

# Controllable supramolecular assembly and architecture transformation by the combination of orthogonal self-assembly and competitive self-sorting assembly

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## Supporting information

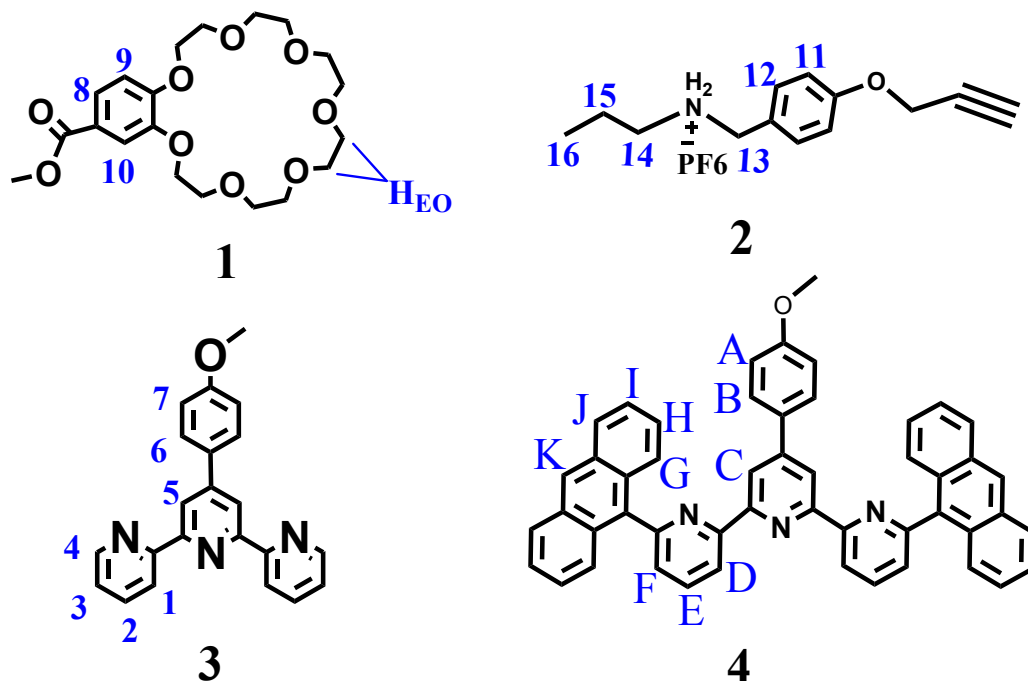
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## 1. Materials and methods

Compound 1<sup>[S1]</sup>, 2<sup>[S1]</sup>, 3<sup>[S2]</sup>, 4<sup>[S2]</sup>, M6<sup>[S2]</sup>, M7<sup>[S2]</sup>, M9<sup>[S2]</sup> were synthesized according to the literature procedure. The other reagents and solvents were either employed as purchased or dried prior to use by usual laboratory methods. Column chromatography was performed on silica gel (200-300 mesh). All reactions were carried out in atmosphere unless noted. 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. MALDI-TOF-MASS spectrometry was performed on a AXIMA-CFR plus mass spectrometer. Viscosity measurements were carried out with Ubbelohde micro viscometers (Shanghai Liangjing Glass Instrument Factory, 0.40 mm inner diameter) at 298 K in chloroform/acetonitrile (3/1, v/v). Transmission electron microscope (TEM) experiments were carried out on a FE-SEM S-4800 instrument. Dynamic light scattering (DLS) measurements were carried out on a Brookhaven BI-9000AT system (Brookhaven Instruments Corporation, USA), using a 200-mW polarized laser source ( $\lambda = 630$  nm).

## 2. Orthogonal complexation and self-sorting complexation studies

### using model compounds 1–4

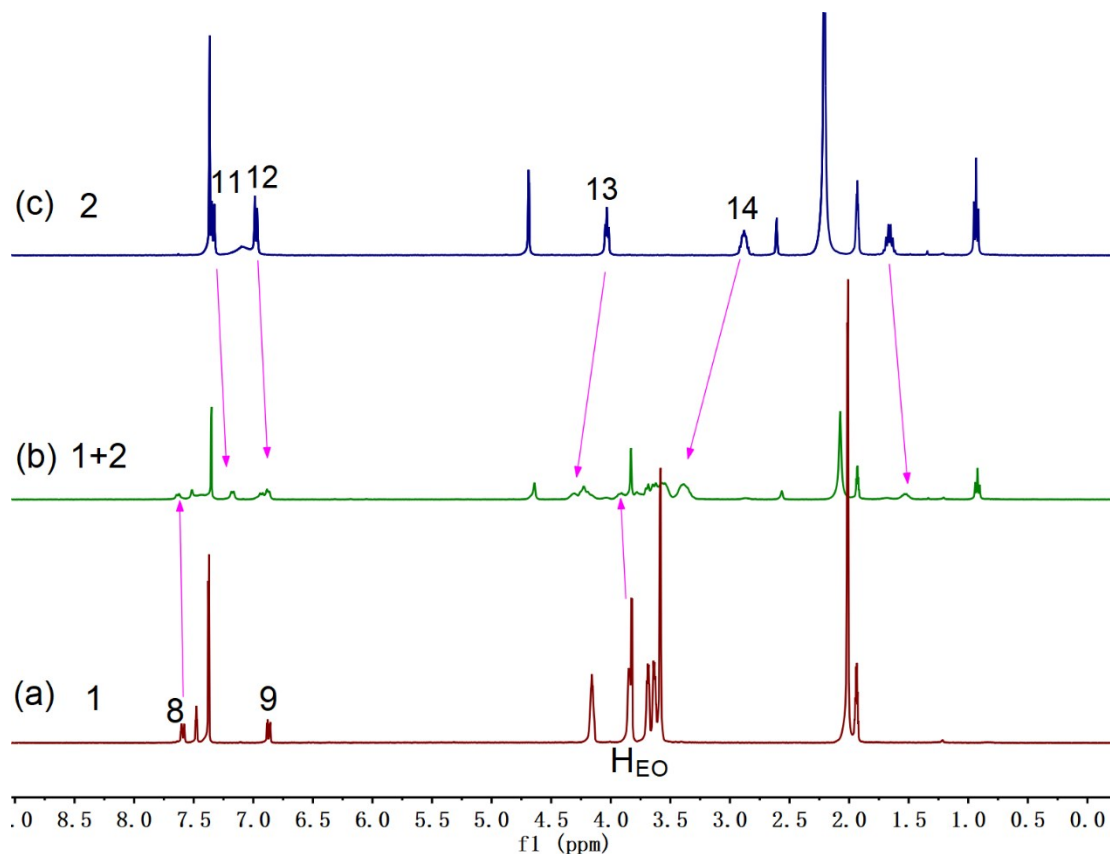


Scheme S1 chemical structures of model compounds 1-4.

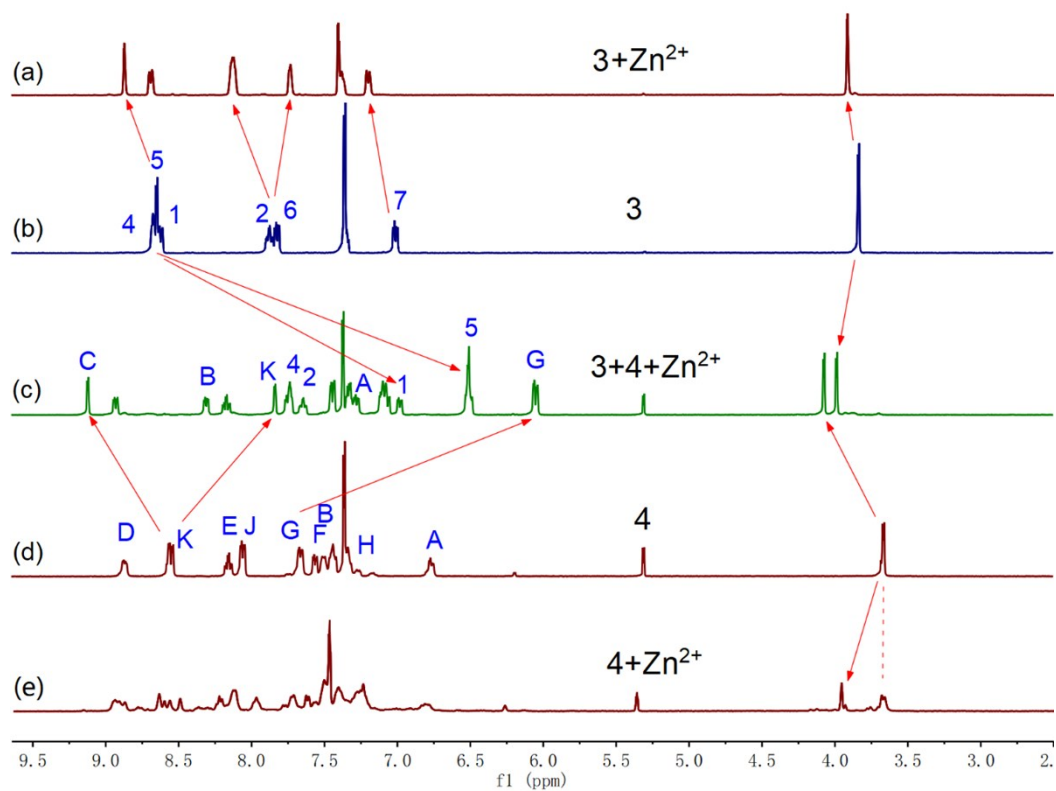
To investigate whether the synthetic three monomers AB, AE, and D<sub>2</sub> can assemble to form supramolecular polymers by orthogonal binding interaction or self-sorting complexation. We prepared four model compounds 1-4 to study the non-covalent interactions in CDCl<sub>3</sub>/CD<sub>3</sub>CN (3:1,

v/v). Firstly, a series of solutions containing two model compounds were prepared and their proton NMR spectra were recorded (Fig. S1–S2). When equimolar **1** and **2** were mixed in CDCl<sub>3</sub>-CD<sub>3</sub>CN (3:1, v/v), a complex <sup>1</sup>H NMR spectrum was observed, the signals of protons 11, 12 of compound **2** were all split into two sets of peaks (Fig. S1), corresponding to uncomplexed monomers and complexed monomers, which reflected the slow-exchange complexation between the B21C and secondary ammonium salt moieties.<sup>[S3]</sup> the metal coordination interaction of **3** with zinc ion was also investigated, as shown in Fig. S2 a-b, peak shifts were observed when zinc ion was added into the solution of **3**, indicating the formation of metal coordination tpy-Zn<sup>2+</sup>-tpy between terpyridyl group and zinc ion. Furthermore, the <sup>1</sup>H NMR spectrum of a mixed solution of equimolar **1**, **2**, **3**, and Zn(OTf)<sub>2</sub> clearly showed that orthogonal noncovalent interactions between **1** and **2** and between **3** and zinc ion occurred (Fig. S3).

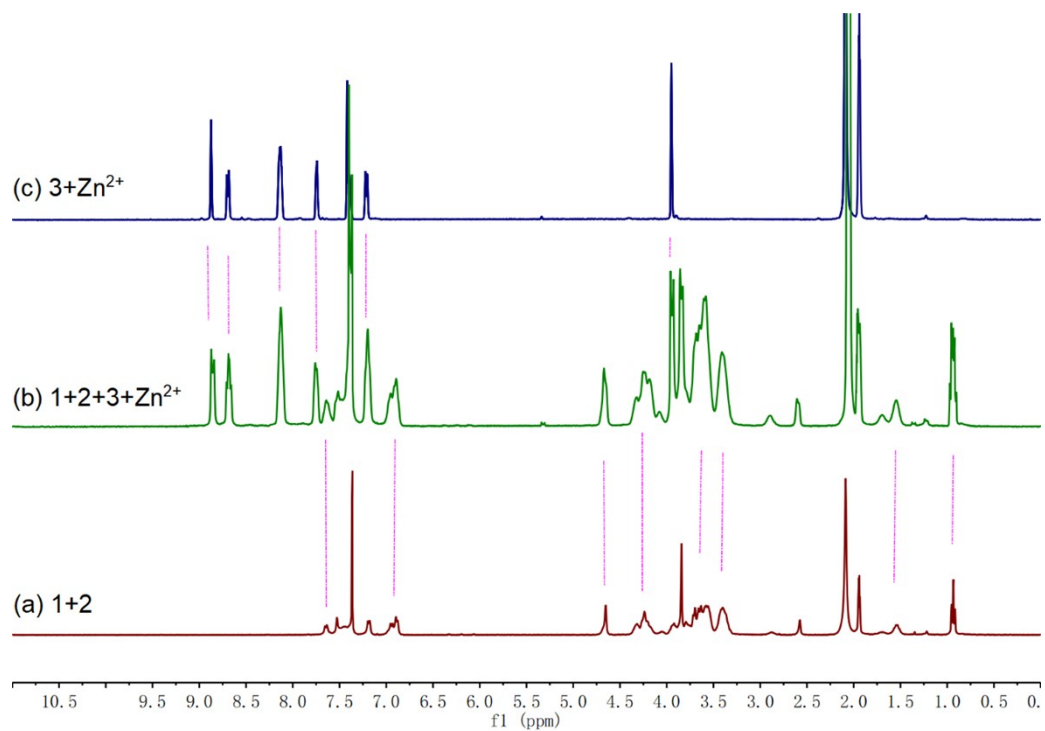
On the other hand, the metal coordination interaction of **4** and zinc ion was also investigated. As shown in Fig. S2e, in comparison with [Zn<sub>3</sub>], the formation ratio for [Zn<sub>4</sub>] was much slower, and an incomplete conversion (58%) was observed, presumably due to the increased bulkiness of the substituents at terpyridinyl 6,6''-positions.<sup>[S2]</sup> Next, we investigated the competitive self-sorting interaction by adding **4** into the [Zn<sub>3</sub>] solution or 1+2+3+Zn(OTf)<sub>2</sub> solution. When **4** was added into the [Zn<sub>3</sub>] solution, as shown in Figure S2c, <sup>1</sup>H NMR peak shifts were observed and the new chemical shifts of protons are similar to the previous report by Chan's group,<sup>[S2]</sup> verifying the disassembly of the original [Zn<sub>3</sub>] structure and the formation of new [Zn<sub>3</sub>4] structure. The experiment result also verified that the complementary tpy-based ligand pair could undergo spontaneous heteroleptic complexation to form tpy-Zn<sup>2+</sup>-tey in the presence of Zn<sup>2+</sup> ion. Finally, the <sup>1</sup>H NMR spectrum of a mixed solution of 1+2+3+4+Zn(OTf)<sub>2</sub> clearly showed that the self-sorting complexation between **1** and **2** and among **3**, **4**, and zinc ions occurred (Figure S4).



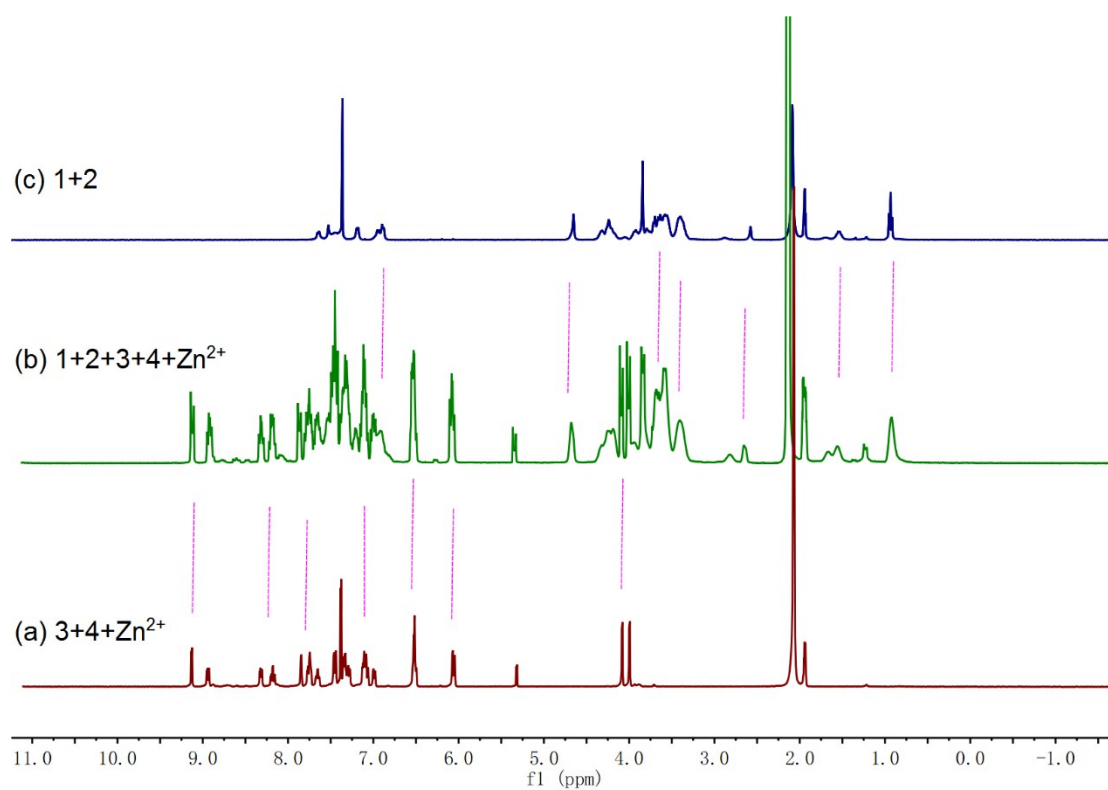
**Fig. S1**  $^1\text{H}$  NMR spectra (400 MHz, chloroform- $d_3$ /acetonitrile- $d_3$ (3/1, v/v), 298 K) of (a) **1**, (b) an equimolar solution of **1** and **2**, (c) **2**



**Fig. S2**  $^1\text{H}$  NMR spectra (400 MHz, chloroform- $d_3$ /acetonitrile- $d_3$ (3/1, v/v), 298 K) of (a) 2:1 molar ratio of  $3+\text{Zn}(\text{OTf})_2$ , (b) **3**, (c) 2: 2 : 1 molar ratio of  $3+4+\text{Zn}(\text{OTf})_2$ , (d) **4**, (e) 2:1 molar ratio of  $4+\text{Zn}(\text{OTf})_2$ .

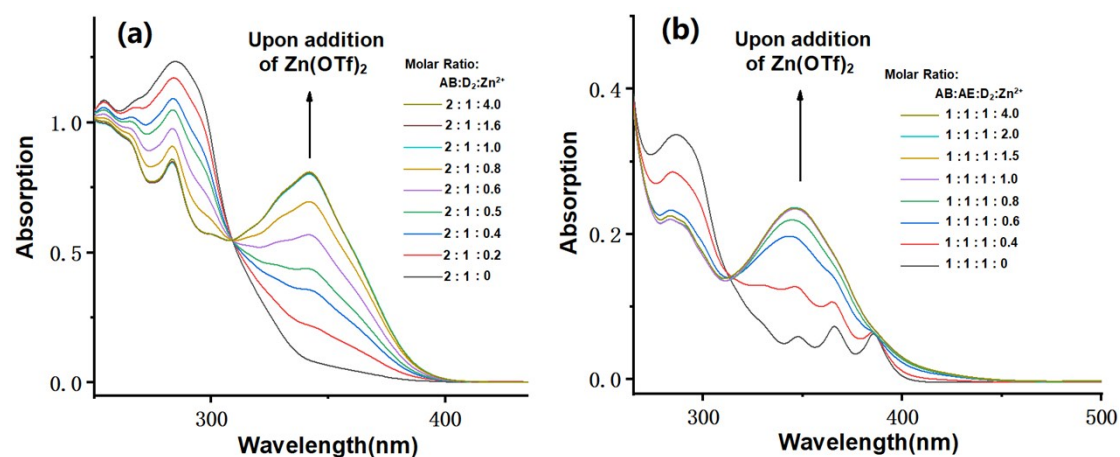


**Fig. S3**  $^1\text{H}$  NMR spectra (400 MHz, chloroform- $d_3$ /acetonitrile- $d_3$ (3/1, v/v), 298 K) of (a) 1: 1 molar ratio of 1+2, (b) 2 : 2 : 2: 1 molar ratio of 1+2+3+ $\text{Zn}(\text{OTf})_2$ , (c) 2 : 1 molar ratio of 3+ $\text{Zn}(\text{OTf})_2$ .



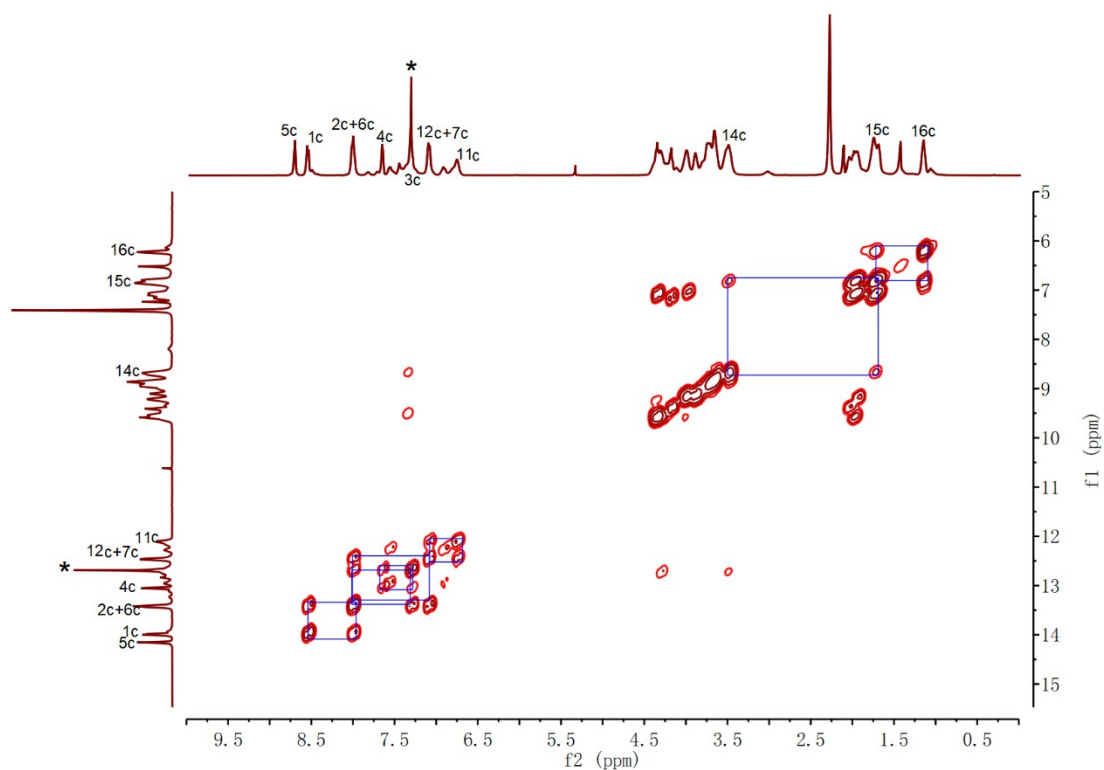
**Fig. S4**  $^1\text{H}$  NMR spectra (400 MHz, chloroform- $d_3$ /acetonitrile- $d_3$ (3/1, v/v), 298 K) of (a) an equimolar 3+4+ $\text{Zn}(\text{OTf})_2$ , (b) an equimolar 1+2+3+4+ $\text{Zn}(\text{OTf})_2$ , (c) an equimolar 1+2.

### 3. UV/Vis titration

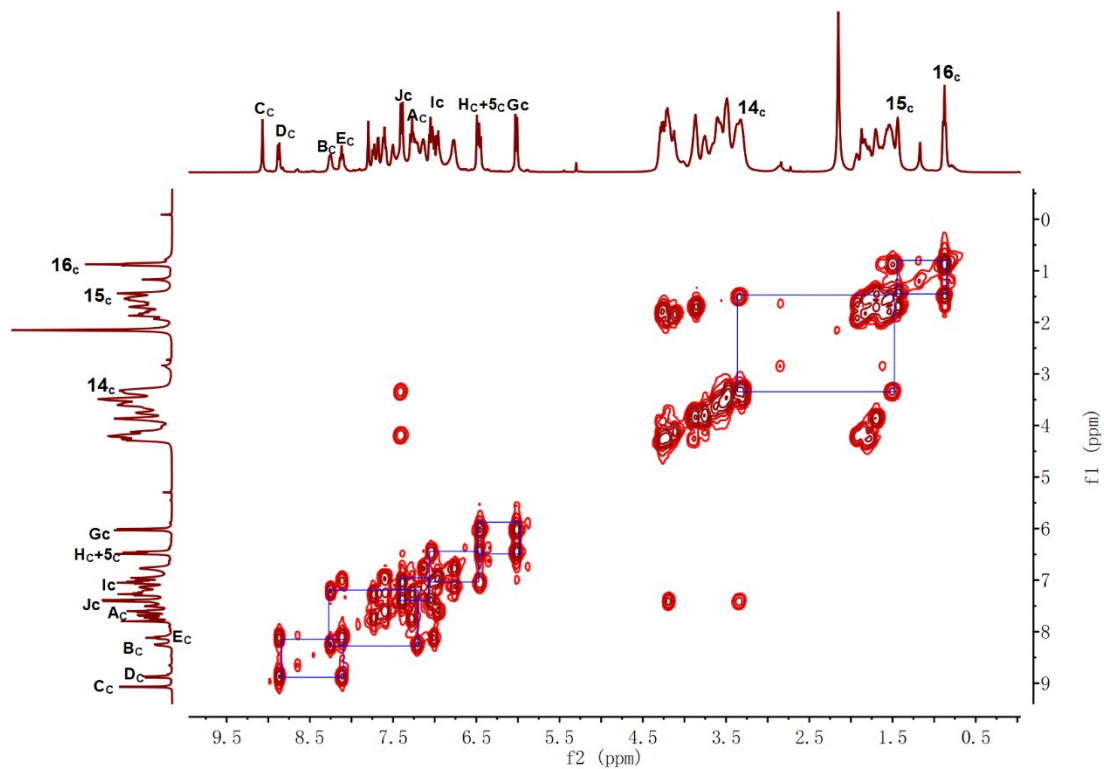


**Fig. S5** Change in the UV/Vis absorption spectra upon stepwise addition of  $\text{Zn}(\text{OTf})_2$  (1.0mM in  $\text{CHCl}_3$ - $\text{CH}_3\text{CN}$  (3/1, v/v)) to a 0.05mM solution of (a) AB+ $\text{D}_2$ , (b)AB+AE+ $\text{D}_2$  in  $\text{CHCl}_3$ - $\text{CH}_3\text{CN}$  (3/1, v/v).

## 4. 2D COSY NMR and NOESY NMR spectra

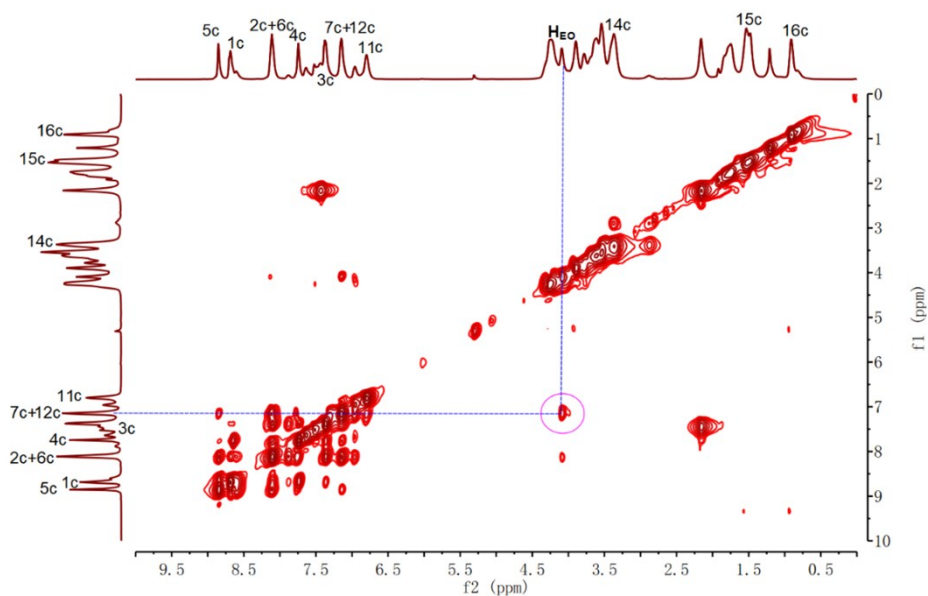


**Fig. S6**  $^1\text{H}$ - $^1\text{H}$  COSY NMR (400 MHz,  $\text{CDCl}_3$ - $\text{CD}_3\text{CN} = 3/1$ , v/v, 298 K, 40mM) spectrum of a solution of AB,  $\text{D}_2$ , and  $\text{Zn}(\text{OTf})_2$ .

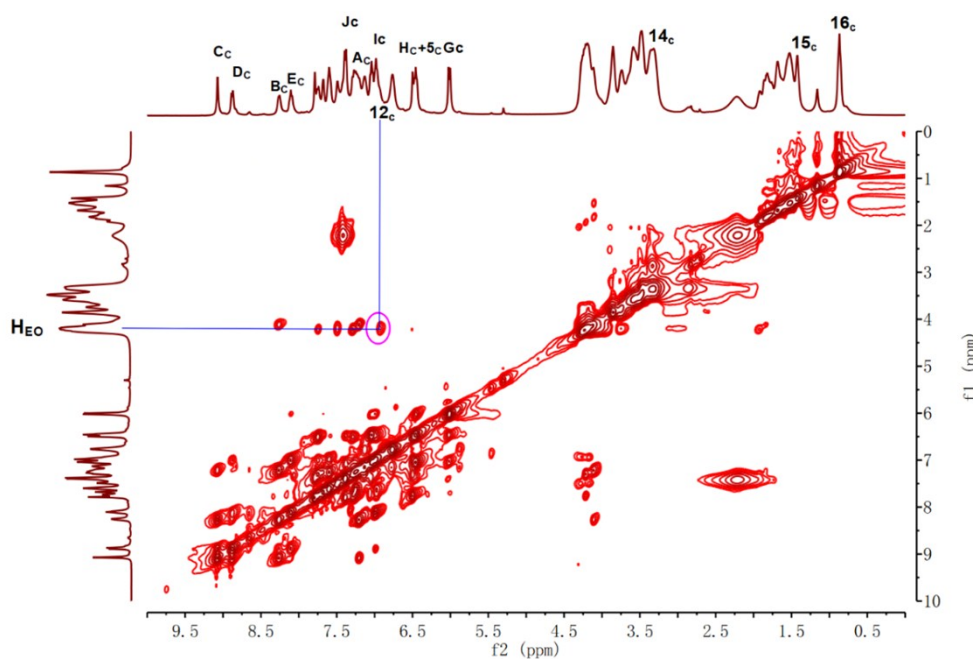


**Fig. S7**  $^1\text{H}$ - $^1\text{H}$  COSY NMR (400 MHz,  $\text{CDCl}_3$ - $\text{CD}_3\text{CN} = 3/1$ , v/v, 298 K, 40mM) spectrum of a solution of AB, AE,  $\text{D}_2$ , and  $\text{Zn}(\text{OTf})_2$ .

NOESY NMR experiments were also performed to study the host-guest complexation of B21C-DAS, the strong correlation between proton 12 from DAS and proton  $\text{H}_{\text{EO}}$  from B21C were both observed for the two systems (Fig. S8, S9), supporting the complexation between B21C and DAS.



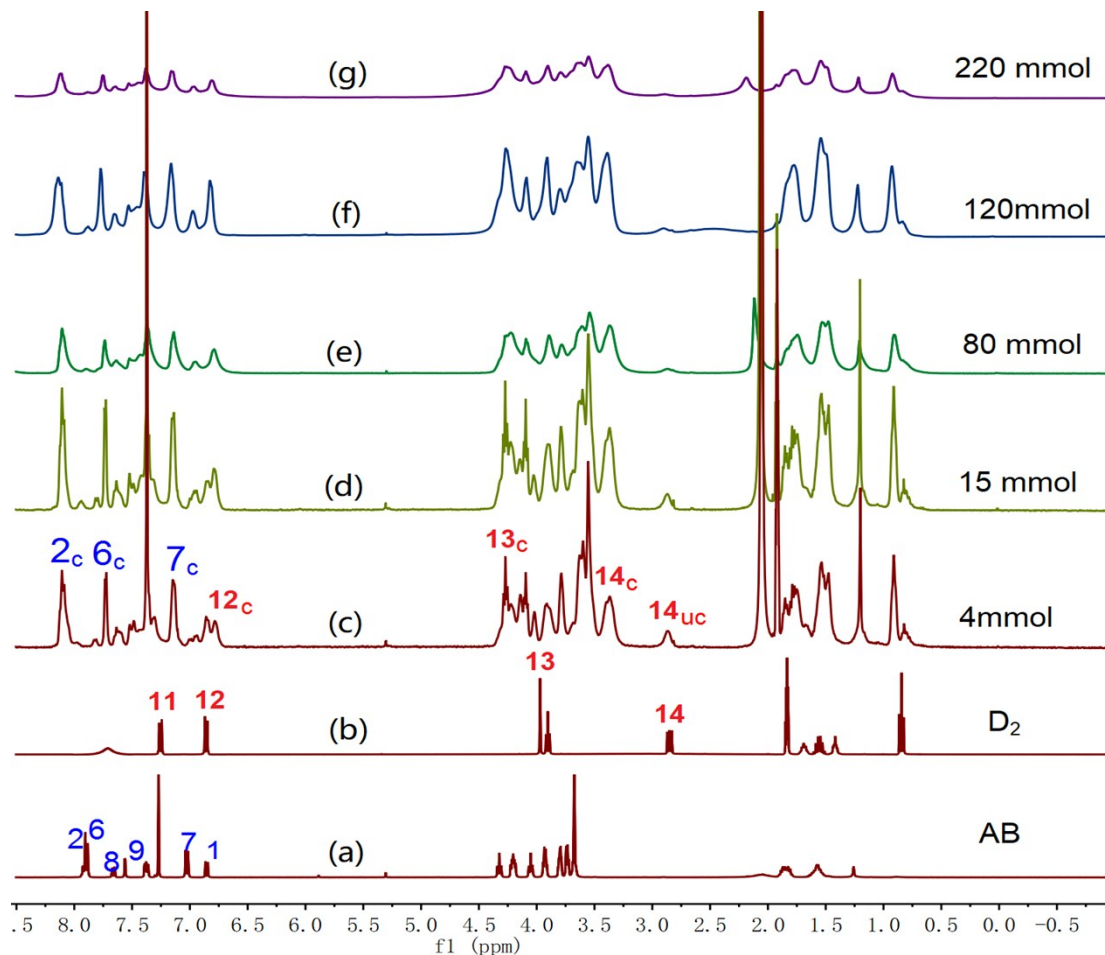
**Fig. S8** NOESY NMR (400 MHz,  $\text{CDCl}_3$ - $\text{CD}_3\text{CN} = 3/1$ , v/v, 298 K, 40mM) spectrum of a solution of AB,  $\text{D}_2$ , and  $\text{Zn}(\text{OTf})_2$ . the strong correlation between 12c from  $\text{D}_2$  and  $\text{H}_{\text{EO}}$  from AB indicated that the dialkylammonium moiety of  $\text{D}_2$  was complexed tightly with the B21C moiety of AB in the mixed solvent.



**Fig. S9** NOESY NMR (400 MHz,  $\text{CDCl}_3$ - $\text{CD}_3\text{CN} = 3/1$ , v/v, 298 K, 40mM) spectrum of a solution of AB, AE,  $\text{D}_2$ ,

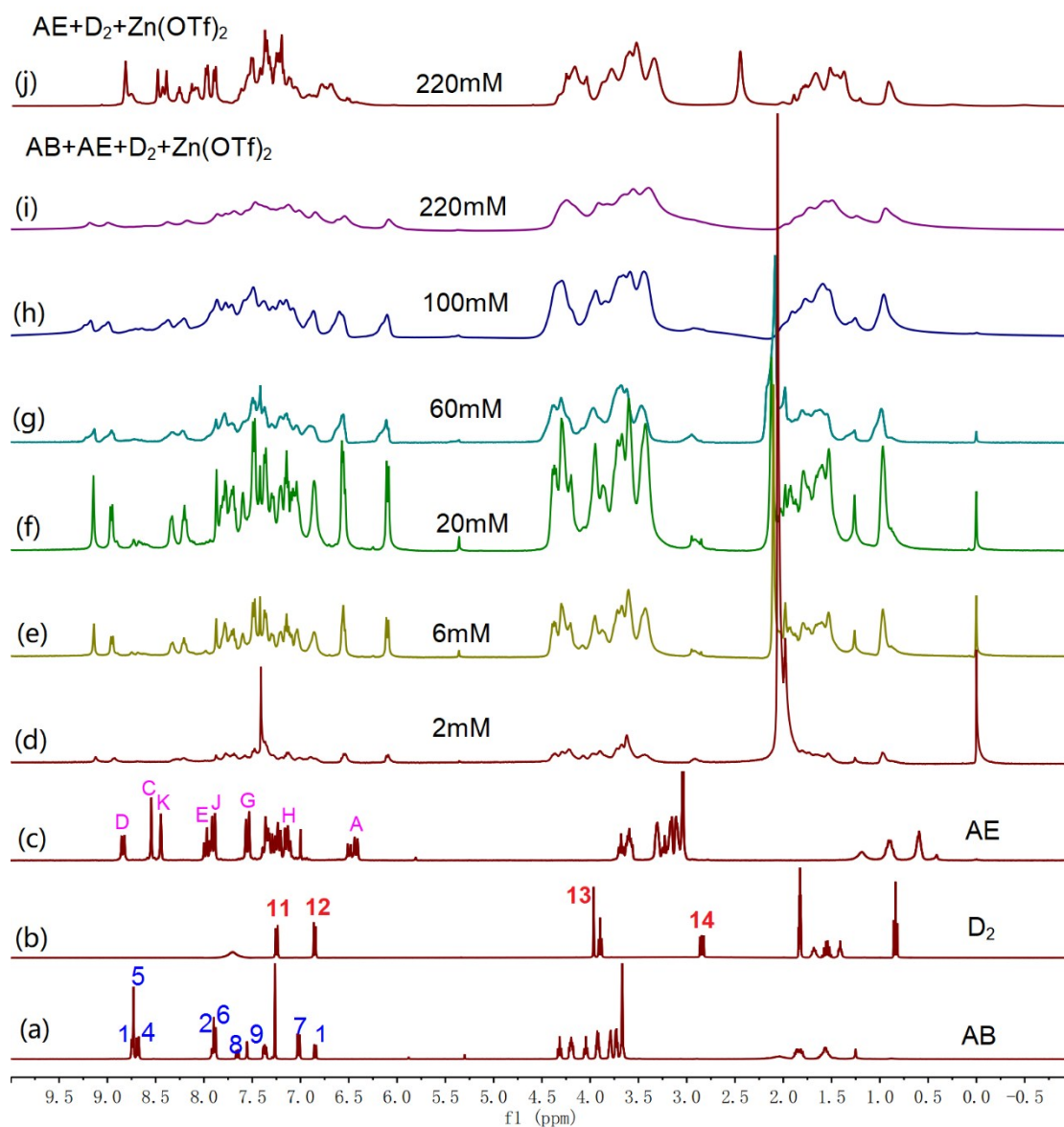
and  $\text{Zn}(\text{OTf})_2$ . the strong correlation between  $12_c$  from  $\text{D}_2$  and  $\text{H}_{\text{EO}}$  from AB and AE indicated that the dialkylammonium moiety of  $\text{D}_2$  was complexed tightly with the B21C moiety of AB and AE in the mixed solvent.

## 5. Concentration-dependent $^1\text{H}$ NMR spectra



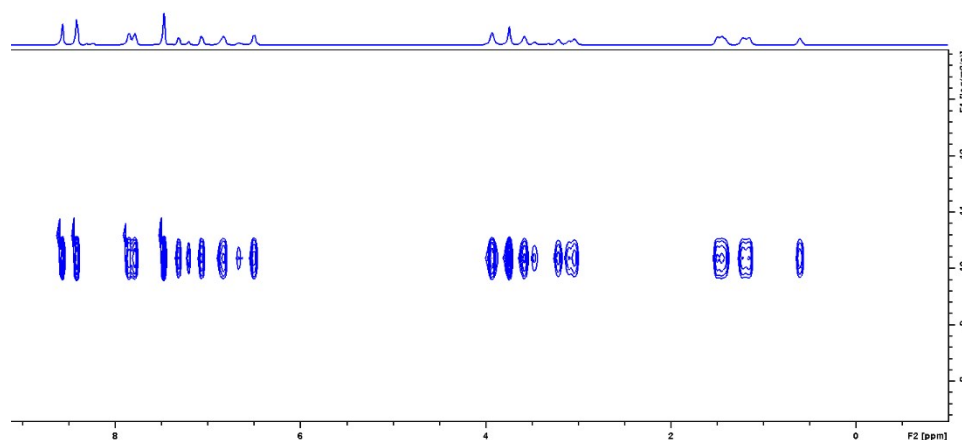
**Fig. S10** Partial  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CDCl}_3\text{-CD}_3\text{CN} = 3/1$ , v/v, 298 K) of individual AB (a),  $\text{D}_2$  (b), mixtures of 2:1:1 molar ratio of AB,  $\text{D}_2$  and  $\text{Zn}(\text{OTf})_2$  at different AB concentrations: (c) 4 mM, (d) 15 mM, (e) 80 mM, (f) 120 mM, (g) 220 mM. Peaks of uncomplexed monomers and complexed monomers are designated as uc and c, respectively.



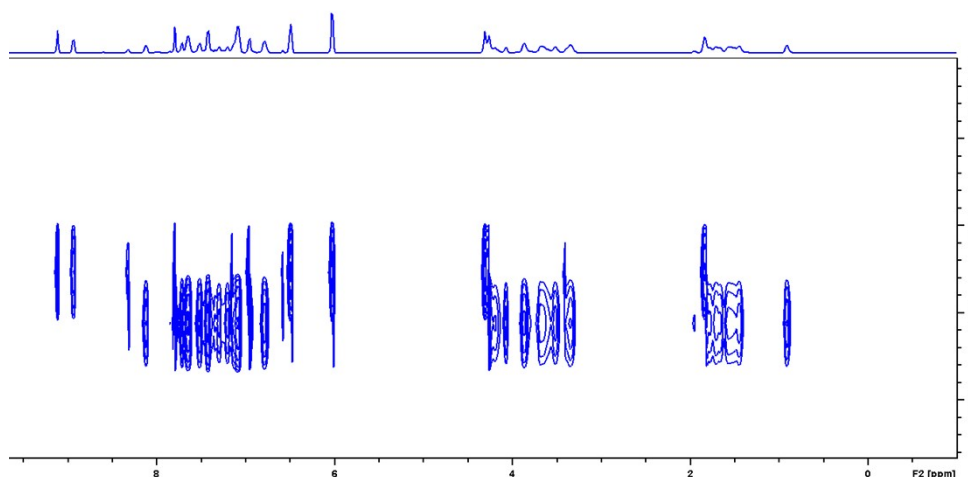


**Fig. S11**  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CDCl}_3\text{-CD}_3\text{CN} = 3/1$ , v/v, 298 K) of individual AB (a),  $\text{D}_2$  (b), and AE (c); mixtures of 1:1:1 molar ratio of AB, AE,  $\text{D}_2$  and  $\text{Zn}(\text{OTf})_2$  at different AB concentrations: (d) 2 mM, (e) 6 mM, (f) 20 mM, (g) 60 mM, (h) 100 mM, (i) 220 mM, and (j) 2:1:1 molar ratio of AE,  $\text{D}_2$  and  $\text{Zn}(\text{OTf})_2$ .

## 6. 2D DOSY NMR spectra



**Fig. S12** Representative DOSY spectrum (500 MHz,  $\text{CDCl}_3\text{-CD}_3\text{CN} = 3/1$ , v/v, 298 K) of 2:1:1 molar ratio of AB,  $\text{D}_2$ , and  $\text{Zn}(\text{OTf})_2$ , the B21C unit concentration is 120mM.

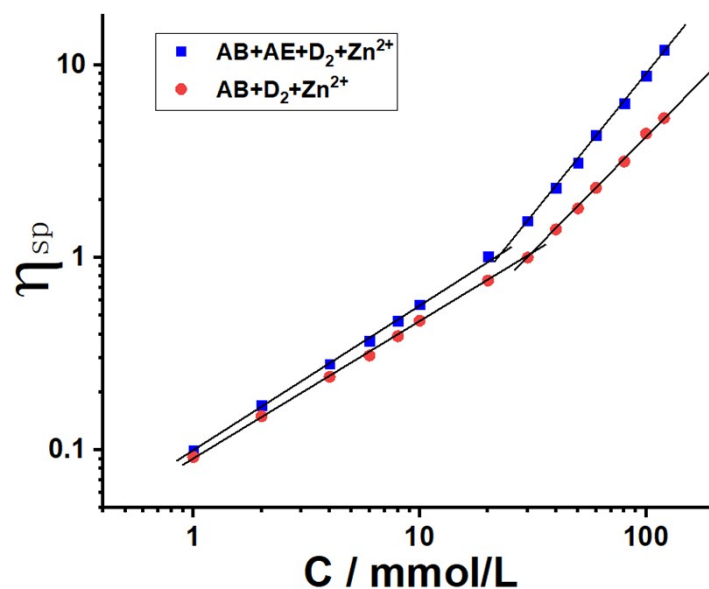


**Fig. S13** Representative DOSY spectrum (500 MHz,  $\text{CDCl}_3\text{-CD}_3\text{CN}_3 = 3/1$ , v/v, 298 K) of 1:1:1:1 molar ratio of AB, AE,  $\text{D}_2$  and  $\text{Zn}(\text{OTf})_2$ , the B21C unit concentration is 120mM.

## 7. Viscosity measurement

Viscosity measurement, as an important characterization method for supramolecular polymerization, was conducted to further study the supramolecular polymerization. The specific viscosities of  $\text{AB}+\text{D}_2+\text{Zn}(\text{OTf})_2$  and the  $\text{AB}+\text{AE}+\text{D}_2+\text{Zn}(\text{OTf})_2$  in  $\text{CHCl}_3\text{-CH}_3\text{CN}$  solutions were measured using a micro-Ubbelohde viscometer. At low concentrations, the slopes of  $\text{AB}+\text{D}_2+\text{Zn}(\text{OTf})_2$  system and  $\text{AB}+\text{AE}+\text{D}_2+\text{Zn}(\text{OTf})_2$  system were 0.91 and 0.98, respectively, showing that oligomers were main species at low concentrations.<sup>[S4]</sup> At higher concentrations, the slopes were changed to 1.66 for the  $\text{AB}+\text{D}_2+\text{Zn}(\text{OTf})_2$  system and 1.90 for the  $\text{AB}+\text{AE}+\text{D}_2+\text{Zn}(\text{OTf})_2$  system (Fig. S14), the CPC concentrations (critical polymerization concentration) were 26 and 21mM, respectively, implying that supramolecular polymers SP1 and

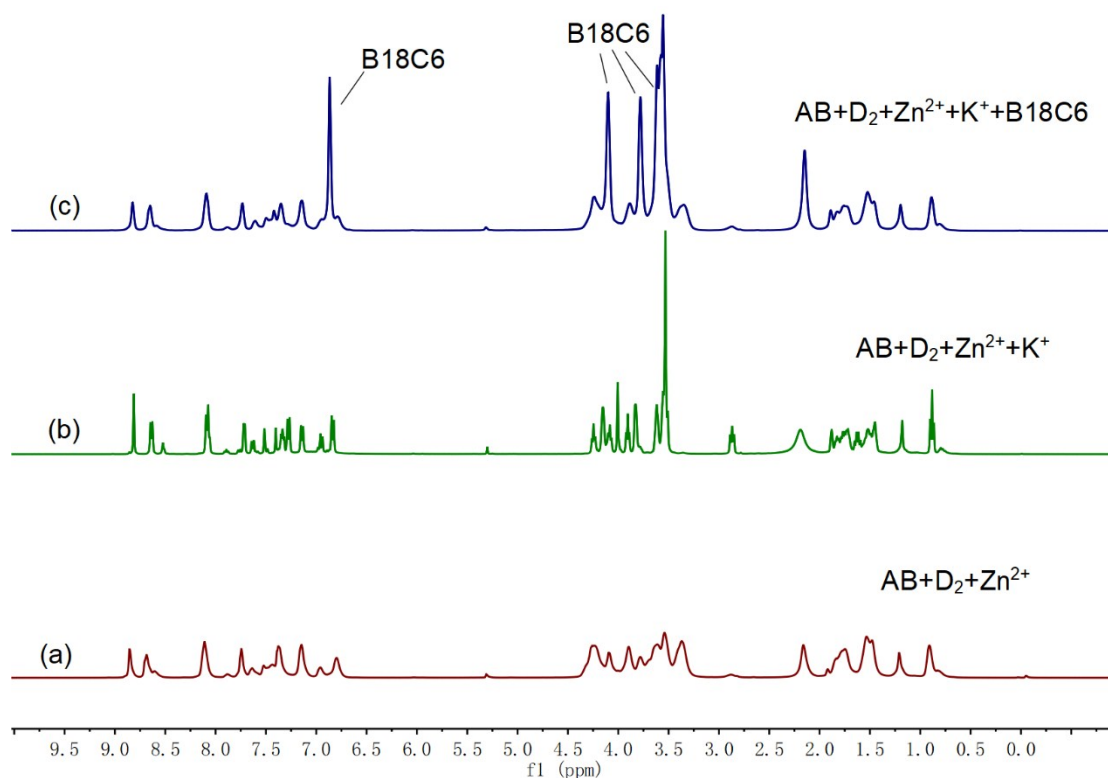
SP2 of increasing size were gradually formed.



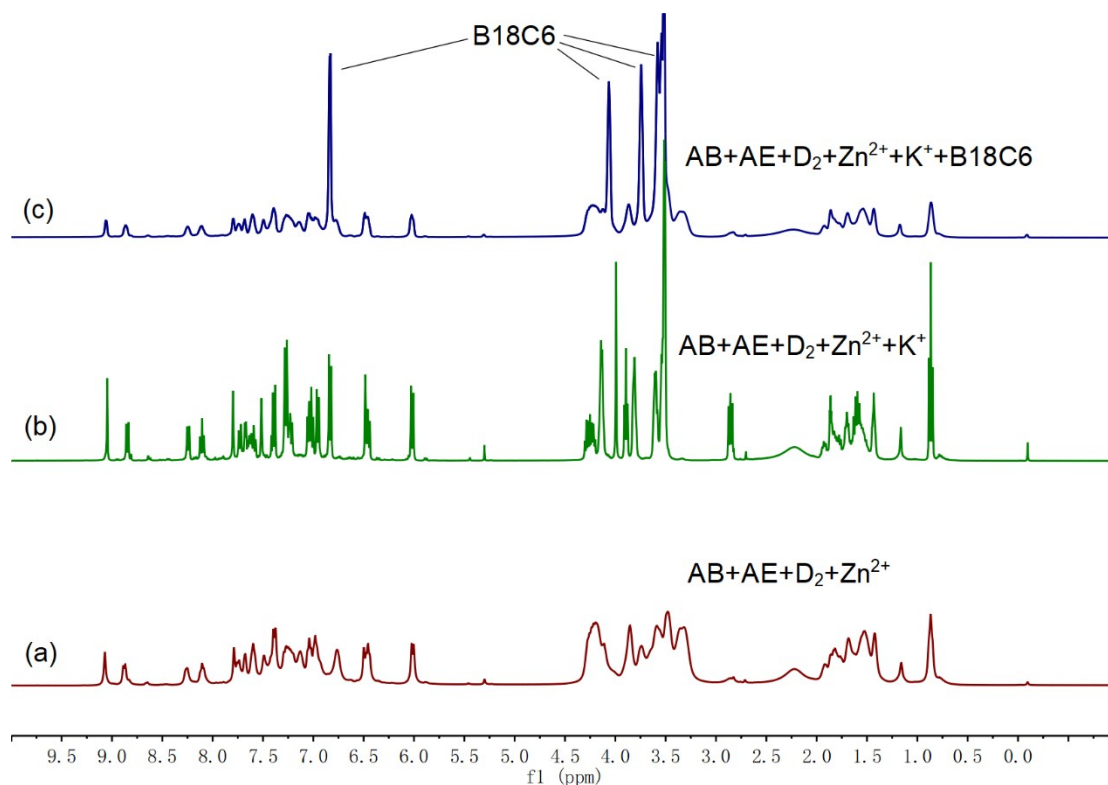
**Fig. S14** Specific viscosity of  $AB+D_2+Zn(OTf)_2$  and  $AB+AE+D_2+Zn(OTf)_2$  in  $CHCl_3-CH_3CN$  (v/v, 3:1) solutions versus the concentration of B21C units.

## 8. Disassembly and reassembly of supramolecular polymers

Given that B21C can capture  $K^+$  more tightly than the secondary ammonium salt, we speculated that the supramolecular polymers SP1 and SP2 may exhibit  $K^+$  responsiveness. After 1 equiv.  $KPF_6$  were added to the solutions of  $AB+D_2+Zn(OTf)_2$  and  $AB+AE+D_2+Zn(OTf)_2$ , the  $^1H$  NMR spectra of the two solutions both became simpler and sharper (Fig. S15-16), indicating the SP1 and SP2 were disassembled into low-molecular-weight species. When 1.2 equiv. benzo-18-crown-6 (B18C6) were subsequently added into the two solutions, the complicated  $^1HNMR$  spectra were both observed again due to the stronger binding ability between B18C6 and  $K^+$  and the recovery complexation between B21C and dialkylammonium salt, suggesting the reformation of supramolecular polymers SP1 and SP2.

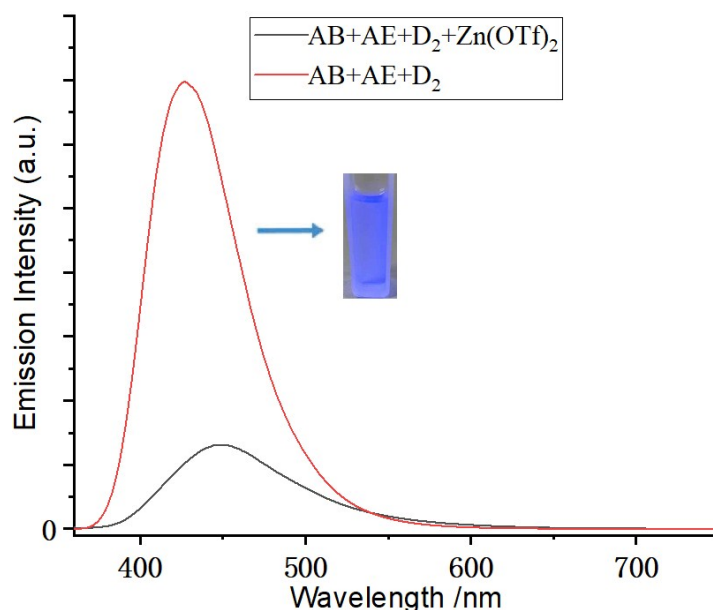


**Fig. S15**  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CDCl}_3\text{-CD}_3\text{CN} = 3/1$ , v/v, 298 K, 50 mM) of a solution of 2:1:1 molar ratio of AB,  $\text{D}_2$ , and  $\text{Zn}(\text{OTf})_2$  (a), after the addition of 1 equiv.  $\text{KPF}_6$  (b), and after the addition of 1.2 equiv. B18C6 (c).



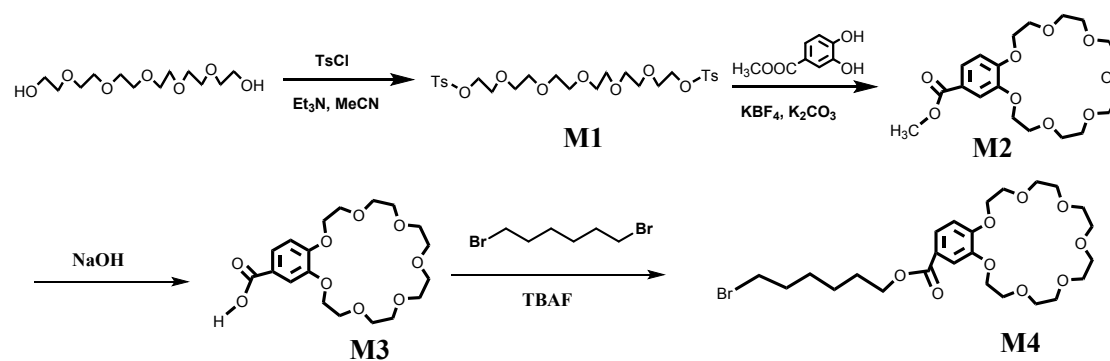
**Fig. S16**  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CDCl}_3\text{-CD}_3\text{CN} = 3/1$ , v/v, 298 K, 50 mM) of a solution of 1:1:1 molar ratio of AB, AE,  $\text{D}_2$ , and  $\text{Zn}(\text{OTf})_2$  (a), after the addition of 1 equiv.  $\text{KPF}_6$  (b), and after the addition of 1.2 equiv. B18C6 (c).

## 9. Fluorescence emission spectra



**Fig. S17** Fluorescence emission spectra of the AB+AE+D<sub>2</sub> and AB+AE+D<sub>2</sub>+Zn(OTf)<sub>2</sub> upon an excitation at 345 nm in CHCl<sub>3</sub>-CH<sub>3</sub>CN (v/v = 3/1, 1.0 × 10<sup>-4</sup> mM). Inset: visual fluorescence emission for AB+AE+D<sub>2</sub> using 365 nm UV lamp irradiation.

## 10. Synthesis of the intermediates and monomers



**Scheme S2.** Synthetic route of the compound **M4**.

### Synthesis of Compound M4

A solution of compound M3 (3.00g, 7.5mmol), 1,6-dibromohexane (5.56g, 23 mmol), and tetrabutylammonium fluoride (1mol/L in THF, 10ml) in tetrahydrofuran (50 mL) was stirred for 12 h at room temperature. The solvent was evaporated under reduced pressure and the residue was partitioned between dichloromethane (60 mL) and water (60 mL). The aqueous layer was further washed with dichloromethane (3 × 150 mL). The organic phases were combined and dried over anhydrous sodium sulfate. After the solvent was removed, the resulting residue was subjected to

column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH= 70:1), to give M4 (4.00g, 95%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.66 (d, *J* = 8.4 Hz, 1H), 7.54 (s, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 4.28 (t, *J* = 6.6 Hz, 2H), 4.20-4.25 (m, 4H), 3.91-3.96 (m, 4H), 3.76-3.81 (m, 4H), 3.71-3.76 (m, 4H), 3.63-3.69 (m, 8H), 3.41 (t, d, *J* = 6.6 Hz, 2H), 1.83-1.91 (m, 2H), 1.74-1.80 (m, 2H), 1.44-1.52 (m, 4H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): δ (ppm) = 166.4, 153.0, 148.4, 123.9, 123.3, 114.8, 112.4, 71.4, 71.3, 71.2, 71.1, 70.7, 69.7, 69.6, 69.4, 69.2, 64.7, 33.7, 32.7, 28.7, 27.9, 25.3. HR-ESI-MS (C<sub>25</sub>H<sub>39</sub>BrO<sub>9</sub>): *m/z* calcd for [M + H]<sup>+</sup> = 563.1850, found = 563.1841, error = 1.6 ppm.

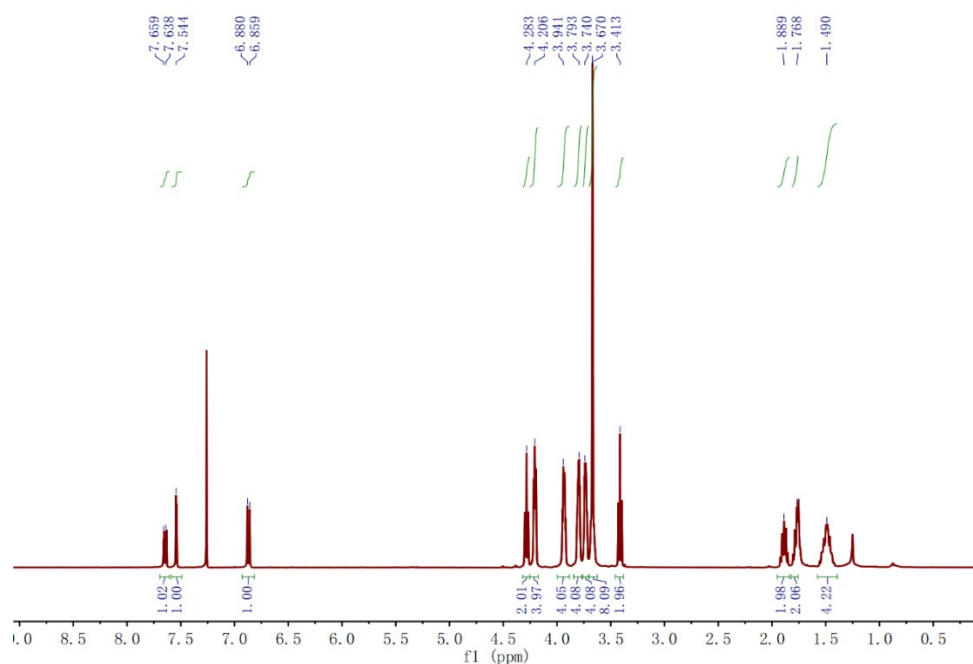
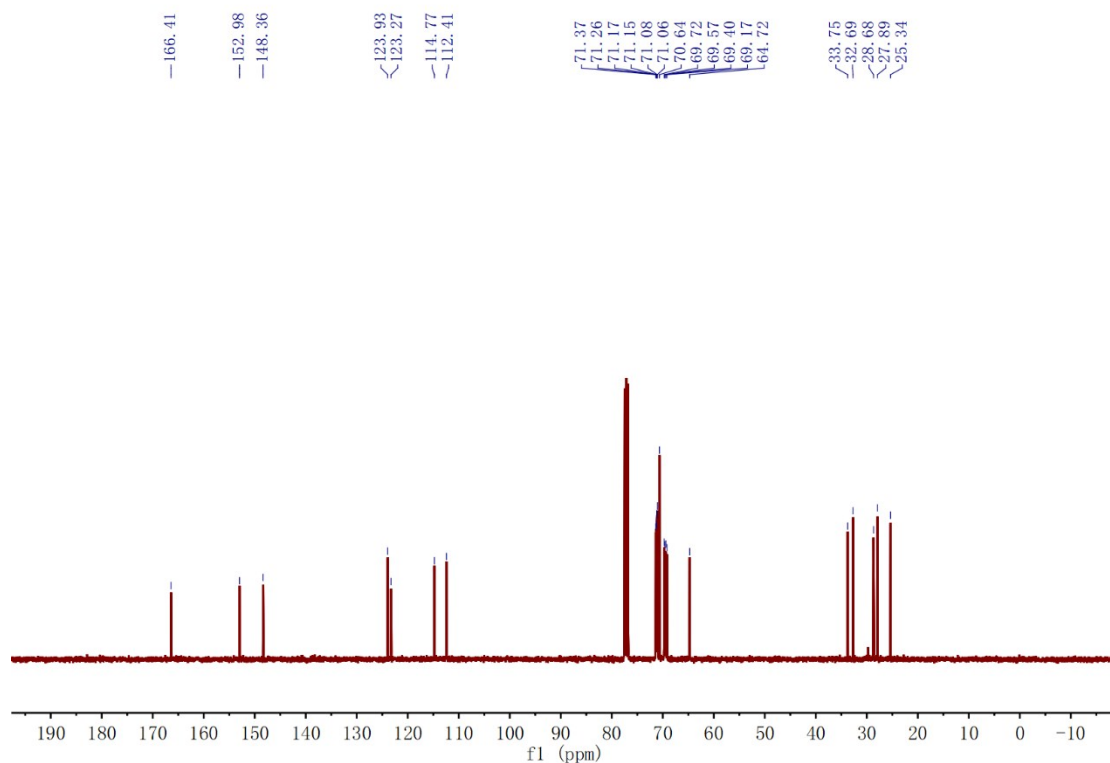
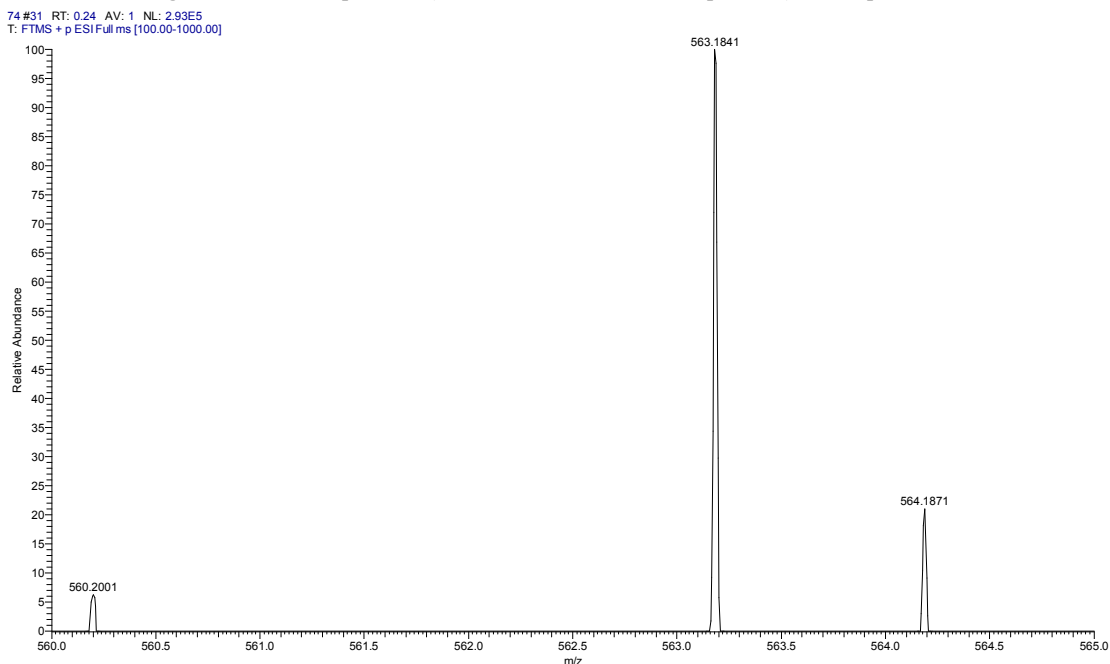


Fig. S18 <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>, room temperature) of compound M4.

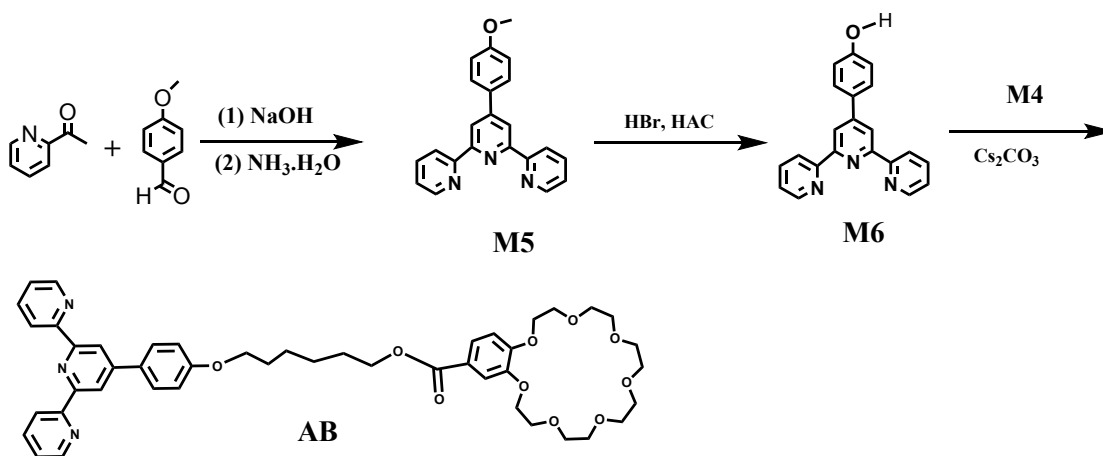


**Fig. S19**  $^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{CDCl}_3$ , room temperature) of compound **M4**.



**Fig. S20** High-resolution electrospray ionization mass spectrum of compound **M4**.

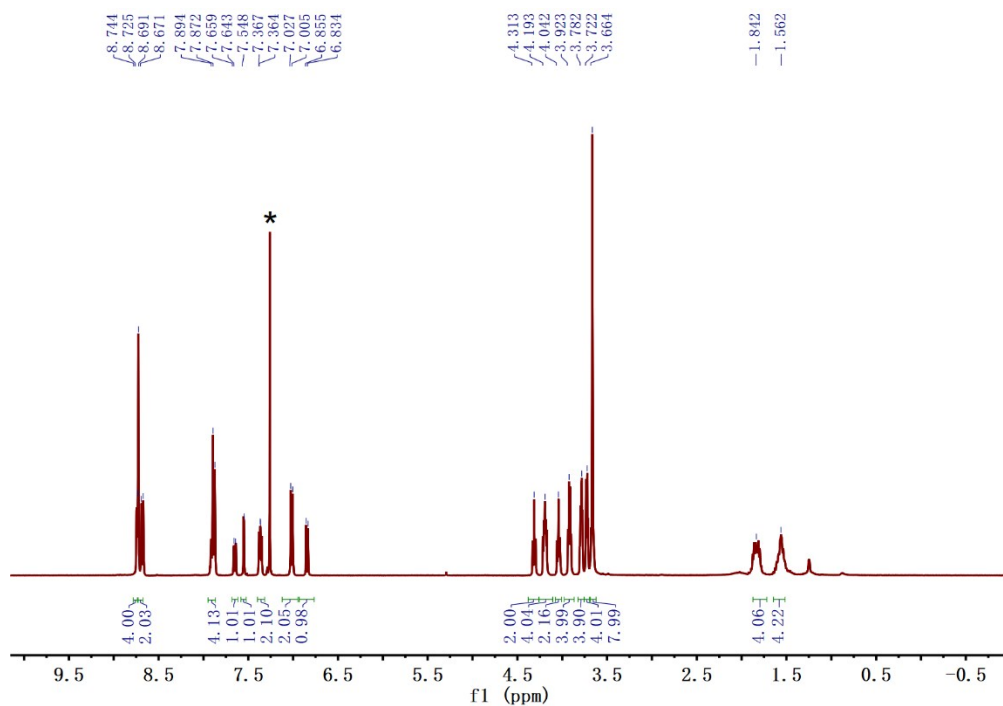
## Synthesis of monomer **AB**



**Scheme S3.** Synthetic route of the monomer **AB**.

A solution of **M6** (3.00g, 9.2 mmol), **M4** (5.18g, 9.2 mmol),  $\text{Cs}_2\text{CO}_3$  (8.97g, 27.6mmol) in DMF (100 mL) was stirred for 16 h at 75 °C. After the reaction mixture was cooled to ambient temperature, the solvent was evaporated under reduced pressure and the residue was partitioned between dichloromethane (80 mL) and water (80 mL). The aqueous layer was further washed with dichloromethane (2 × 40 mL). The organic phases were combined and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After the solvent was removed, the resulting residue was subjected to column chromatography (dichloromethane/ methyl alcohol = 60:1), to give **AB** (5.20g, 70 %) as a white solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K): ppm = 8.74 (s, 2H), 8.73 (s, 2H), 8.68 (d,  $J$  = 8.0 Hz,

2H), 7.86-7.92 (m, 4H), 7.65 (d,  $J = 6.8$  Hz, 1H), 7.55 (s, 1H), 7.36 (d,  $J = 1.2$  Hz, 2H), 7.33-7.38 (m, 2H), 7.02 (d,  $J = 8.8$  Hz, 2H), 6.84 (d,  $J = 8.4$  Hz, 1H), 4.31 (t,  $J = 1.2$  Hz, 2H), 4.16-4.21 (m, 4H), 4.04 (t,  $J = 6.4$  Hz, 2H), 3.88-3.98 (m, 4H), 3.77-3.84 (m, 4H), 3.70-3.75 (m, 4H), 3.57-3.69 (m, 8H), 1.80-1.87 (m, 4H), 1.52-1.59 (m, 4H).  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 166.5, 160.2, 156.4, 155.9, 153.0, 149.9, 149.1, 148.4, 137.0, 130.6, 128.6, 124.0, 123.4, 121.5, 118.4, 115.0, 114.8, 112.4, 71.4, 71.30, 71.2, 71.1, 71.1, 70.7, 69.8, 69.6, 69.2, 68.0, 64.3, 29.8, 29.3, 28.8, 26.0, 25.9. HR-ESI-MS ( $\text{C}_{46}\text{H}_{53}\text{N}_3\text{O}_{10}$ ):  $m/z$  calcd for  $[\text{M}+\text{H}]^+ = 808.3804$ , found = 808.3796, error 1.0 ppm.



**Fig. S21**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , room temperature) of compound **AB**.



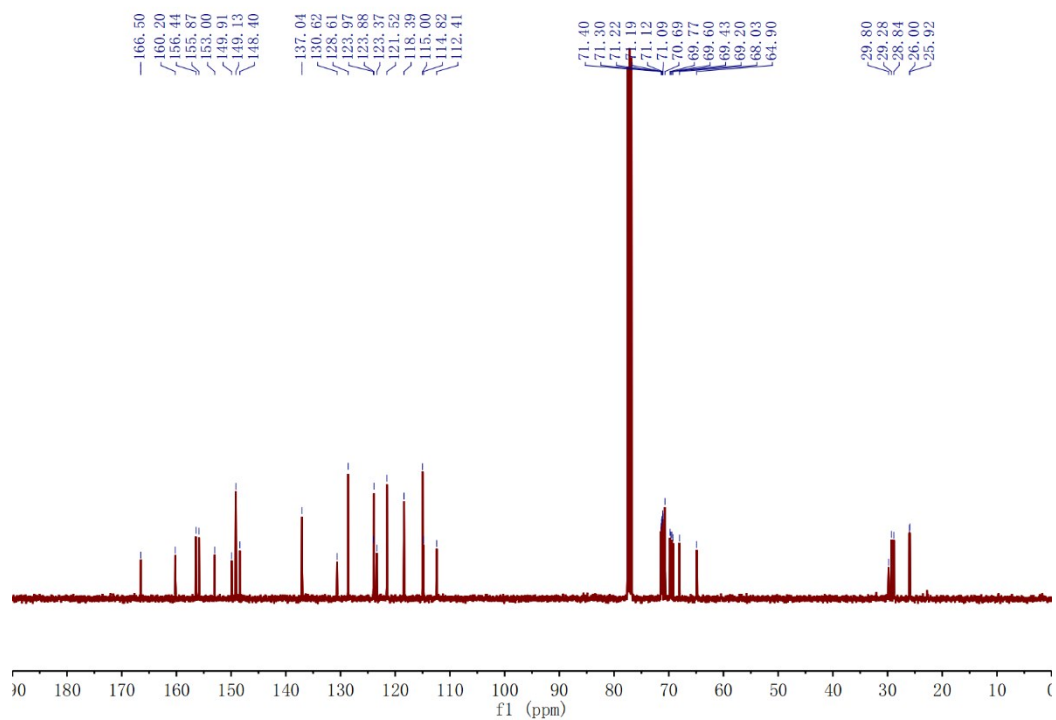


Fig. S22  $^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{CDCl}_3$ , room temperature) of compound AB.

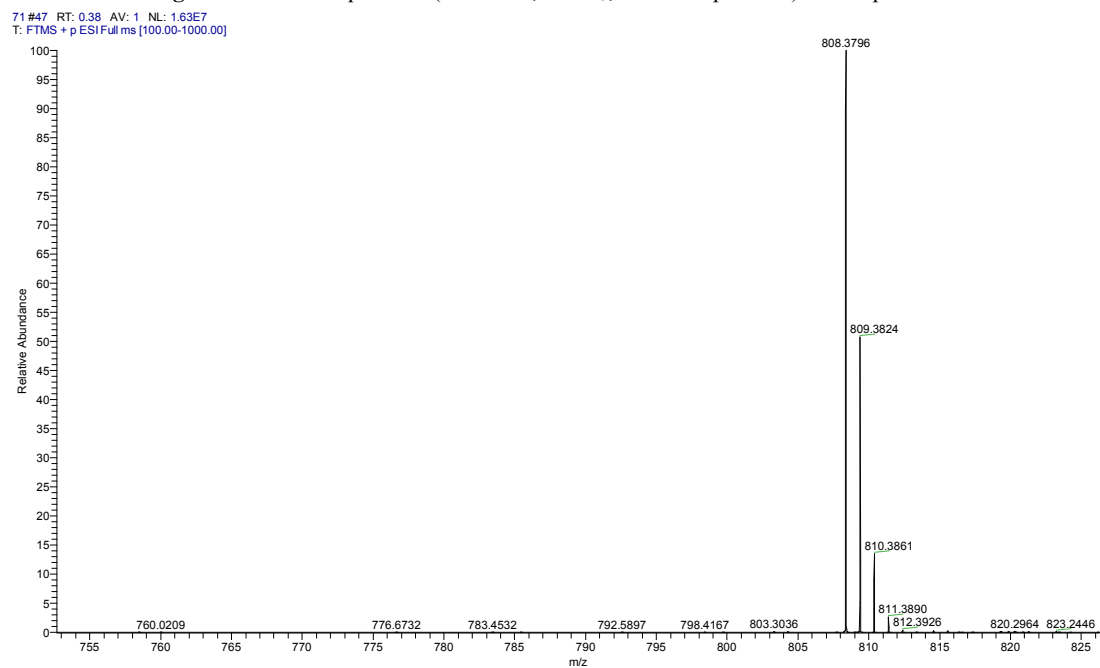
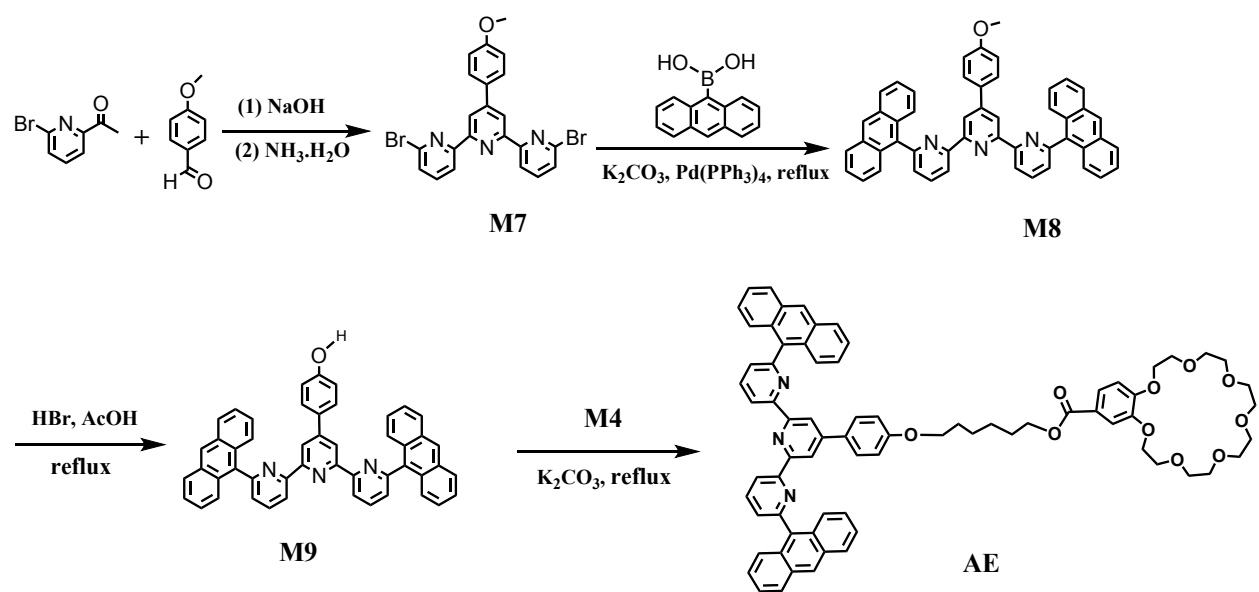


Fig. S23 High-resolution electrospray ionization mass spectrum of compound AB.

## Synthesis route of monomer AE



**Scheme S4.** Synthetic route of the monomer **AE**.

### Synthesis of Compound M7

Compound M7 was synthesized according to the literature procedure.<sup>[S2]</sup> To an ethanol solution of 2-acetyl-6-bromopyridine (2.0 g, 10 mmol), NaOH (0.45 g, 11.2 mmol) and p-anisaldehyde (0.6 g, 4.5 mmol) were added at 0 °C. After the solution was stirred at 25 °C for 14 h, NH<sub>4</sub>OH(aq) (28 wt%, 25 mL) was added into the solution and the reaction mixture was then refluxed for 14 h. After the reaction mixture was cooled to ambient temperature, the solution was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the combined organic phases was washed with H<sub>2</sub>O, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then evaporated under reduced pressure. The crude product was recrystallized from methanol to give M7 (1.1g, 2.3 mmol) in 50% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.64 (s, 2H), 8.57 (d, *J* = 7.7 Hz, 2H), 7.84 (d, *J* = 8.6 Hz, 2H), 7.70 (t, *J* = 7.8 Hz, 2H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 3.89 (s, 3H).

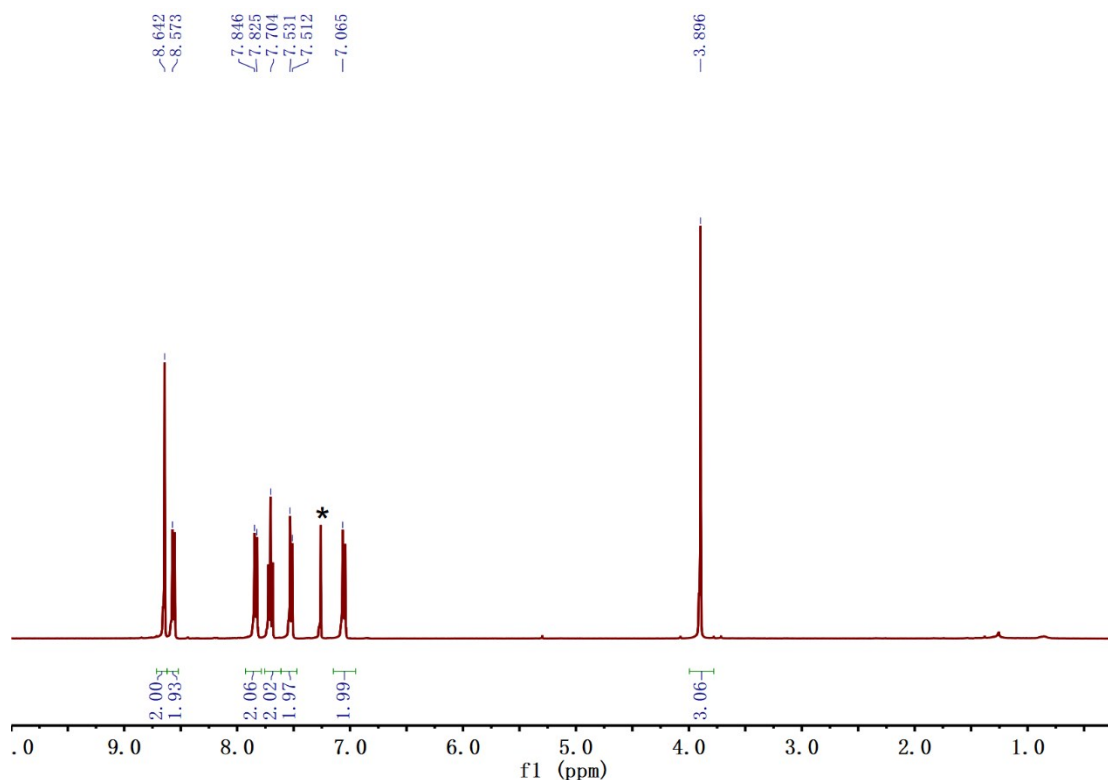


Fig. S24  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , room temperature) of compound **M7**.

### Synthesis of Compound **M8**

Compound **M8** was synthesized according to the literature procedure.<sup>[S2]</sup> To a solution of **M7** (5.0 g, 10.1 mmol), 9-anthraceneboronic acid (6.7 g, 22.0 mmol), and  $\text{Na}_2\text{CO}_3$  (10.6 g, 0.1 mol) in a mixed solvent (150 mL) of toluene/ $\text{H}_2\text{O}$ /*t*-BuOH (3:3:1, v/v/v),  $\text{Pd}(\text{PPh}_3)_4$  (577.8 mg, 0.5 mmol) was added. The reaction mixture was refluxed for 1 day under  $\text{N}_2$ . After cooling to 25 °C, the mixture was extracted with  $\text{CH}_2\text{Cl}_2$ , and the combined organic phases was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and then evaporated to dryness under reduced pressure. The residue was recrystallized from MeOH to give **M8** as a white solid (5.6 g, 8.0 mmol) in 80% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.90 (d,  $J = 7.9$  Hz, 2H), 8.62 (s, 2H), 8.57 (s, 2H), 8.17–8.04 (m, 6H), 7.76 (d,  $J = 8.8$  Hz, 2H), 7.53–7.60 (m, 4H), 7.43–7.51 (m, 4H), 7.34–7.41 (m, 4H), 6.75 (d,  $J = 8.9$  Hz, 2H), 3.69 (s, 3H).

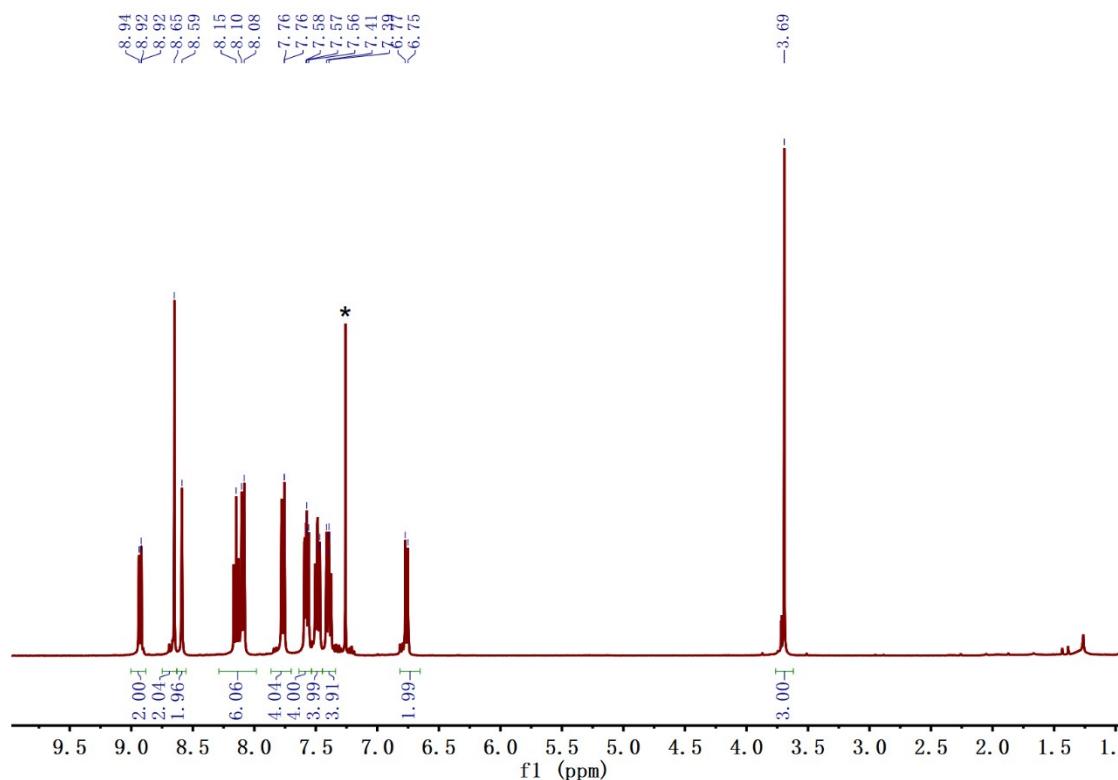


Fig. S25  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , room temperature) of compound **M8**.

### Synthesis of monomer **AE**

A solution of **M9** (2.00g, 2.95 mmol), **M4** (1.66g, 2.95 mmol),  $\text{Cs}_2\text{CO}_3$  (2.91g, 9mmol) in DMF (50 mL) was stirred 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 (80 mL) and water (80 mL). The aqueous layer was further washed with dichloromethane ( $2 \times 40$  mL). The organic phases were combined and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After the solvent was removed, the resulting residue was subjected to column chromatography (dichloromethane/methanol=70:1), to give **AE** (2.56g, 75 %) as a white solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.94 (d,  $J = 8.0$  Hz, 2H), 8.67 (s, 2H), 8.57 (s, 2H), 8.10-8.17 (m, 6H), 7.80 (d,  $J = 8.0$  Hz, 4H), 7.55-7.61 (m, 5H), 7.47-7.51 (m, 5H), 7.36-7.41 (m, 4H), 6.82 (d,  $J = 8.0$  Hz, 1H), 6.75 (d,  $J = 8.0$  Hz, 2H), 4.26 (t,  $J = 6.6$  Hz, 2H), 4.15-4.20 (m, 4H), 3.88-3.96 (m, 4H), 3.87 (t,  $J = 4.0$  Hz, 2H), 3.76-3.84 (m, 4H), 3.70-3.74 (m, 4H), 3.61-3.69 (m, 8H), 1.71-1.78 (m, 4H), 1.42-1.48 (m, 4H).  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 166.4, 159.9, 157.6, 156.6, 155.8, 152.8, 148.3, 137.1, 135.5, 131.5, 130.2, 128.5, 128.5, 127.5, 127.0, 126.3, 125.8, 125.2, 120.1, 119.0, 115.0, 112.3, 71.3, 71.2, 71.1, 71.1, 71.0, 70.6, 69.7, 69.5, 69.3, 69.1, 67.8, 64.8, 29.0, 28.7, 25.8, 25.7. MALDI-TOF-MS ( $\text{C}_{74}\text{H}_{69}\text{N}_3\text{O}_1$ ):  $m/z$  calcd for  $[\text{M}]^+ = 1159.4983$ , found = 1159.4971, error 1.0 ppm.

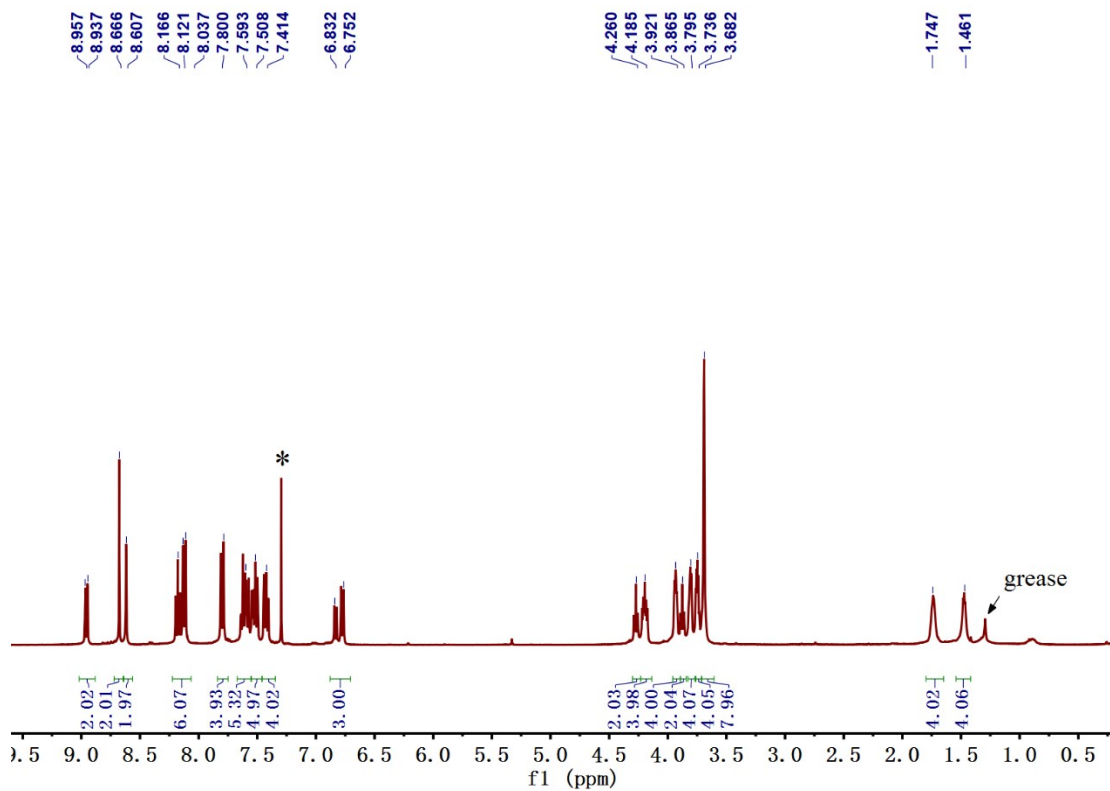


Fig. S26  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , room temperature) of AE.

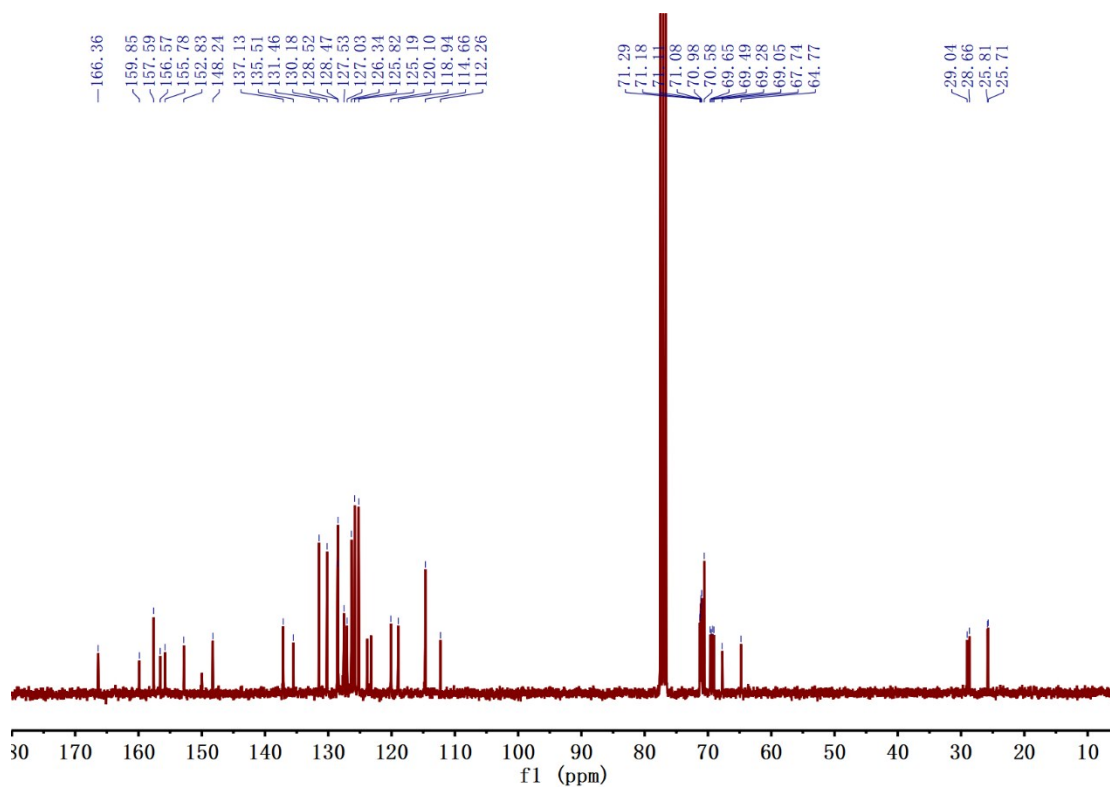


Fig. S27  $^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{CDCl}_3$ , room temperature) of AE.

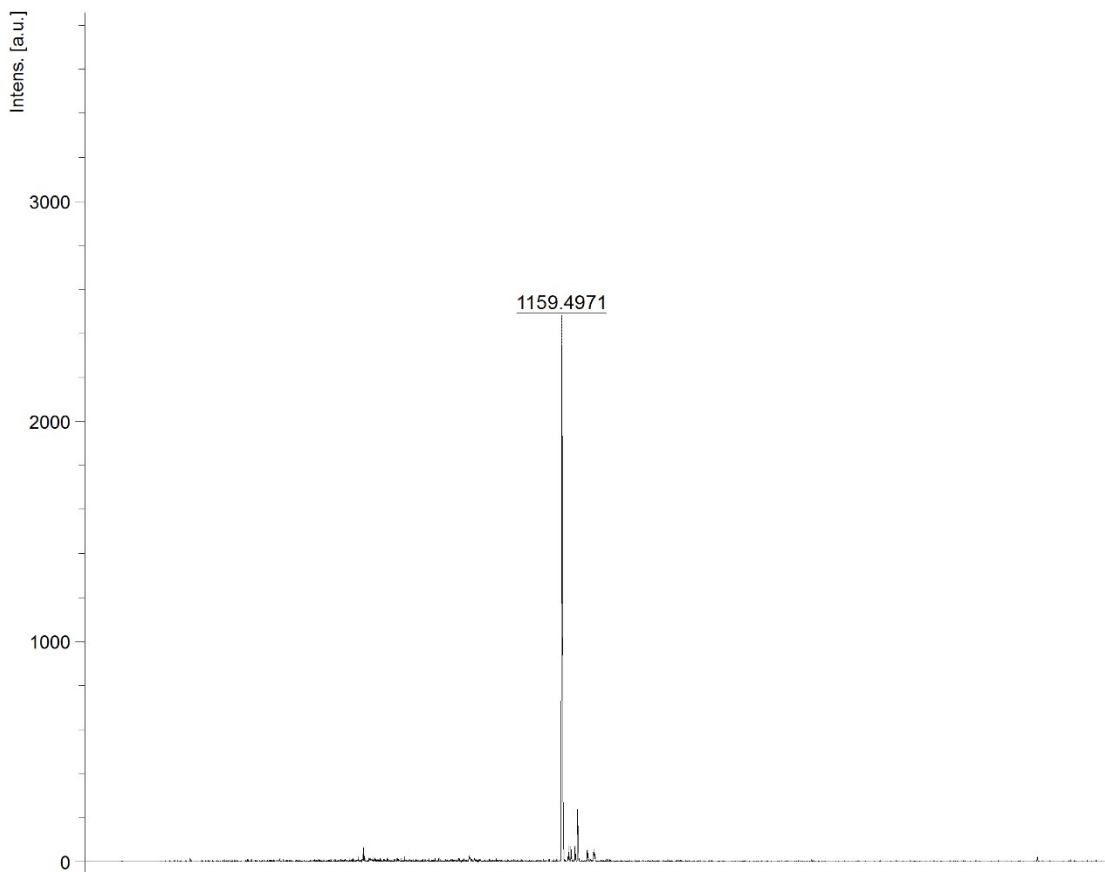
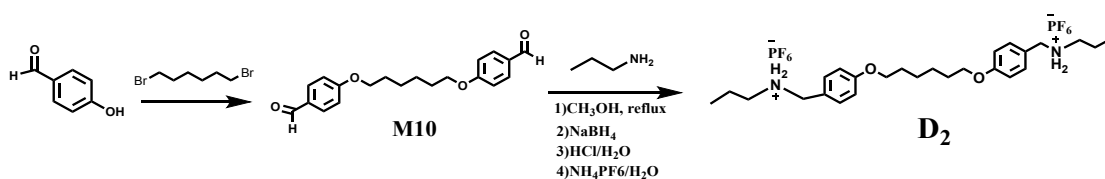


Fig. S28 High-resolution MALDI-TOF-MS of compound AE.

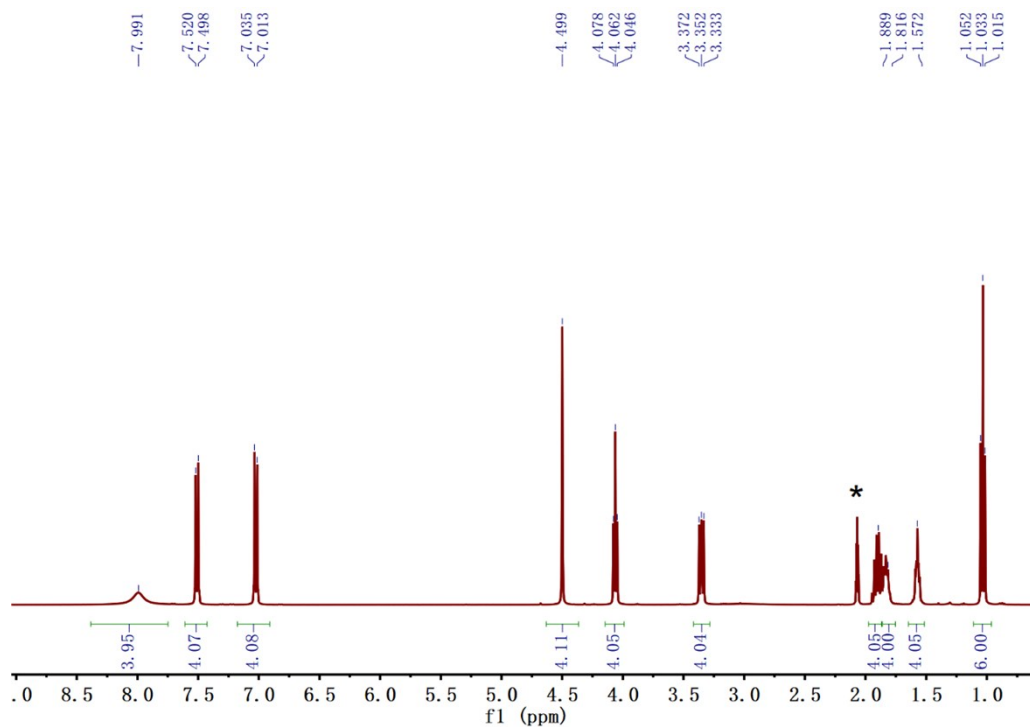
## Synthesis of Compound D<sub>2</sub>



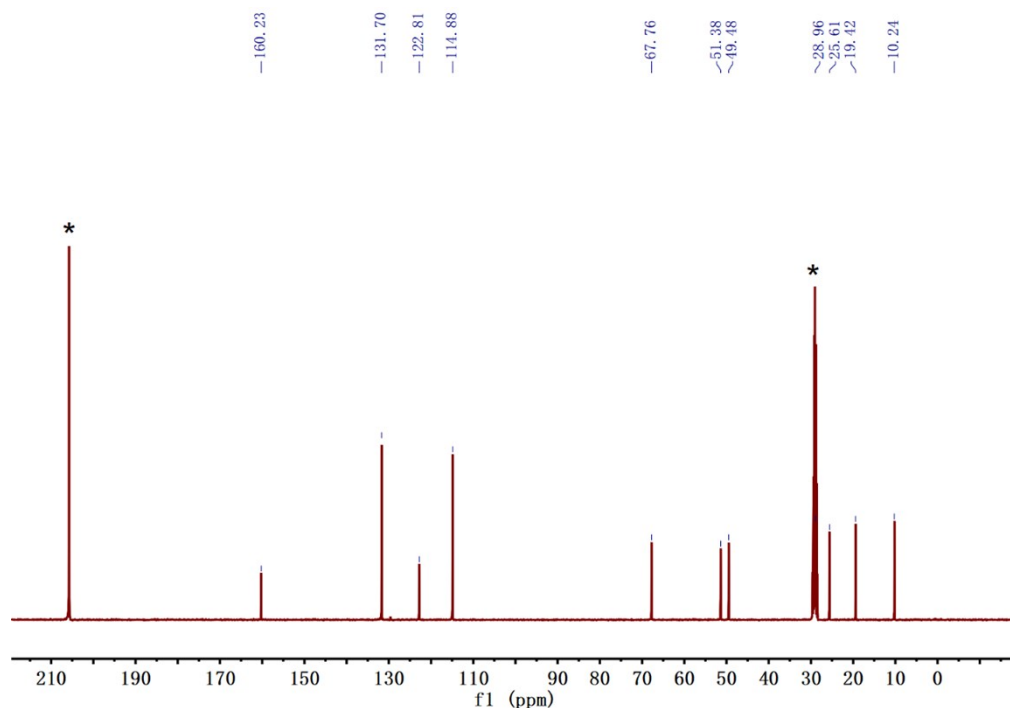
Scheme S5. Synthetic route of the monomer D<sub>2</sub>.

Bisaldehyde M10 (2.42g, 7.4mmol) and propylamine (0.88g, 14.8mmol) were dissolved in ethanol (60 mL) and was stirred at 70 °C under N<sub>2</sub> atmosphere overnight. After the reaction mixture was cooled to ambient temperature, NaBH<sub>4</sub>(0.56 g, 15.0mmol) was added to the solution in small portion and the mixture was stirred at room temperature for another 10 h. Water (60 mL) was added to quench the remaining NaBH<sub>4</sub>, and 2 M HCl was added to acidify the amine. The solvent was removed under reduced pressure to give a white solid which was suspended in acetone (40 mL). Saturated aqueous NH<sub>4</sub>PF<sub>6</sub> solution was added until the suspension become clear. The resulting

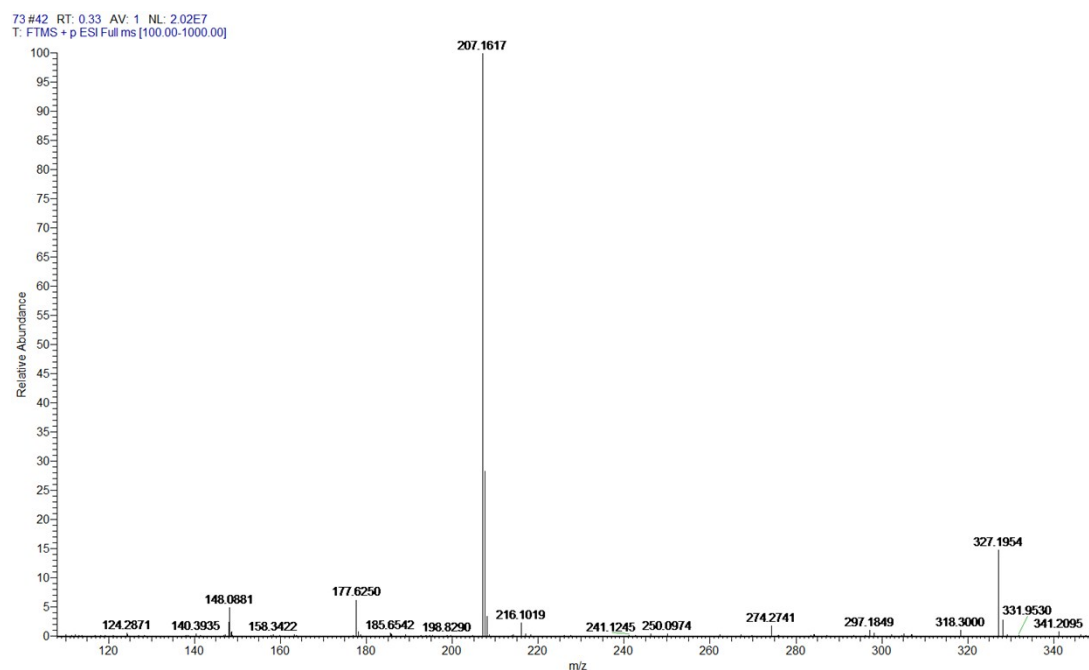
solution was evaporated under reduced pressure. The residue was washed with copious amount of water and filtrated to afford the product (2.61 g, 50%).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ , 298 K): ppm = 7.99 (br, 4H), 7.51 (d,  $J = 8.8$  Hz, 4H), 7.02 (d,  $J = 8.8$  Hz, 4H), 4.49 (s, 4H), 4.06 (t,  $J = 6.4$  Hz, 4H), 3.35 (t,  $J = 7.8$  Hz, 4H), 1.84-1.92 (m, 4H), 1.79-1.83(m, 4H), 1.53-1.59 (m, 4H), 1.03(t,  $J = 7.4$  Hz, 6H),  $^{13}\text{C}$  NMR(100MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  (ppm) = 160.2, 131.7, 122.8, 114.9, 67.8, 51.4, 49.5, 29.0, 25.6, 19.4, 10.2. HR-ESI-MS ( $\text{C}_{26}\text{H}_{42}\text{F}_{12}\text{N}_2\text{O}_2\text{P}_2$ ):  $m/z$  calcd for  $[\text{M}-2\text{PF}_6]^{2+} = 207.1618$ , found = 207.1617, error 0.5 ppm.



**Fig. S29**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , room temperature) of compound **D<sub>2</sub>**.



**Fig. S30**  $^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{CDCl}_3$ , room temperature) of compound **D<sub>2</sub>**.



**Fig. S31** High-resolution electrospray ionization mass spectrum of compound **D<sub>2</sub>**.

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- [S4] T. X. Xiao, X. Q. Feng, Q. Wang, C. Lin, L. Y. Wang and Y. Pan, *Chem. Commun.*, 2013, **49**, 8329-8331.