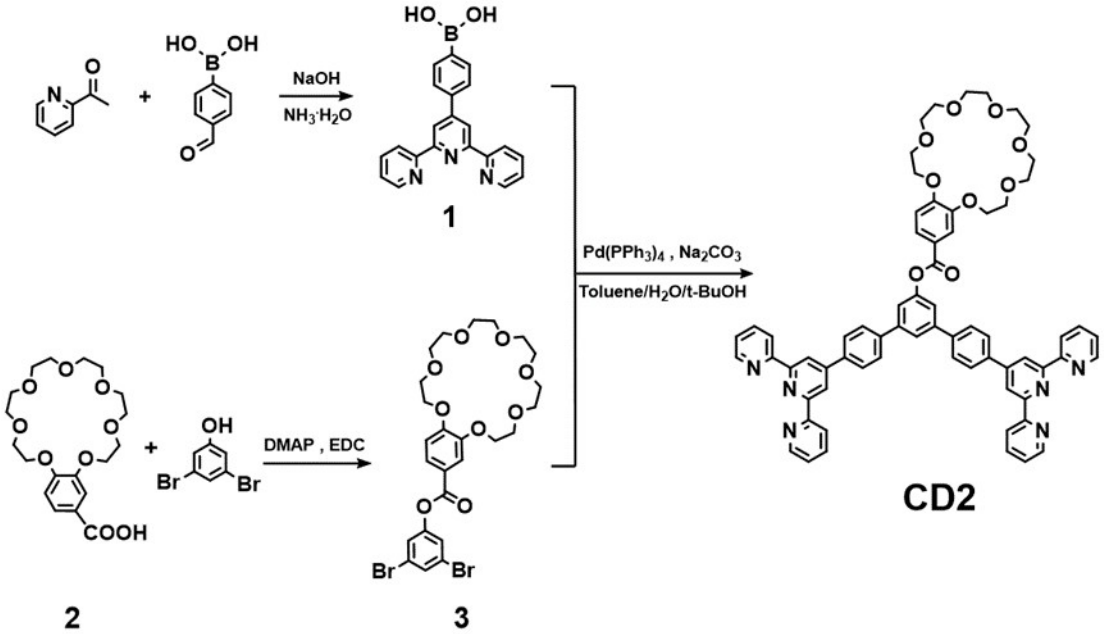
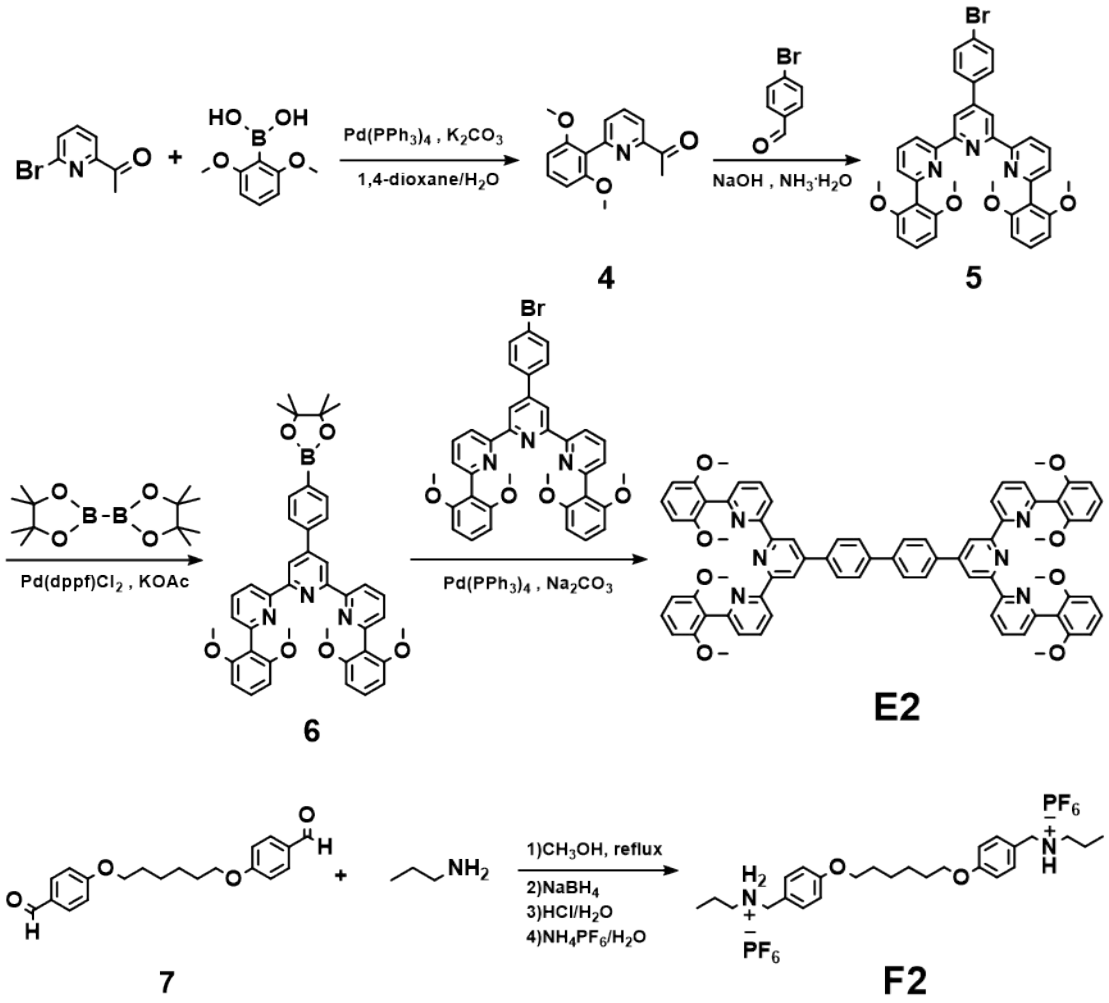


Fig. S22 The self-healing behavior of SCP3 gel. The gel was prepared at a concentration of 125mM.

10. The synthesis of intermediates and monomers





Scheme S1. Synthetic routes of monomers

The synthesis of compound 1

In a 100 mL beaker, solid sodium hydroxide (3.2 g, 80 mmol) was dissolved in a small amount of water and the solution was cooled to room temperature and set aside. Then, 2-acetylpyridine (3.6 g, 29.4 mmol), 4-formylphenylboronic acid (2.0 g, 13.3 mmol), and ethanol (120 mL) were sequentially added to a 250 mL round-bottomed flask, and the reaction solution was stirred for 15 min at 5 °C. The previously prepared sodium hydroxide solution was then slowly added to the reaction mixture. The reaction solution was continuously stirred at room temperature for 24 h. Then 20 ml of ammonia solution at a concentration of 28 wt% was added to the solution and the reaction system was heated to 55 °C. The reaction mixture was stirred at 55 °C for another 12 hours. At the end of the reaction, the reaction solution was cooled to room temperature and the suspension was transferred to a sand core funnel for filtration to obtain a residue, and the residue was washed with ethanol. Finally, the residue was

dried in a vacuum drying oven to obtain the white solid compound 1 (yield 76.4%, 3.6 g).

^{1}H NMR (400 MHz, MeOD, 298 K): δ (ppm) = 8.72 (d, J = 4.8 Hz, 2H), 8.69 (s, 2H), 8.68 (d, J = 8.0 Hz, 2H), 8.05-8.01 (m, 2H), 7.81-7.74 (m, 4H), 7.52-7.49 (m, 2H).

^{13}C NMR (100 MHz, MeOD, 298K): δ (ppm) = 156.26, 155.63, 152.21, 148.67, 137.37, 133.79, 124.56, 123.90, 121.62, 118.20.

HR-ESI-MS ($C_{21}H_{16}BN_3O_2$): m/z calcd for $[M+K]^+$ = 392.0967, found =392.1081.

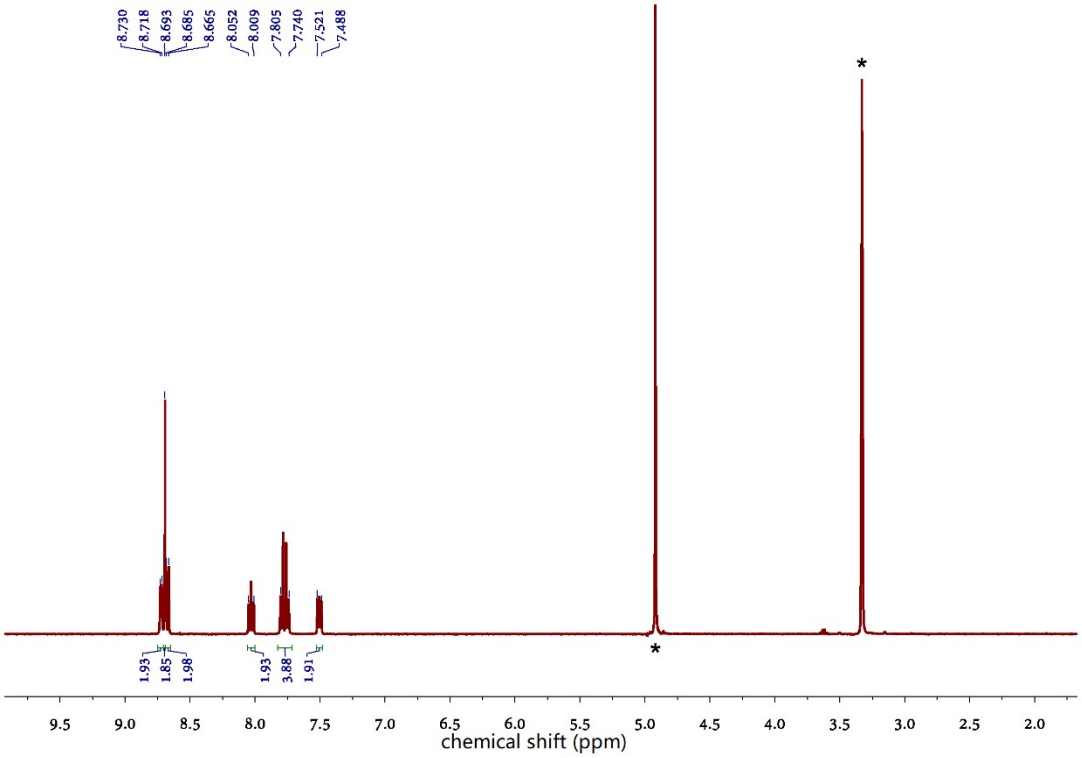


Fig. S23 The ^{1}H NMR of compound 1 (400 MHz, CD_3OD, 298 K).

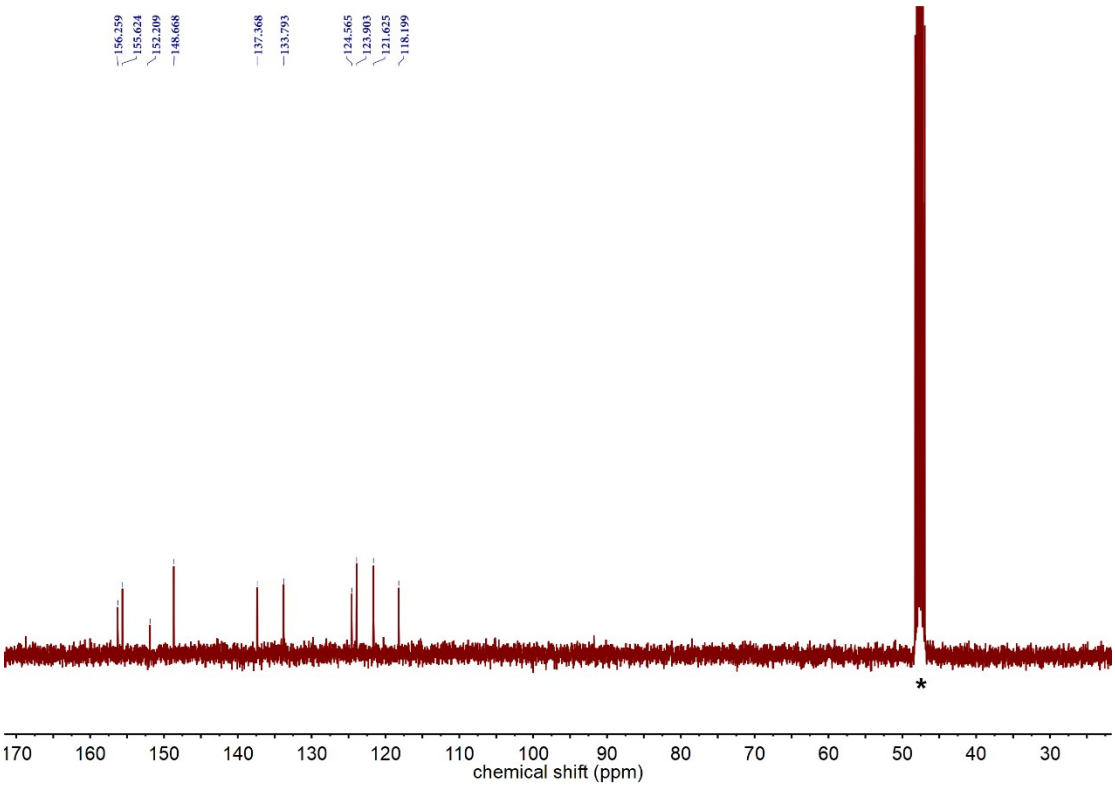


Fig. S24 The ^{13}C NMR of compound 1 (100 MHz, $CDCl_3$, 298 K).

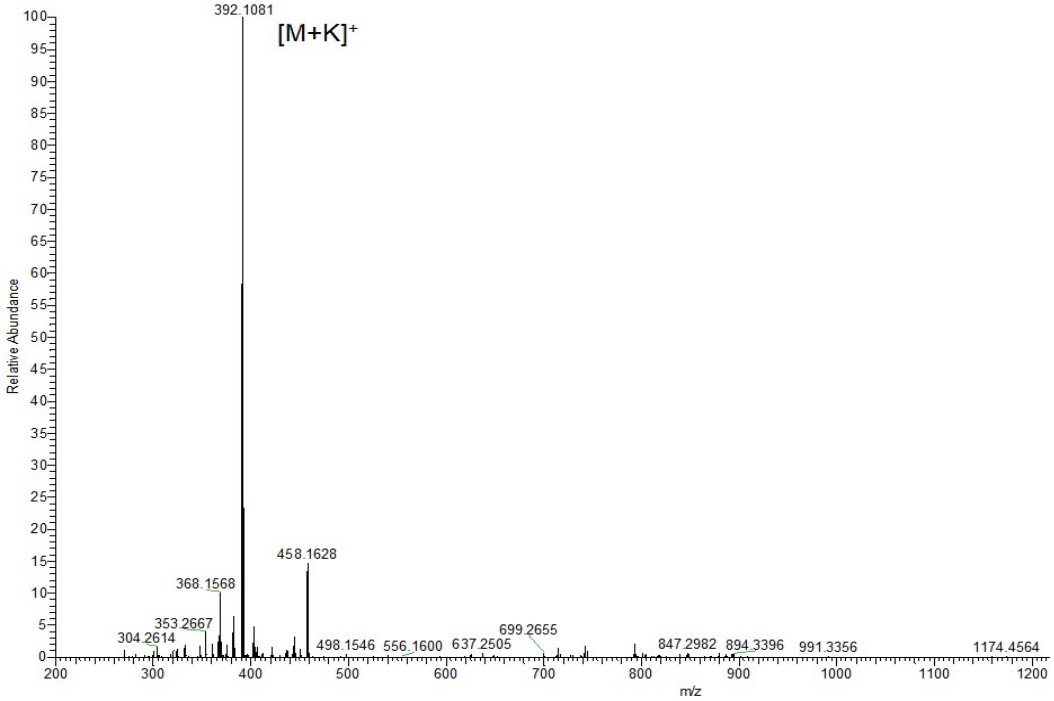


Fig. S25 The ESI-MS of compound 1.

The synthesis of compound 3

In a 250 mL round bottom flask, compound 2 (4.82 g, 12.0 mmol), 3,5-dibromophenol (3.34 g, 13.2 mmol), 4 -dimethylaminopyridine (DMAP) (1.62 g, 13.2 mmol), and dichloromethane (160 mL) were added sequentially. After the reaction mixture was stirred at 0 °C for 10 min, 1-(3-dimethylaminopropyl)-3-ethylcarbamoyl imide (EDC, 5.08 g, 26.5 mmol) was added to the reaction system. The reaction system was stirred at room temperature for 24 hours. After completing the reaction, the reaction mixture was filtered, the organic solvent was removed in a rotary evaporator to obtain the crude product. The crude product was purified by silica gel column chromatography (eluent: methanol/dichloromethane=1:200, v/v) to give white solid compound 3 (6.00 g, 78.6%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 7.78 (d, J = 10.4 Hz, 1H), 7.62 (d, J = 2.0 Hz, 1H), 7.57 (t, J = 1.6 Hz, 1H), 7.36 (d, J = 1.6 Hz, 2H), 6.93 (d, J = 8.5 Hz, 1H), 4.24 (m, 4H), 3.96 (m, 4H), 3.81 (m, 4H), 3.75 (m, 4H), 3.68 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 164.32, 154.28, 152.15, 148.84, 131.85, 125.25, 124.64, 123.05, 121.32, 115.30, 112.64, 71.69, 71.56, 71.45, 71.41, 71.34, 71.31, 70.88, 69.90, 69.75, 69.73, 69.50.

HR-ESI-MS ($C_{25}H_{30}Br_2O_9$): m/z calcd for $[M+Na]^+$ = 657.01283, found =657.01215, error = 1.0 ppm.

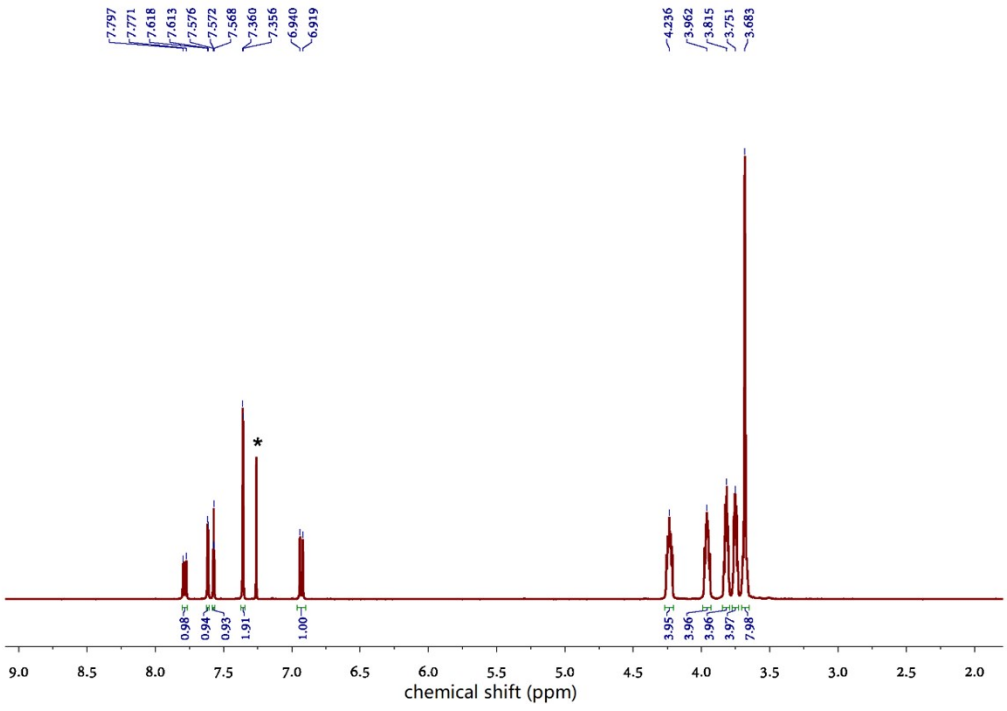


Fig. S26 The ^{1}H NMR of compound 3 (400 MHz, $CDCl_3$, 298 K).

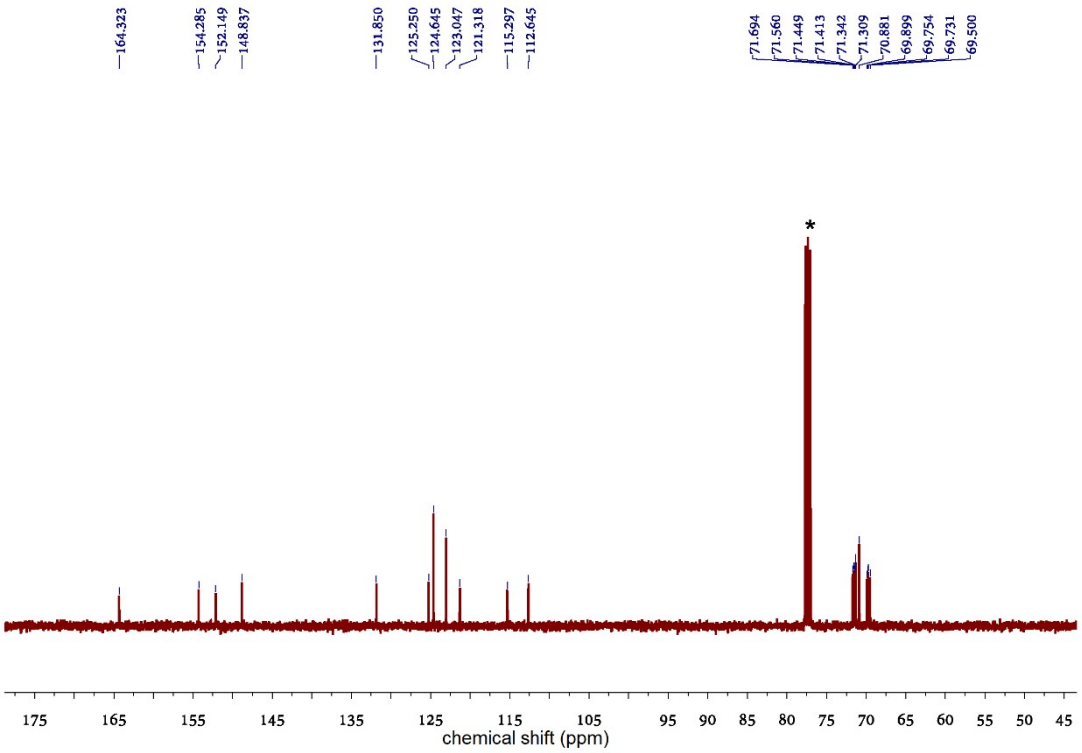


Fig. S27 The ^{13}C NMR of compound 3 (100 MHz, $CDCl_3$, 298 K).

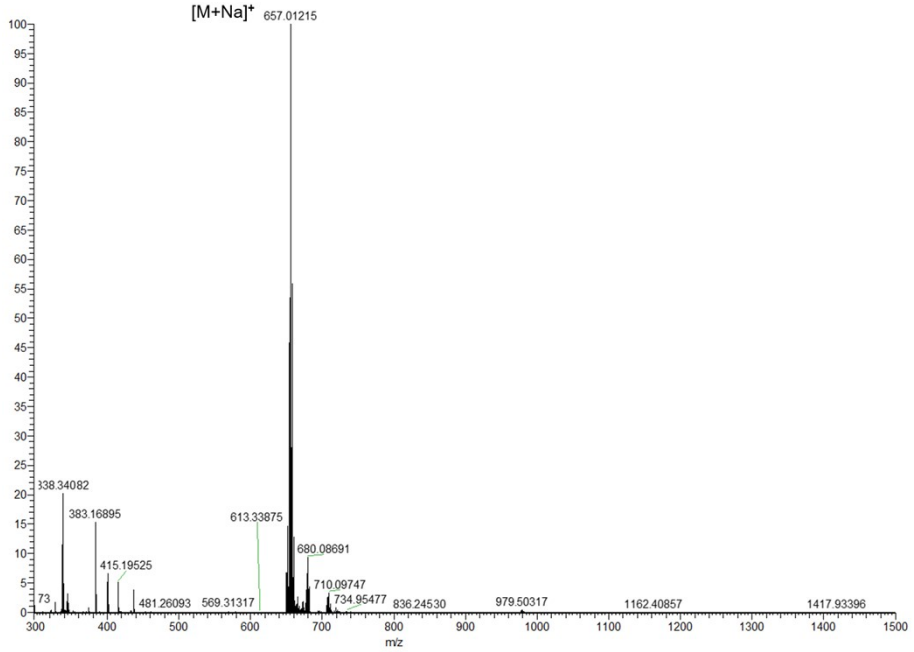


Fig. S28 The ESI-MS of compound 3.

The synthesis of monomer CD2

In a 250 mL round bottomed flask, compound 1 (8.35 g, 23.65 mmol), compound 3 (5 g, 7.88 mmol), sodium carbonate (5 g, 47.3 mmol), $Pd(PPh_3)_4$ (0.91 g, 0.79 mmol), and a mixed solvent (160 mL, toluene/water/t-butanol (3:3:1, v/v/v))

were added in sequence under N2 atmosphere. The reaction system was heated to 80 ° C and stirred for 36 hours, After the reaction was completed, the reaction mixture was cooled to room temperature, the mixture was transferred to a separatory funnel, dichloromethane and water was added and the water phase was extracted using dichloromethane for three times, the organic layer solution was combined and dried with anhydrous sodium sulfate for two hours, the organic solvent was removed in a rotary evaporator to obtain the crude product. The crude product was purified by silica gel column chromatography (eluent: methanol/dichloromethane=1:100, v/v) to obtain a yellow solid CD2 (6.20 g, 72.1%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 8.83 (s, 4H), 8.77 (d, *J* = 4.3 Hz, 4H), 8.71 (d, *J* = 7.9 Hz, 4H), 8.06 (d, *J* = 8.2 Hz, 4H), 7.91 (t, *J* = 7.8 Hz, 5H), 7.85 (d, *J* = 8.4 Hz, 5H), 7.76 (d, *J* = 1.9 Hz, 1H), 7.53 (d, *J* = 1.3 Hz, 2H), 7.42-7.35 (m, 4H), 6.98 (d, *J* = 8.6 Hz, 1H), 4.28 (m, 4H), 3.98 (m, 4H), 3.83 (m, 4H), 3.77 (m, 4H), 3.69 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 165.10, 156.33, 156.09, 153.79, 152.15, 149.80, 149.24, 148.65, 142.70, 140.98, 138.01, 137.07, 127.98, 127.95, 125.01, 123.99, 122.16, 121.56, 119.89, 118.93, 115.16, 112.52, 71.52, 71.39, 71.28, 71.24, 71.16, 70.75, 69.79, 69.63, 69.54, 69.32.

HR-ESI-MS ($C_{67}H_{58}N_6O_9$): m/z calcd for $[M+H]^+$ = 1091.4338, found =1091.0872, error = 4.0 ppm.

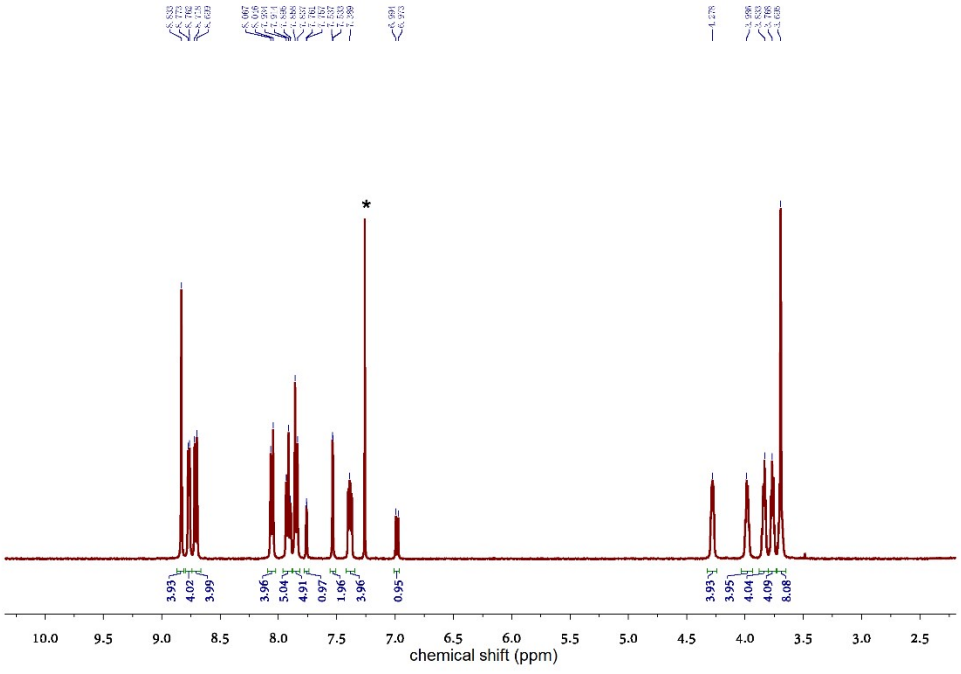


Fig. S29 The ^{1}H NMR of compound CD2 (400 MHz, $CDCl_3$, 298 K).

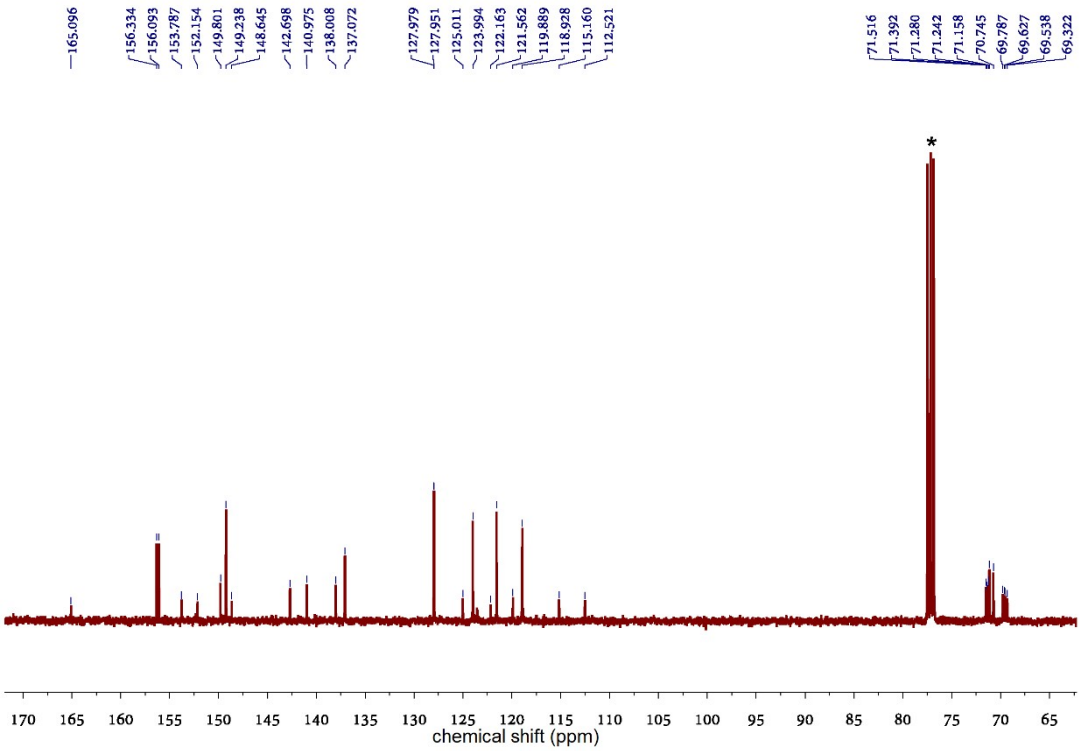


Fig. S30 The ^{13}C NMR of compound CD2 (100 MHz, $CDCl_3$, 298 K).

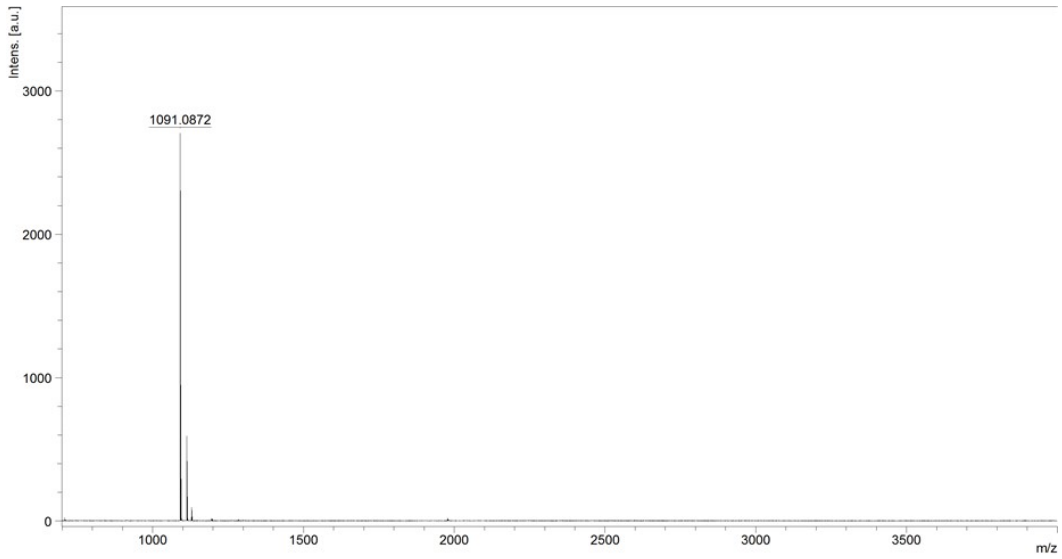


Fig. S31 The ESI-MS of compound CD2.

The synthesis of compound 4

2-acetyl-6-bromopyridine (5.00 g, 25 mmol), 2,6-dimethoxyphenylboronic acid (5.09 g, 28 mmol), potassium carbonate (6.91 g, 50 mmol), $Pd(PPh_3)_4$ (0.87 g, 0.75

mmol) were added to a 250 mL round bottom flask, solvents (160 mL of 1,4-dioxane/water (3:1, v/v)) was then added. The reaction system was heated to 80 °C and stirred for 12 hours. After the reaction was completed and cooled down to room temperature, the mixture was transferred to a dispensing funnel, water was added into the system, the reaction mixture was extracted using dichloromethane for three times, the organic phases were combined and dried with anhydrous sodium sulfate, the sodium sulfate was then filtered, and the organic solvent was removed in a rotary evaporator to obtain the crude product. The crude product was purified by silica gel column chromatography (eluent: pure dichloromethane) to obtain a yellow solid as compound 4 (5.50 g, 85.52%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 7.98 (d, J = 7.8 Hz, 1H), 7.84 (t, J = 7.7 Hz, 1H), 7.48 (d, J = 7.7 Hz, 1H), 7.36 (t, J = 8.4 Hz, 1H), 6.69 (d, J = 8.4 Hz, 2H), 3.75 (s, 6H), 2.73 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 200.79, 158.24, 153.84, 153.11, 136.44, 130.17, 129.96, 119.77, 118.45, 104.67, 56.18, 26.14.

HR-ESI-MS ($C_{15}H_{15}NO_3$): m/z calcd for $[M+Na]^+$ = 280.0944, found =280.0943, error = 0.1 ppm.

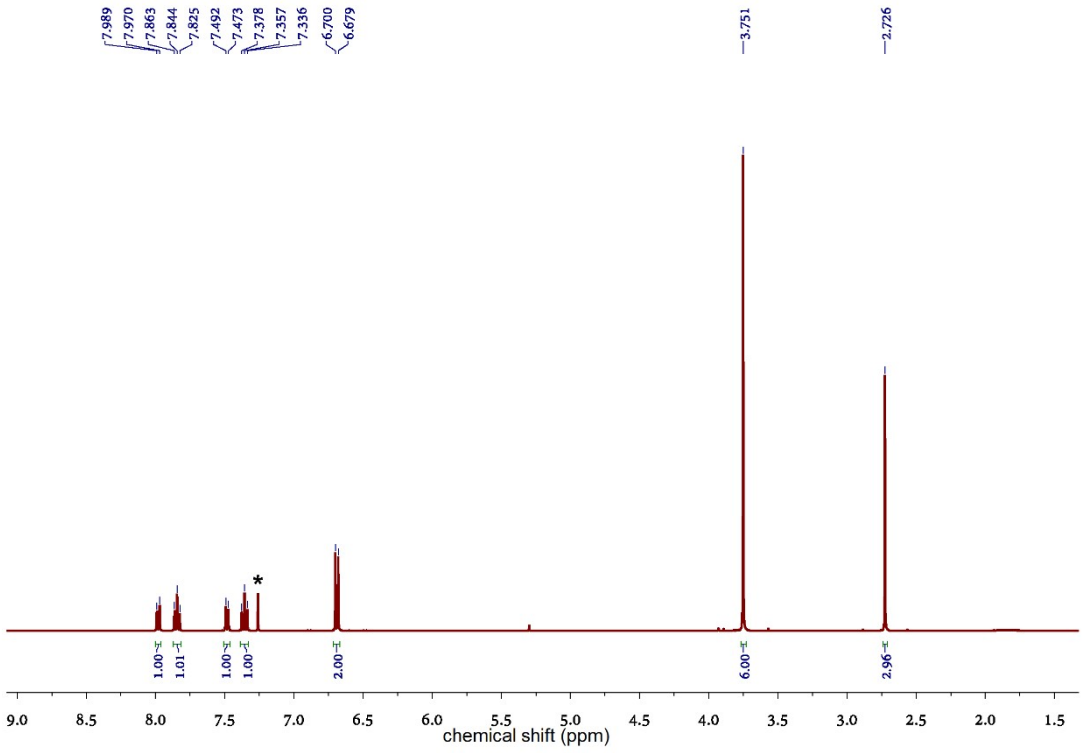


Fig. S32 The ^{1}H NMR of compound 4 (400 MHz, $CDCl_3$, 298 K).

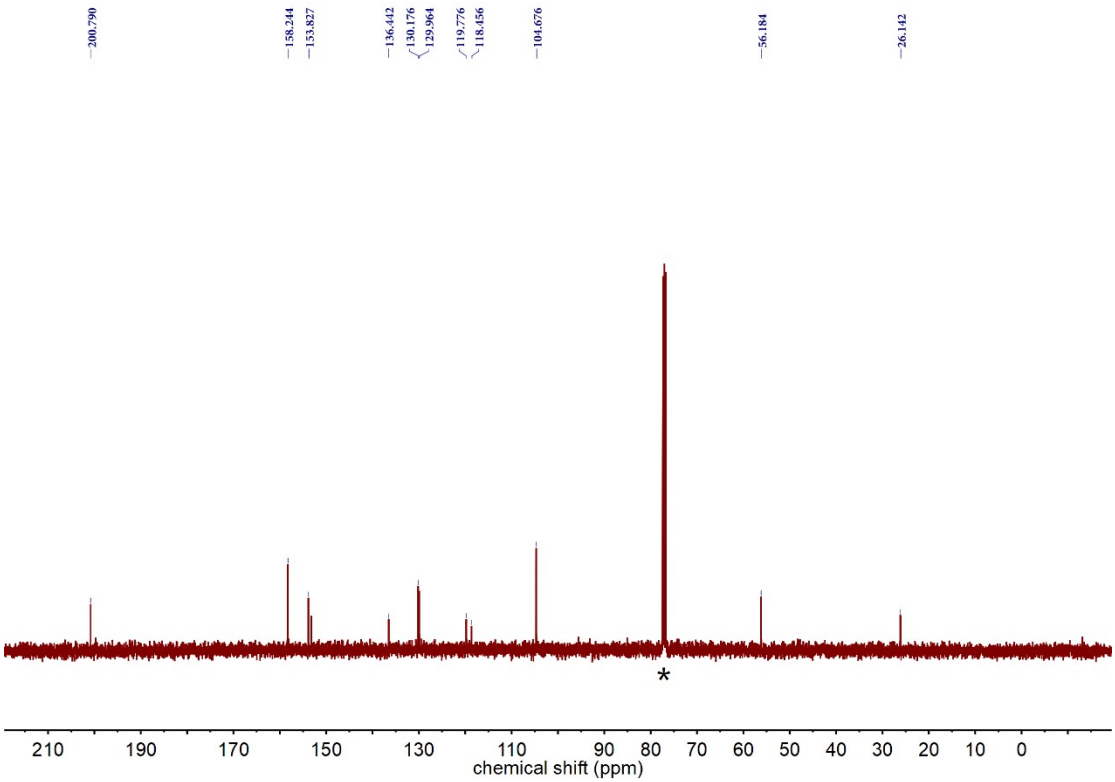


Fig. S33 The ^{13}C NMR of compound 4 (100 MHz, $CDCl_3$, 298 K).

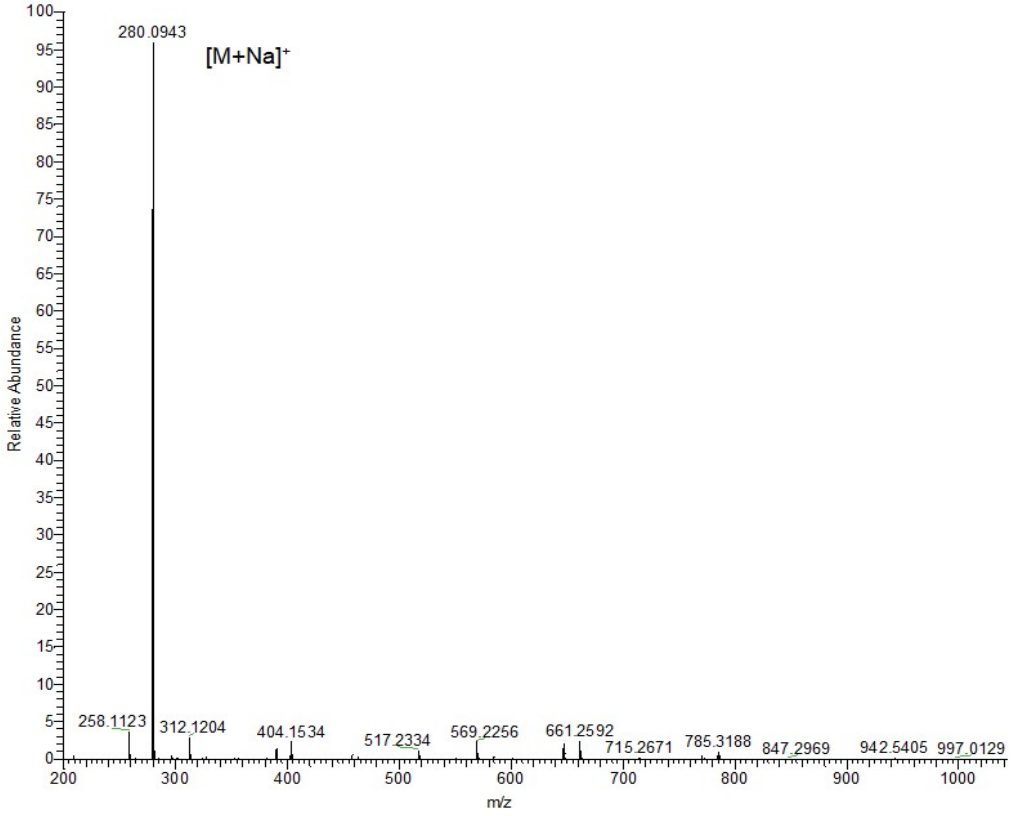


Fig. S34 The ESI-MS of compound 4.

The synthesis of compound 5

In a 100 mL beaker, solid sodium hydroxide (1.06 g, 26.6 mmol) was dissolved in a small amount of water and the solution was cooled to room temperature and set aside. Then, compound 4 (6 g, 23.27 mmol), 4-bromobenzaldehyde (2.05 g, 11.08 mmol), and ethanol (130 mL) were sequentially added to a 250 mL round-bottomed flask, and the reaction solution was stirred for 15 min at 5 °C. The previously prepared sodium hydroxide solution was then slowly added to the reaction mixture. The reaction solution was continuously stirred at room temperature for 24 h. Then 30 ml of ammonia solution at a concentration of 28 wt% was added to the solution and the reaction system was heated to 55 °C. The reaction mixture was stirred at 55 °C for 12 hours. At the end of the reaction, the reaction solution was cooled to room temperature and the suspension was transferred to a sand core funnel for filtration to obtain a residue, and the residue was washed with ethanol. Finally, the residue was dried in a vacuum drying oven to obtain the white solid compound 5 (3.71 g, 50.6%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 8.66 (s, 2H), 8.62 (d, J = 7.8 Hz, 2H), 7.93 (t, J = 7.8 Hz, 2H), 7.70 (d, J = 8.5 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H), 7.38 (t, J = 7.5 Hz, 4H), 6.73 (d, J = 8.4 Hz, 4H), 3.79 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 158.45, 156.42, 153.81, 140.65, 137.32, 131.89, 128.99, 125.71, 118.95, 104.77, 56.21.

HR-ESI-MS ($C_{15}H_{15}NO_3$): m/z calcd for $[M+Na]^+$ = 280.0944, found =280.0943, error = 0.1 ppm.

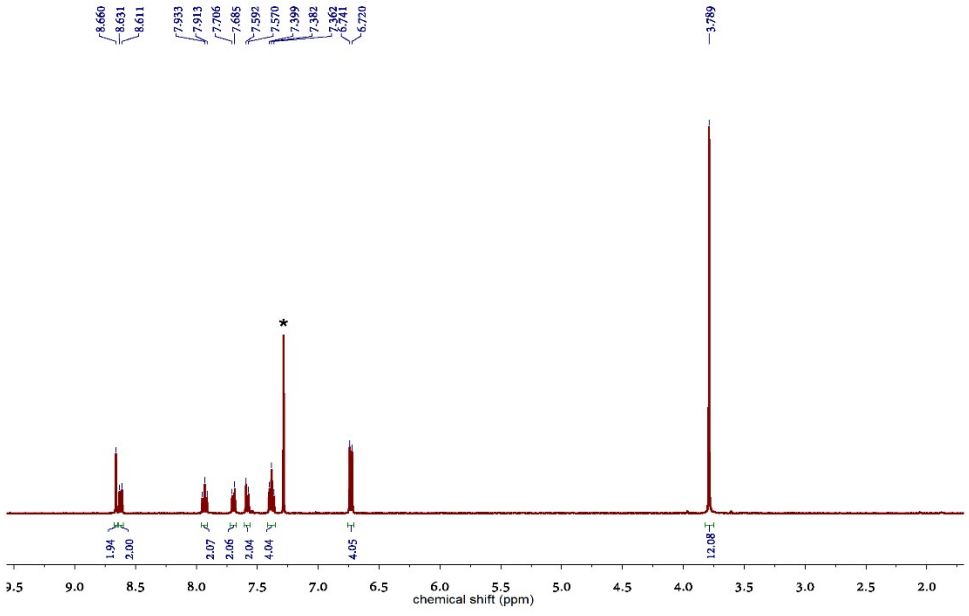


Fig. S35 The ^{1}H NMR of compound 5 (400 MHz, $CDCl_3$, 298 K).

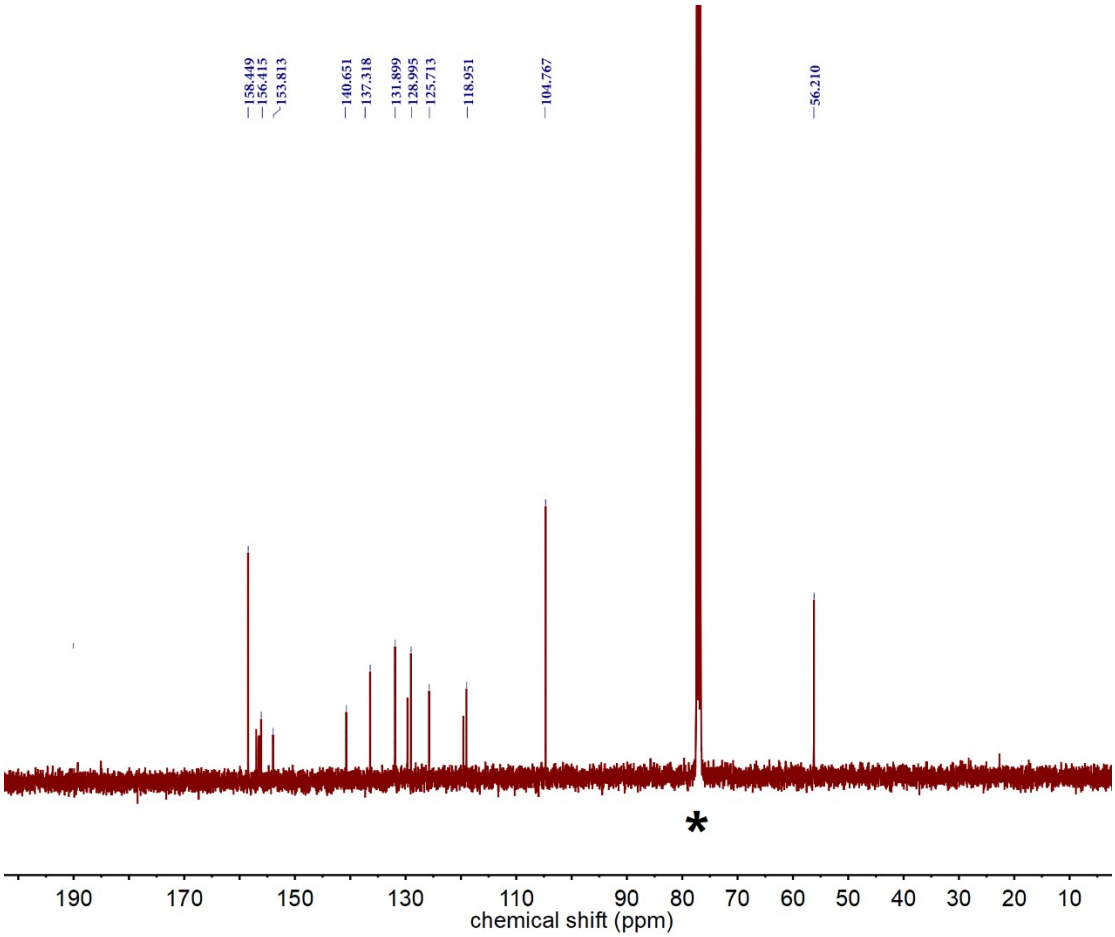


Fig. S36 The ^{13}C NMR of compound 5 (100 MHz, $CDCl_3$, 298 K).

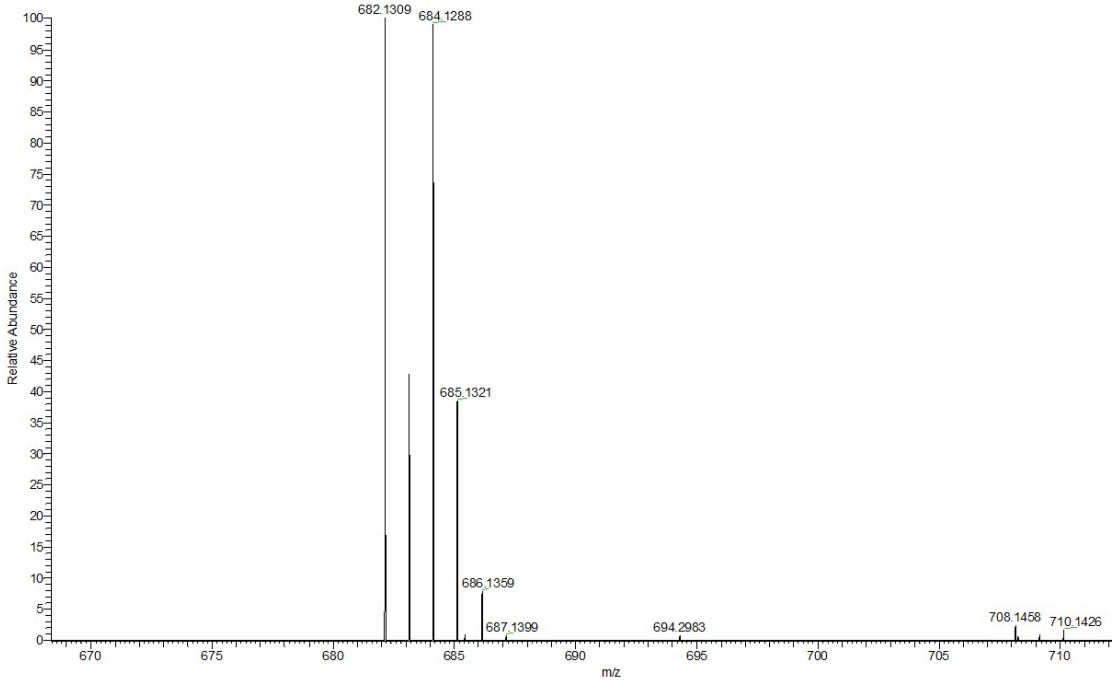


Fig. S37 The ESI-MS of compound 5.

The synthesis of compound 6

In a 250 mL round bottomed flask, compound 5 (2.00 g, 3.0 mmo1), bis(pinacolato)diboron (1.00 g, 3.9 mmo1), potassium acetate (0.89 g, 9.1 mmo1), Pd(dppf)Cl_2 (0.33 g, 0.45mmo1), and anhydrous dimethyl sulfoxide (150 mL) were added sequentially at N2 atmosphere, the reaction mixture was heated to 80 ℃ and stirred for 18 hours. After the reaction was completed, the reaction mixture was cooled down to room temperature, water was added to the reaction mixture and the water phase was extracted using dichloromethane for three times, the organic phases were combined and dried with anhydrous sodium sulfate. After the sodium sulfate was filtered, the organic solvent was removed in a rotary evaporator to obtain the crude product. The crude product was purified by silica gel column chromatography (eluent: tetrahydrofuran/dichloromethane=1:200, v/v) to give a white solid as compound 6 (1.81 g, 84%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 8.73 (s, 2H), 8.61 (d, *J* = 8.8 Hz, 2H), 7.96-7.84 (m, 6H), 7.42-7.36 (m, 4H), 6.73 (d, *J* = 8.4 Hz, 4H), 3.80 (s, 12H), 1.39 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 158.41, 156.14, 153.77, 138.92, 135.19, 129.72, 126.68, 126.33, 119.63, 104.74, 83.89, 56.24, 24.92.

HR-ESI-MS ($C_{43}H_{42}BN_3O_6$): m/z calcd for $[M+H]^+$ = 708.3239, found =708.3240, error = 0.1 ppm.

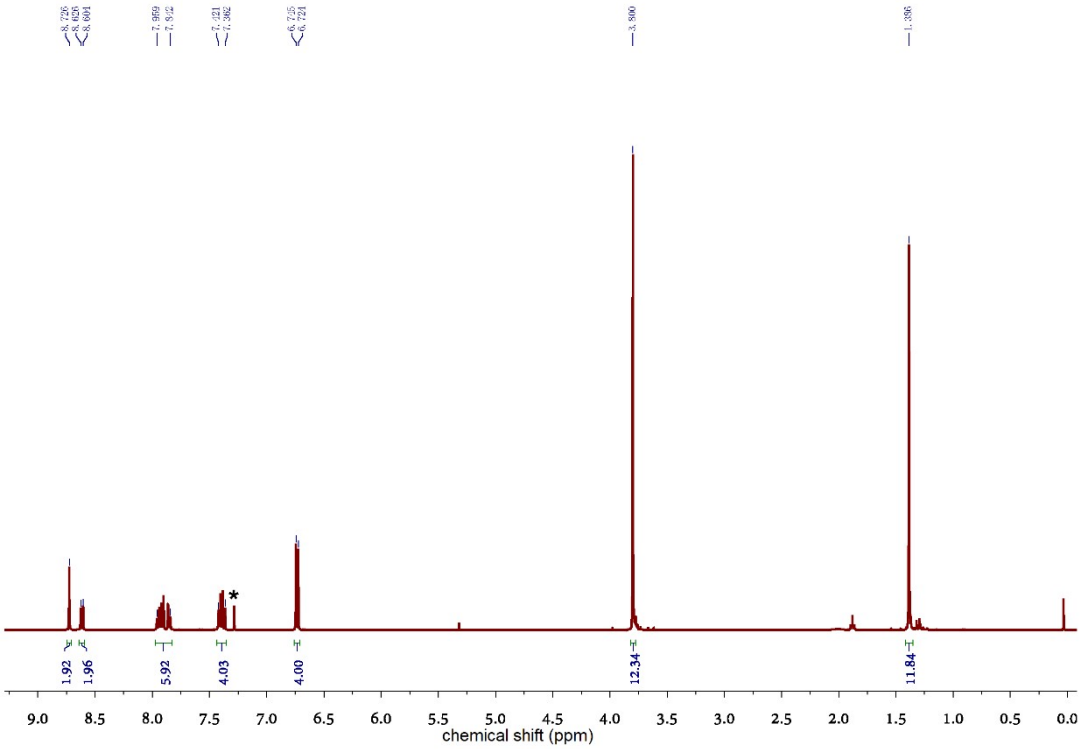


Fig. S38 The ^{1}H NMR of compound 6 (400 MHz, $CDCl_3$, 298 K).

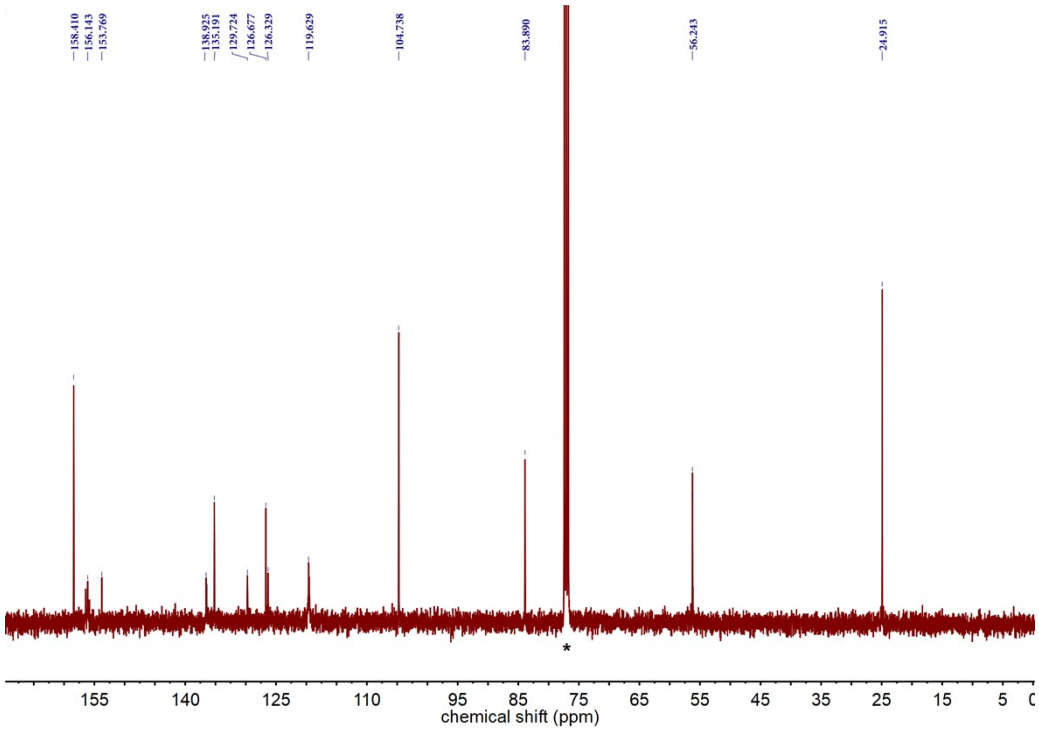


Fig. S39 The ^{13}C NMR of compound 6 (100 MHz, $CDCl_3$, 298 K).

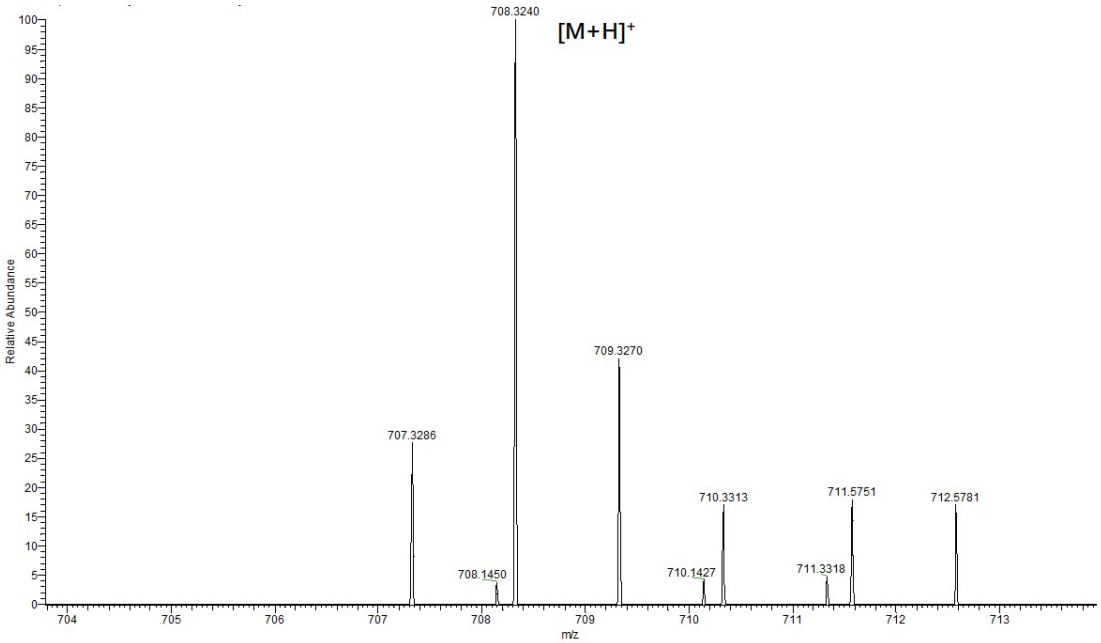


Fig. S40 The ESI-MS of compound 6.

The synthesis of compound E2

In a 250 mL round bottom flask, compound 6 (1.00 g, 1.5 mmol), compound 5 (1.61 g, 2.3 mmol), sodium carbonate (1.40 g, 13.6 mmol), $Pd(PPh_3)_4$ (0.22 g, 0.3 mmol), and 120ml mixed solvent (dimethyl sulfoxide/water (5:1, v/v)) were added sequentially under N2 atmosphere. the reaction system was heated up to 80 °C and stirred for 20 hours. After the reaction was completed and cooled to room temperature, the mixture was transferred to a partition funnel, water was added to the reaction mixture and the water phase was extracted using dichloromethane for three times, the organic phases were combined and dried with anhydrous sodium sulfate. After the sodium sulfate was filtered, the organic solvent was removed in a rotary evaporator to obtain the crude product. The crude product was purified by silica gel column chromatography (eluent: tetrahydrofuran/dichloromethane=1:100, v/v) to give the yellow solid as compound E2 (0.91 g, 51.2%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 8.58 (d, J = 7.6 Hz, 4H), 8.43 (s, 4H), 7.93 (t, J = 7.8 Hz, 4H), 7.40-7.30 (m, 12H), 6.67 (d, J = 8.4 Hz, 8H), 6.61 (d, J = 8.5 Hz, 4H), 3.73 (s, 24H).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 158.63, 154.21, 137.04, 130.12, 128.47, 126.65, 120.39, 119.29, 116.09, 104.80, 68.28, 56.06.

MALDI-TOF-MS ($C_{74}H_{60}N_6O_8$): m/z calcd for $[M]^+$ = 1161.3280, found =1161.3298, error = 2.0 ppm.

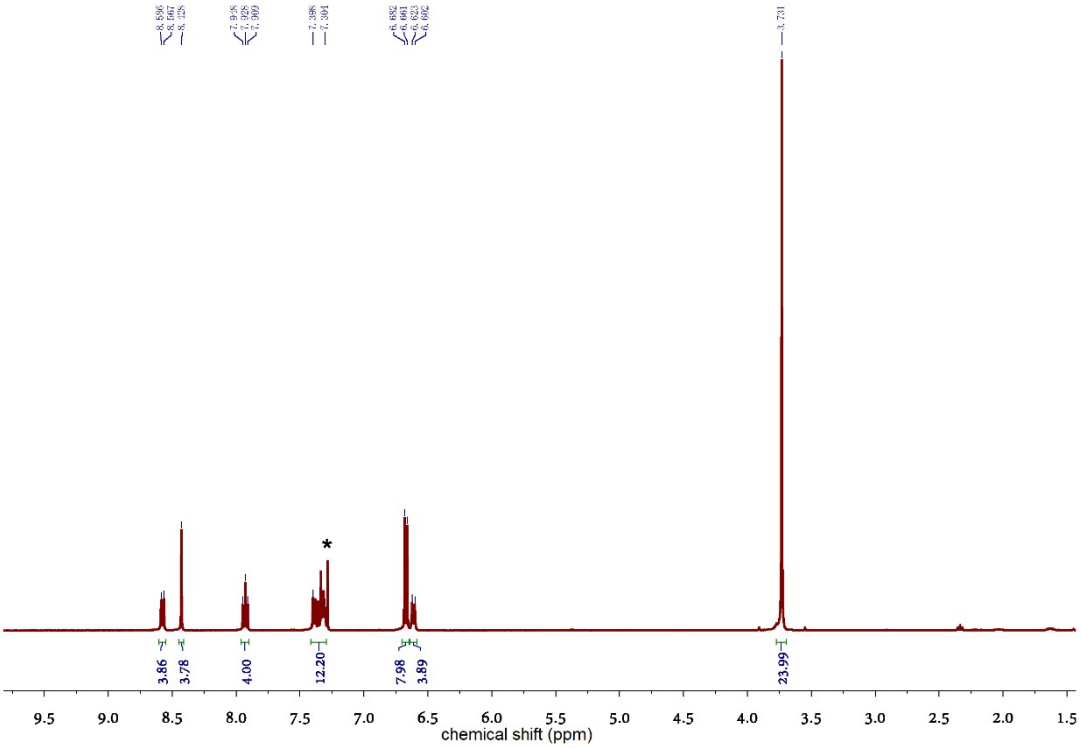


Fig. S41 The ^{1}H NMR of monomer E2 (400 MHz, $CDCl_3$, 298 K).

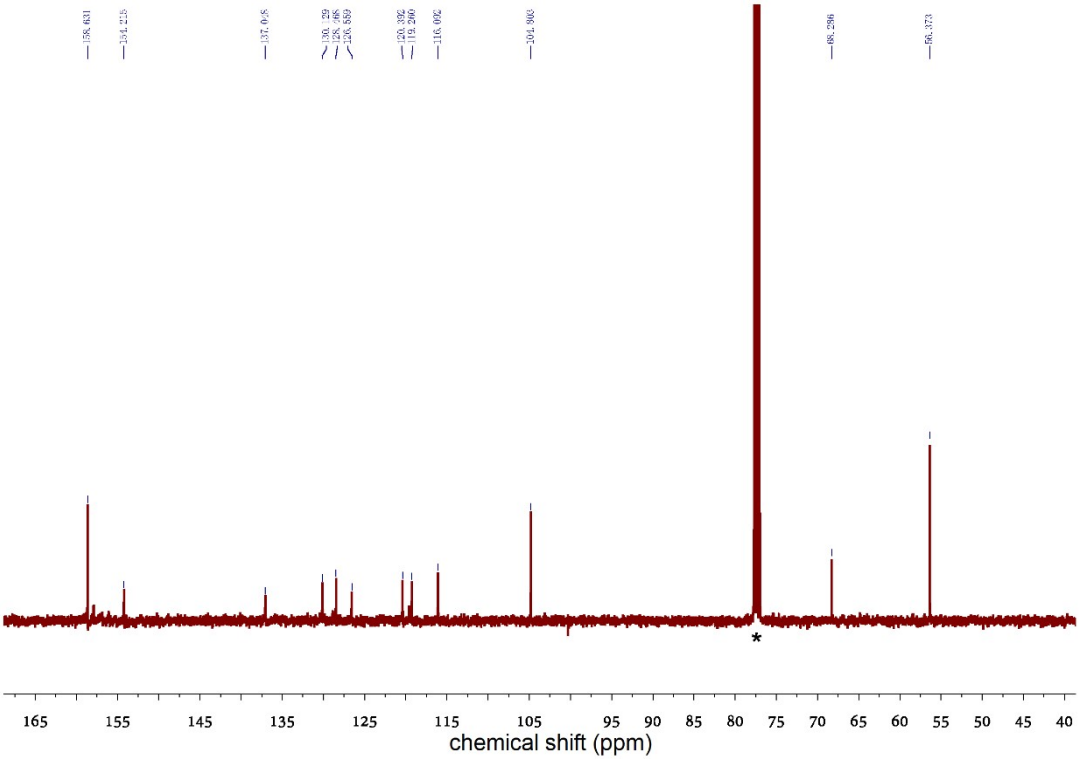


Fig. S42 The ^{13}C NMR of monomer E2 (400 MHz, $CDCl_3$, 298 K).

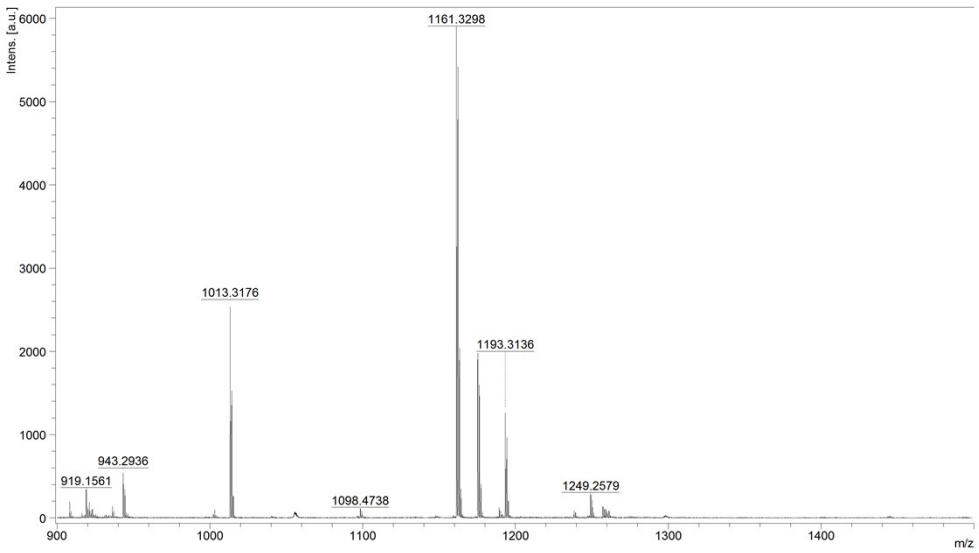


Fig. S43 The ESI-MS of monomer E2.

References:

S1: Likussar, W., and Boltz, D.F. Theory of continuous variations plots and a new method for spectrophotometric determination of extraction and formation constants. *Anal. Chem*. 1971, **43**, 1265–1272.

S2: Zhang, C. J.; Li, S. J.; Zhang, J. Q.; Zhu, K. L.; Li, N.; Huang, F. H. Benzo-21-Crown-7/Secondary Dialkylammonium Salt [2]Pseudorotaxane- and [2]Rotaxane-Type Threaded Structures, Org. Lett., 2007, **9**, 5553–5556.