**Electronic Supplementary Information**

# Multiple stimuli-responsive supramolecular gel constructed from metal-organic cycle

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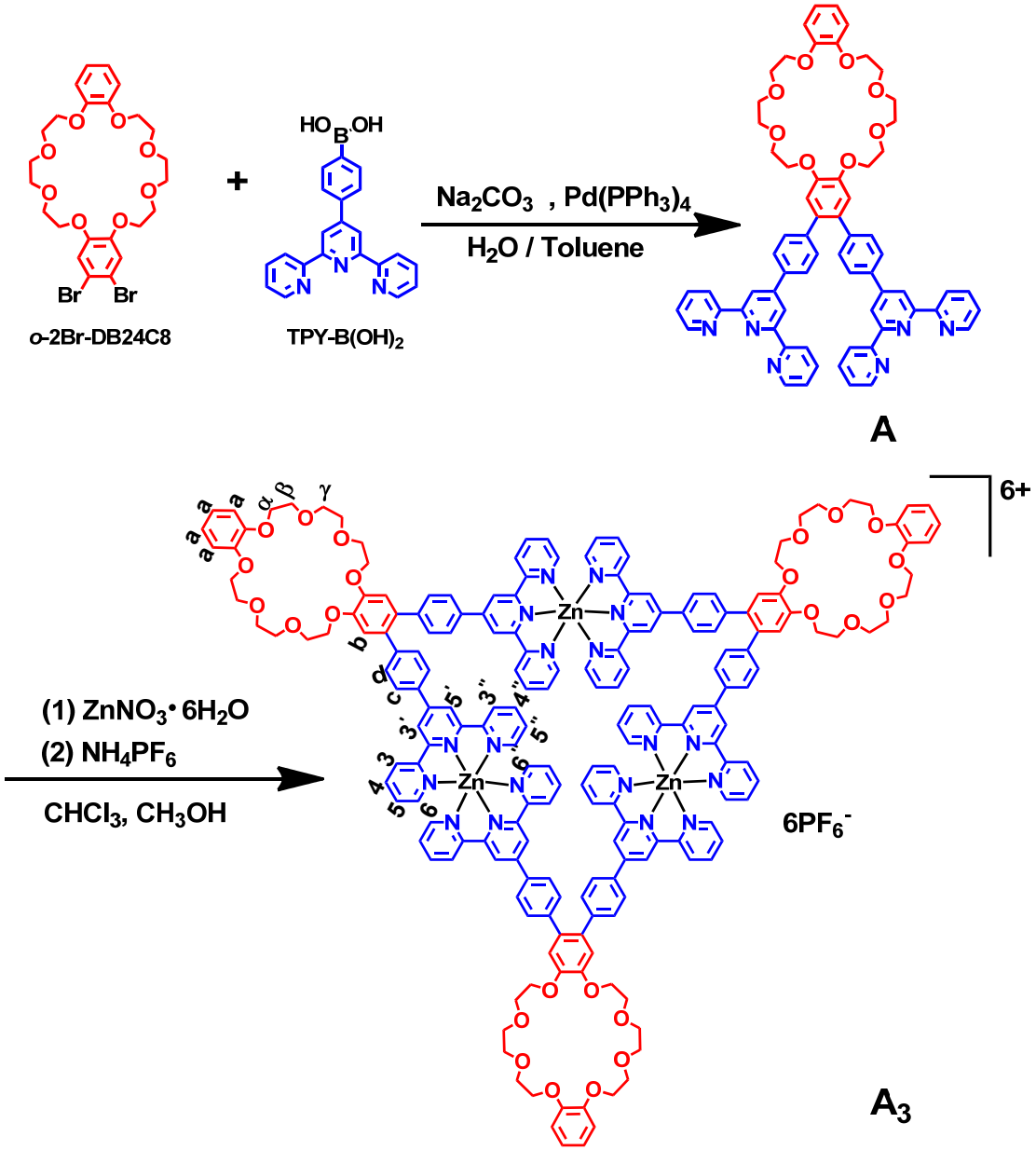
## Instruments and Materials

$^{1}H$ and $^{13}C$ NMR spectra were recorded on a JNM-ECS400 spectrometer in $CD_3CN$ and/or $CDCl_3$ with TMS as an internal standard. High-resolution electrospray ionization mass spectra (ESI-MS) were obtained on a Bruker APEX II FT-MS mass spectrometer. UV-vis absorption spectra were recorded by using a SHIMADZU UV-2550 spectrophotometer. Luminescence measurements were made on a Hitachi -7000 spectrofluorimeter with a xenon lamp as the excitation source. SEM images were obtained with JSM-5600LV. Dynamic viscosity ($\eta$) of supramolecular networks was determined on a HAAKE RS6000 rotational rheometer. All measurements were carried out at room temperature. All reaction operations were performed under an anhydrous Ar atmosphere. Toluene was distilled over Na. $\varepsilon$-Caprolactone (CL) was dried over $CaH_2$ and distilled before polymerization.

## Synthesis of A and $A_3$




Scheme S1 Synthesis of **A** and $\mathbf{A_3}$.

***o*-2Br-DB24CB**[s1] and **TPY-B(OH)$_2$**[s2] were synthesized according to the procedures in the related literatures and showed identical $^1$H NMR spectra to those reported therein.

**A: *o*-2Br-DB24CB** (304 mg, 0.502 mmol), **TPY-B(OH)$_2$** (533 mg, 1.51 mmol), $Na_2CO_3$ (427 mg, 4.03 mmol) and Pd $(PPh_3)_4$ (58 mg, 0.05 mmol) were added to a mixture solvent of toluene (10 mL) and $H_2O$ (2 mL) in an oven dried Schlenk flask under an argon atmosphere. The resulting mixture was stirred at 100 °C for 3 days.

The formed solid was obtained by filtration which precipitated from methanol. The crude product purification was achieved by flash column chromatography ($SiO_2$) using chloroform as eluent to afford **A** as white solid (400 mg, 75% yield). $^1$H NMR (400 MHz, $CDCl_3$, ppm), $\delta$: 8.73 (s, 4H, Ar), 8.69-8.68 (d, $J$ = 4.8 Hz, 4H, Ar), 8.65-8.63 (d, $J$ = 8.0 Hz, 4H, Ar), 7.87-7.83 (td, $J_1$ = 8.0 Hz, $J_2$ = 2.0 Hz, 4H, Ar), 7.82-7.80 (d, $J$ = 8.4 Hz, 4H, Ar), 7.33-7.30 (m, 6H, Ar), 7.28 (s, 2H, Ar), 7.02 (s, 2H, Ar), 6.90 (s, 4H, Ar), 4.30-4.28 (m, 4H, $OCH_2$), 4.19-4.17 (m, 4H, $OCH_2$), 4.00-3.95 (m, 8H, $OCH_2$), 3.89 (s, 8H, $OCH_2$). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm), $\delta$: 156.2, 155.8, 149.7, 149.0, 148.9, 148.4, 142.0, 136.7, 136.3, 133.0, 130.4, 127.0, 123.6, 121.4, 121.2, 118.7, 116.3, 114.0, 71.3, 69.7, 69.4. HR-ESI-MS (m/z), $[C_{66}H_{58}N_6O_8 + H]^+$ calculated: 1063.4389, found: 1063.4373.

**$A_3$:** A solution of ligand **A** (7.0 mg, 6.6 μmol) in $CHCl_3$ (1 mL), a solution of Zn $(NO_3)_2$•$6H_2O$ (1.96 mg, 6.6 μmol) in MeOH (3 mL) was added to the round-bottom flask. Then the mixture was stirred at 50 ºC for 8 h. After cooling to room temperature, 162 mg $NH_4PF_6$ was added to give a white precipitate. And the crude product was washed by water and methanol to obtain pure product (9.36 mg, yield: 83%).$^1$H NMR (400 MHz, $CDCl_3$, ppm), $\delta$: 8.96 (s, 12H, Ar), 8.71-8.69 (d, $J$ = 8.4 Hz, 12H, Ar), 8.12-8.07 (m, 24H, Ar), 7.83-7.81 (d, $J$ = 4.8 Hz, 12H, Ar), 7.60-7.58 (d, $J$ = 8.4 Hz, 12H, Ar), 7.36-7.33 (t, $J$ = 6.4 Hz, 12H, Ar), 7.23 (s, 6H, Ar), 6.97-6.91 (m, 12H, Ar), 4.35-4.33 (m, 12H, $OCH_2$), 4.15-4.13 (m, 12H, $OCH_2$), 3.93-3.91 (m, 12H, $OCH_2$), 3.86-3.84 (m, 12H, $OCH_2$), 3.77-3.76 (m, 24H, $OCH_2$). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm), $\delta$: 156.3, 150.4, 149.4, 148.6, 148.5, 141.8, 134.9, 133.0, 132.0, 128.4, 128.2, 123.9, 122.1, 121.9, 118.0, 116.8, 114.7, 71.1, 70.1, 69.8. 69.3. Elemental Analysis: $C_{198}H_{174}F_{36}N_{18}O_{24}P_6Zn_3$+$11H_2O$: Experimental: N: 5.23%, C: 53.28%, H: 4.18%. Calculated: N: 5.66%, C: 53.40%, H: 4.44%.

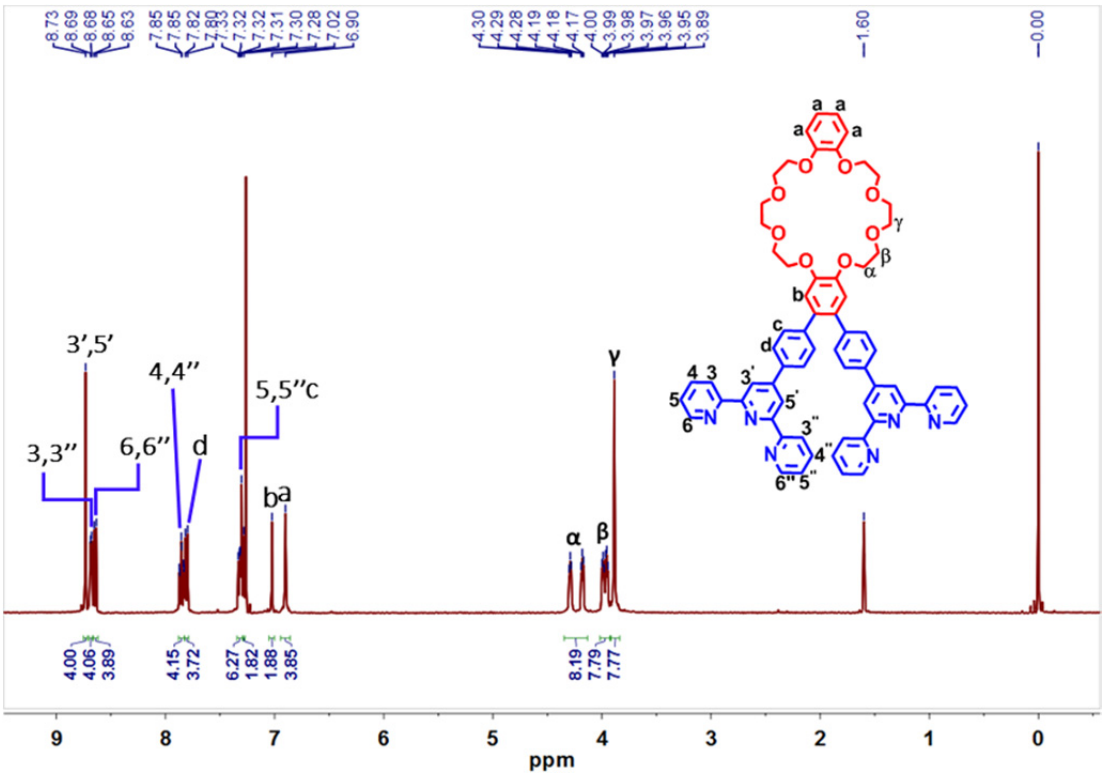



**Fig. S1** $^{1}$H NMR spectrum of **A**.

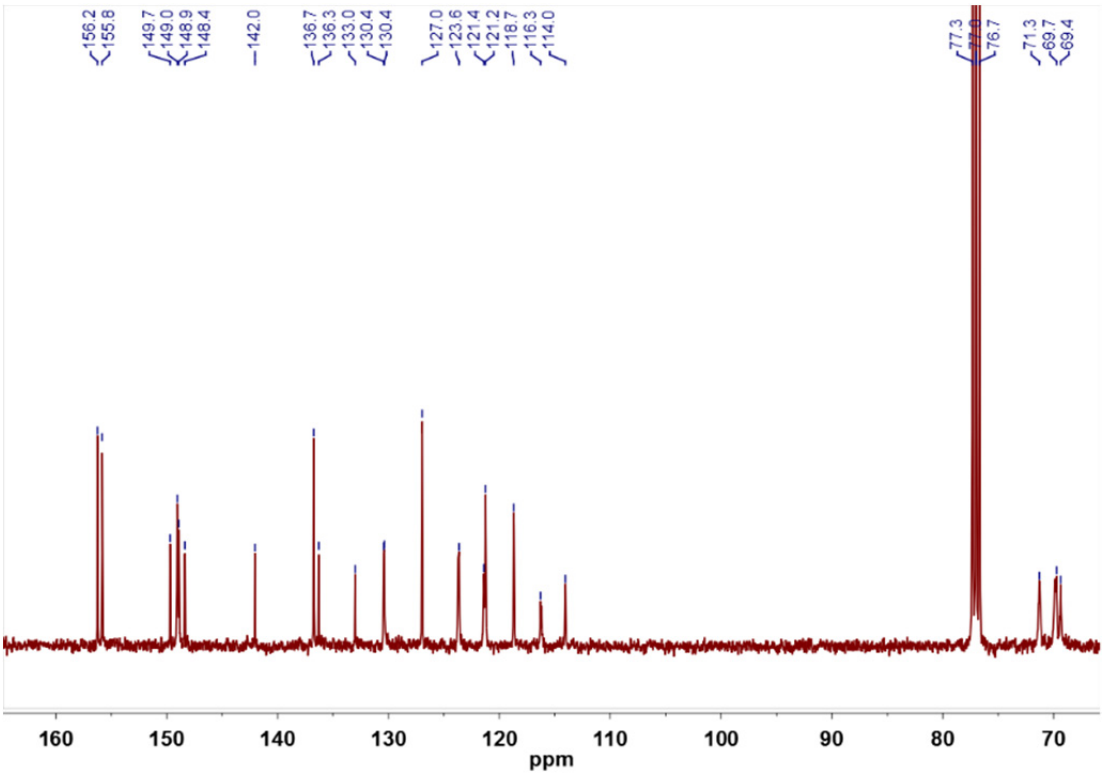



**Fig. S2** $^{13}$C NMR spectrum of **A**.

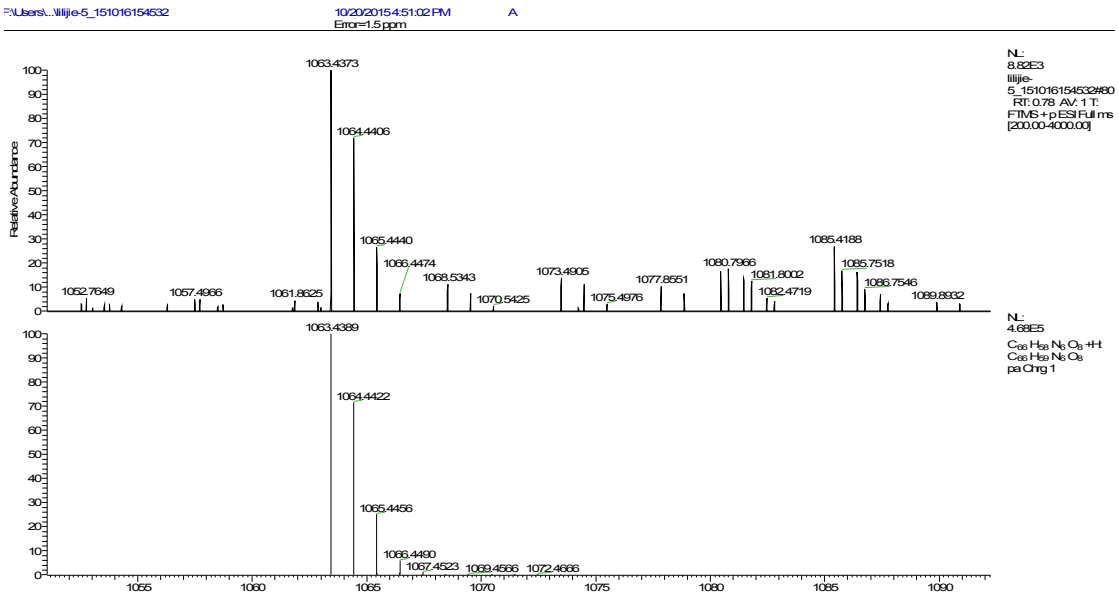



**Fig. S3** ESI-MS of A, $[C_{66}H_{58}N_6O_8 + H]^+$ calculated: 1063.4389, found: 1063.4373.

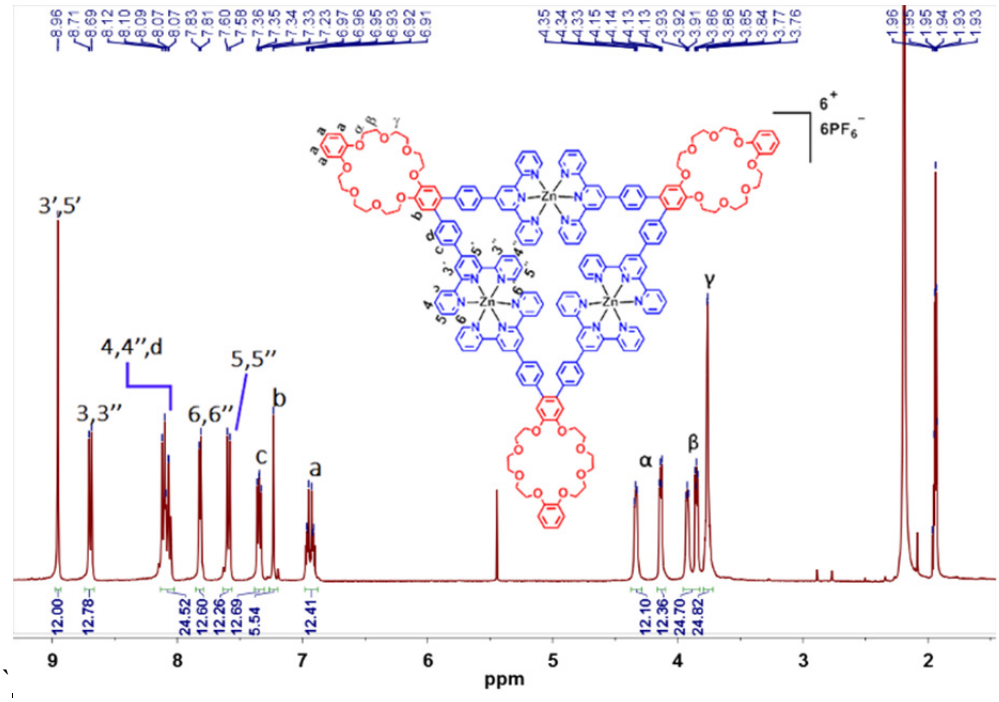



**Fig. S4** $^1$H NMR spectrum of $\mathbf{A_3}$.

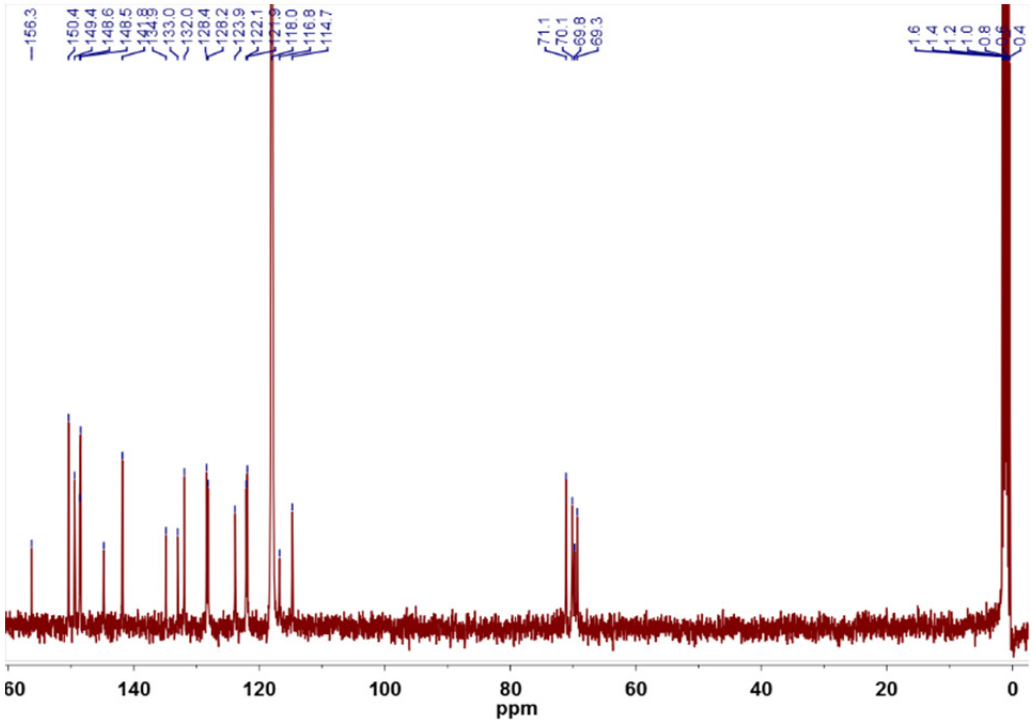



**Fig. S5** $^{13}$C NMR spectrum of $\mathbf{A_3}$.

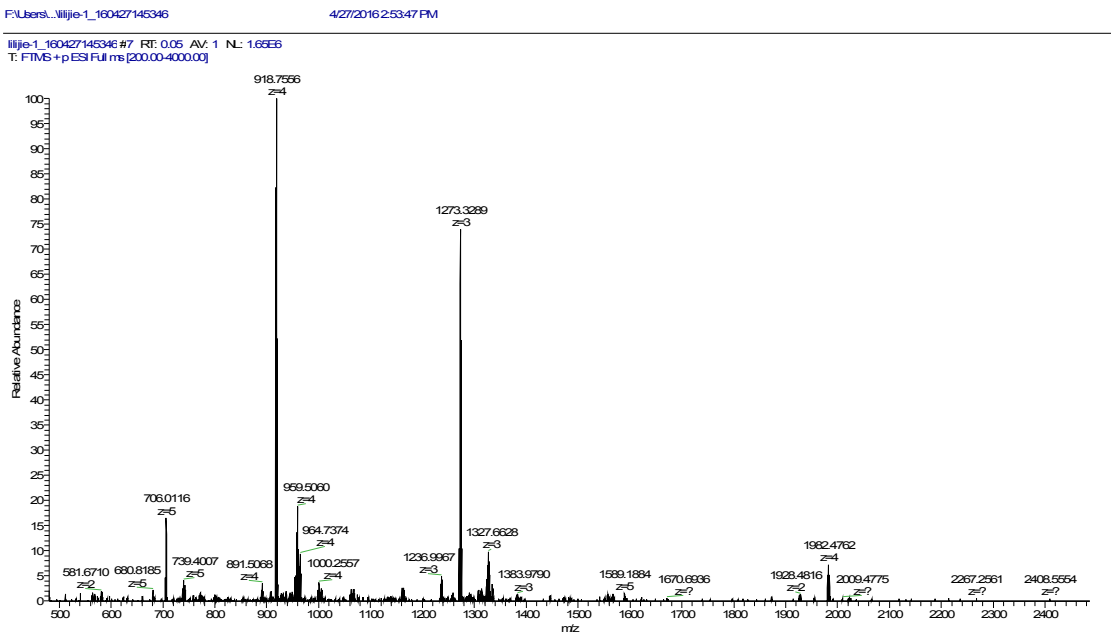



**Fig. S6** ESI-MS of $\mathbf{A_3}$.

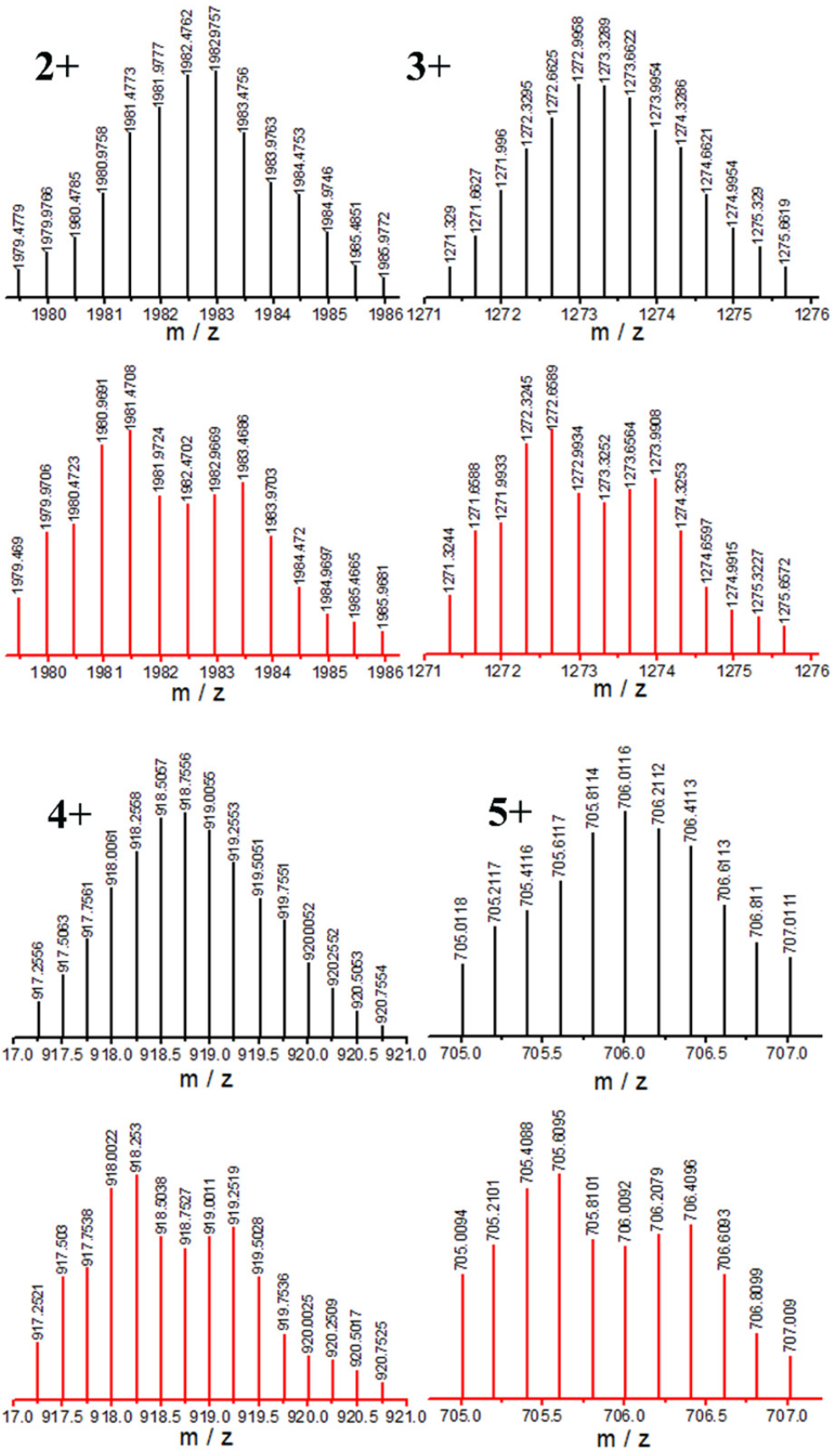



**Fig. S7** Measured (black at top) and calculated (red at bottom) isotope patterns for the different charges observed from the ESI-MS of $\mathbf{A_3}$.

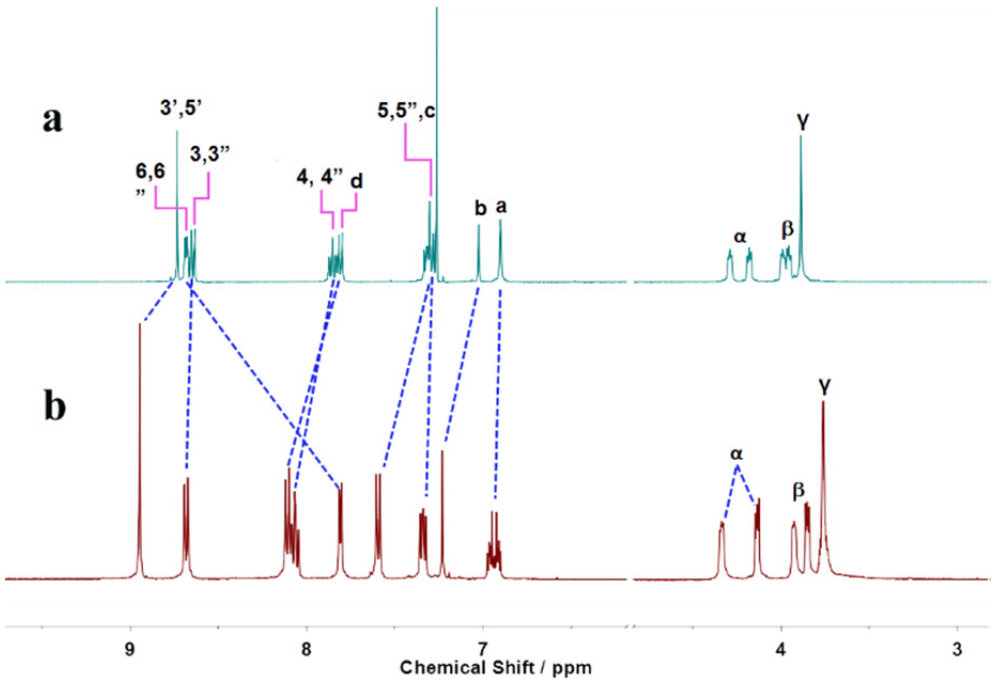



**Fig. S8** $^{1}$H NMR spectrum of (a) **A** and (b) $\mathbf{A_3}$.

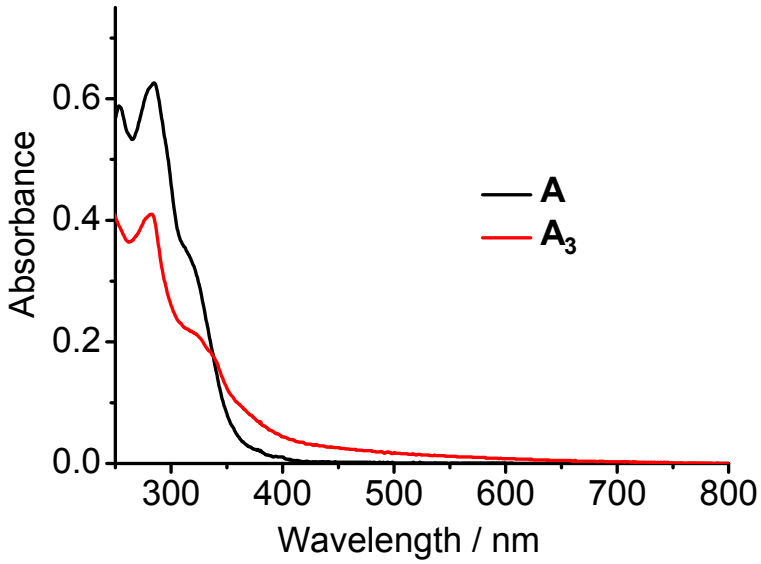



**Fig. S9** UV-vis absorption spectra of **A** (8 μM, $CHCl_3$) and $\mathbf{A_3}$ (2.66 μM, $CH_3CN$).

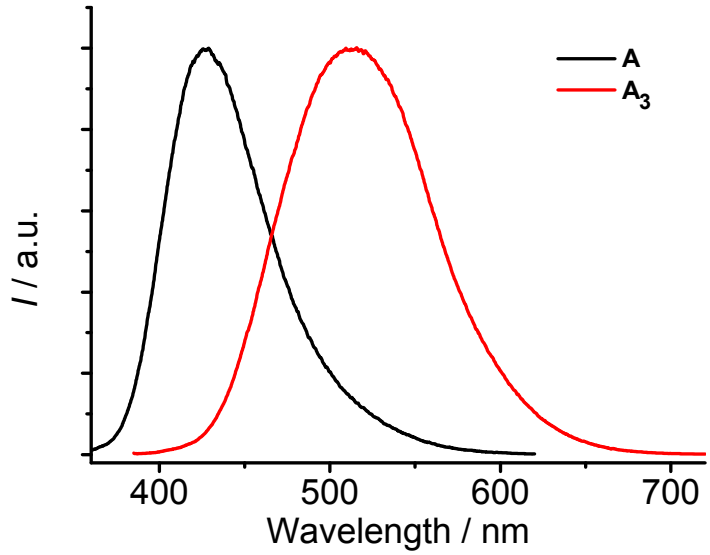
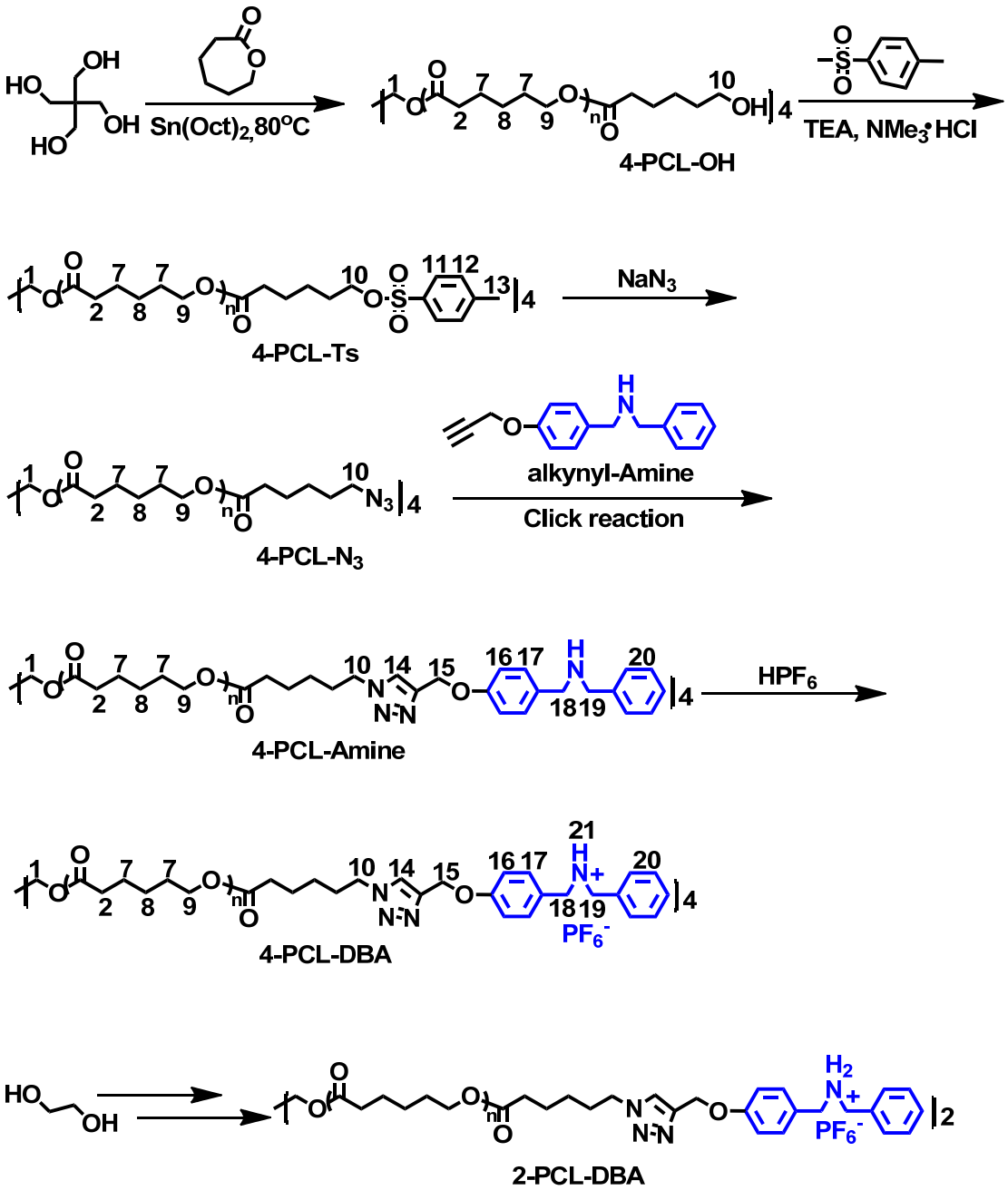



**Fig. S10** Fluorescence spectra of **A** (60 μM, $CHCl_3$) and $\mathbf{A_3}$ (20 μM, $CH_3CN$).

## Synthesis of 4-PCL-DBA and 2-PCL-DBA




**Scheme S2** Schematic illustrations for the preparation of **4-PCL-DBA** and **2-PCL-DBA**.

Alkynyl-Amine[s3] was synthesized according to the procedures in the related literature and showed identical $^1$H NMR spectra to those reported therein.

**4-PCL-OH:** The oven dried reaction bottle was degassed by vacuum pump and pentaerythritol (94.99 mg, 0.7mmol), $Sn(Oct)_2$ (11.14mg, 0.028 mmol), CL (8.0 g, 70

mmol) and toluene (6 ml) were injected rapidly. Then the reaction bottle was degassed by three freeze-punp-thaw-cycles, sealed under vacuum, and then put it in the oil bath at 80 °C for 24 h. The reaction mixture was dissolved in THF, which then precipitated into an excess of diethyl ether. The sediments were obtained by filtration. This dissolution-precipitation cycle was repeated for three times. **4-PCL-OH** was obtained as a white solid (5.6 g, yield: 70%, $M_{n,\,GPC}$=10.7 KDa, $M_w/M_n$ = 1.06). The degree of polymerization (DP) was determined to be 15 for the PCL arm by $^1$H NMR analysis in $CDCl_3$ (Figure S11).

**4-PCL-Ts: 4-PCL-OH** (4.0 g, 0.59 mmol), trimethylamine (0.30 g, 2.97 mmol), trimethylamine hydrochloride (32 mg, 0.33 mmol) and dry $CH_2Cl_2$ were added to a round-bottom flack. After cooling to 0 °C, tosyl chloride (1.93 g, 10.12 mmol) was added and the resulting mixture stirred for overnight at room temperature. After removing the solvents on a rotary evaporator, the residues were dissolved in THF and passed through a neutral alumina column to remove insoluble salts. After concentration and repeated precipitation into an excess of diethyl ether, **4-PCL-Ts** was obtained as a white solid (3.96 g, yield: 93.4%, $M_{n,}$ GPC=11.4 KDa, $M_w/M_n$ = 1.04).

**PCL-$N_3$:** To a 100 mL reaction flask, **4-PCL-Ts** (3.0 g, 0.41 mmol), $NaN_3$ (0.55 g, 8.46 mmol) and DMF (20 ml) were added and stirred at 45 °C for 24 h under an argon atmosphere. After ending the reaction, the crude product was extracted by $CH_2Cl_2$ and washed with water. Further purification was achieved by concentration and repeated precipitation into an excess of diethyl ether. **4-PCL-$N_3$** was obtained as a white solid (2.67 g, yield: 91.4%, $M_{n,\,GPC}$=11.1 KDa, $M_w/M_n$ = 1.05).

**4-PCL-Amine: 4-PCL-$N_3$** (1.30 g, 0.18 mmol), alkynyl-Amine (0.35 g, 1.4 mmol), $CuSO_4$•$5H_2O$ (44.94 mg, 0.18 mmol) and sodium ascorbate (71.32 mg, 0.36 mmol) in DMF (10 mL) was stirred at 50 °C for 24 h under nitrogen gas. After stopping the reaction, the crude product was extracted by $CH_2Cl_2$ and washed with water. Then the reaction mixture was diluted with THF and passed through a basic alumina column. After removal of most of the solvent under a reduced pressure, the residue was purified by precipitation (three times) into excess cold diethyl ether. After drying in a

vacuum oven overnight at room temperature, **4-PCL-Amine** was obtained as a pale yellow solid (0.98 g, yield: 73%, $M_{n,\,GPC}$ = 12.0 KDa, $M_w/M_n$ = 1.10).

**4-PCL-DBA: 4-PCL-Amine** (1.0 g, 0.13 mmol) was dissolved in THF (20 mL). Then the $HPF_6$ (60 wt% in water, 1.5 g, 6.16 mmol) was slowly added at 0 °C. After the mixture was stirred for 30 min at room temperature, the reaction was quenched with water and extracted by $CH_2Cl_2$. The combined organic fractions were dried ($MgSO_4$) and the solution was concentrated under a reduced pressure. The crude product was added to excess diethyl ether and the resultant precipitate was obtained by filtration and dried in a vacuum oven overnight at room temperature, affording **4-PCL-DBA** as a pale yellow solid ( 0.87 g, yield: 85 %).

**2-PCL-DBA: 2-PCL-DBA** was similarly prepared for the preparation **4-PCL-DBA**. **2-PCL-OH** was synthesized by ROP of **CL** using ethylene glycol as the initiator ($M_{n,\,GPC}$=7.5 KDa, $M_w/M_n$ = 1.06). The DP of **2-PCL-OH** was determined to be 19 for the PCL arm by $^1$H NMR analysis in $CDCl_3$ (Figure S9). Then the **2-PCL-Ts** ($M_{n,\,GPC}$=8.1 KDa, $M_w/M_n$ = 1.05), **2-PCL-N$_3$** ($M_{n,\,GPC}$=7.7 KDa, $M_w/M_n$ = 1.04), **2-PCL-Amine** ($M_{n\ ,\ GPC}$ = 8.1 KDa, $M_w/M_n$ = 1.24) were synthesized, respectively.

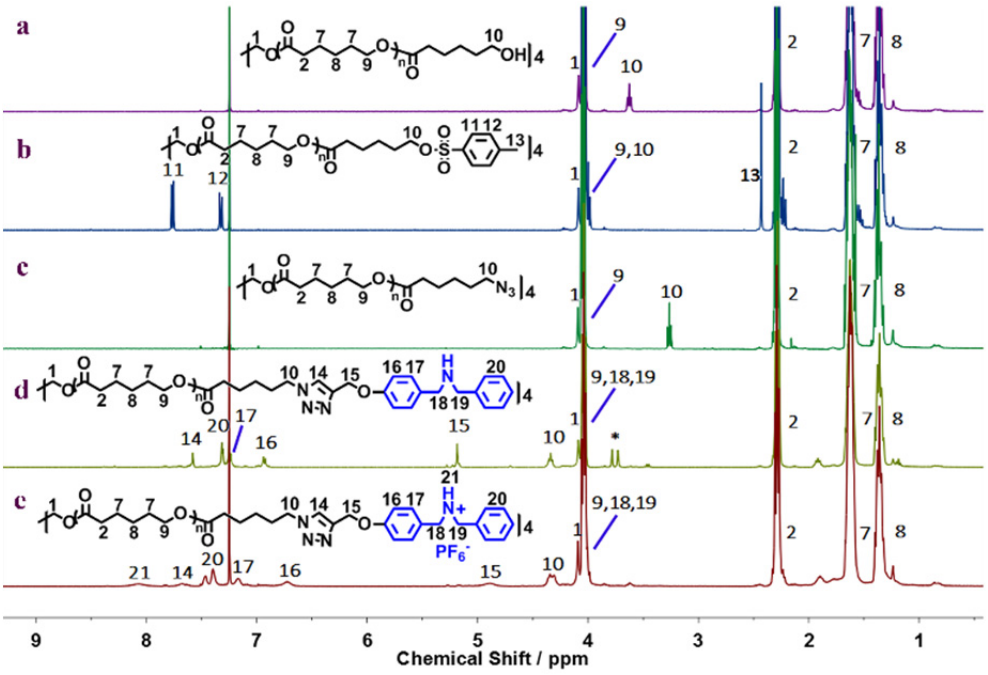



**Fig. S11** $^1$H NMR spectrum of (a) **4-PCL-OH**, (b) **4-PCL-OTs**, (c) **4-PCL-N$_3$**, and (d) **4-PCL-Amine**, (e) **4-PCL-DBA** in $CDCl_3$.

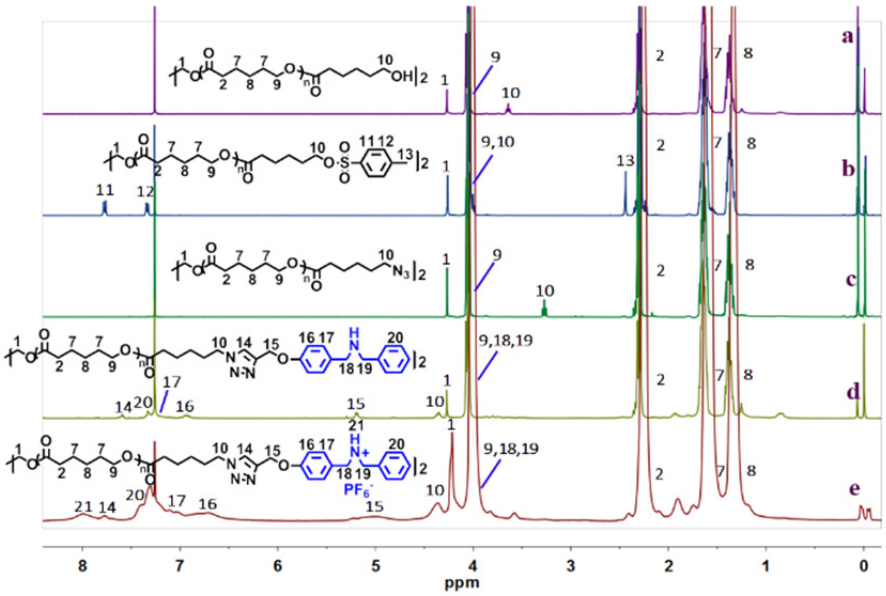



**Fig. S12** $^{1}$H NMR spectrum of (a) **2-PCL-OH**, (b) **2-PCL-OTs**, (c) **2-PCL-N$_3$**, (d) **2-PCL-Amine** and (e) **2-PCL-DBA** in $CDCl_3$.

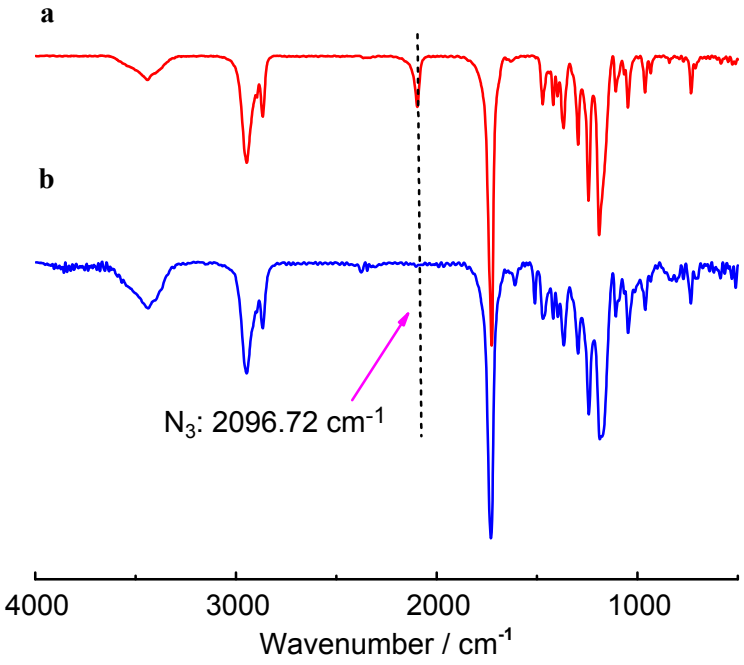



**Fig. S13** FT-IR spectra of (a) **4-PCL-N$_3$** and (b) **4-PCL-Amine**.

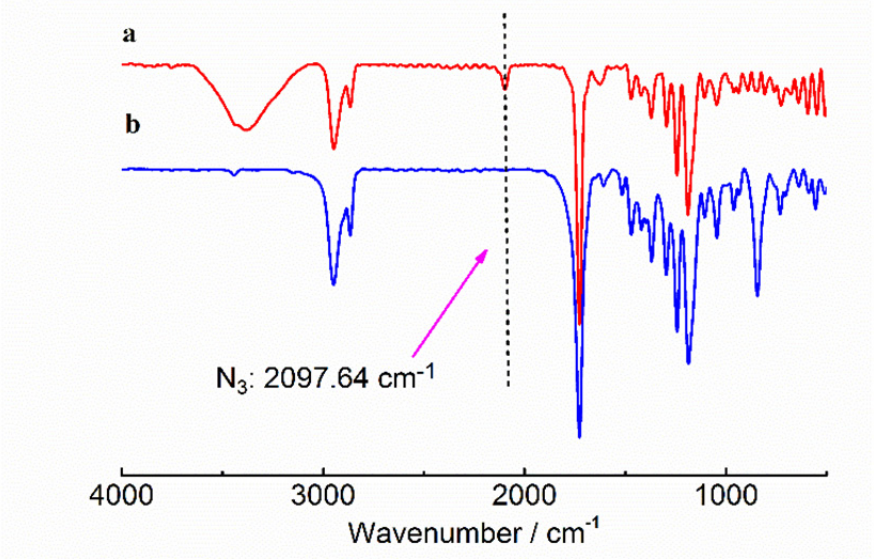



**Fig. S14** FT-IR spectra of (a) **2-PCL-N$_3$** and (b) **2-PCL-Amine**

**Discussion:** After azidation, the stretching vibration peaks of -$N_3$ at 2097 $cm^{-1}$ were not detected, suggesting **2-PCL-N$_3$** and **4-PCL-N$_3$** have been transformed into **4-PCL-Amine** and **2-PCL-Amine**, completely (Fig. S13 and S14).

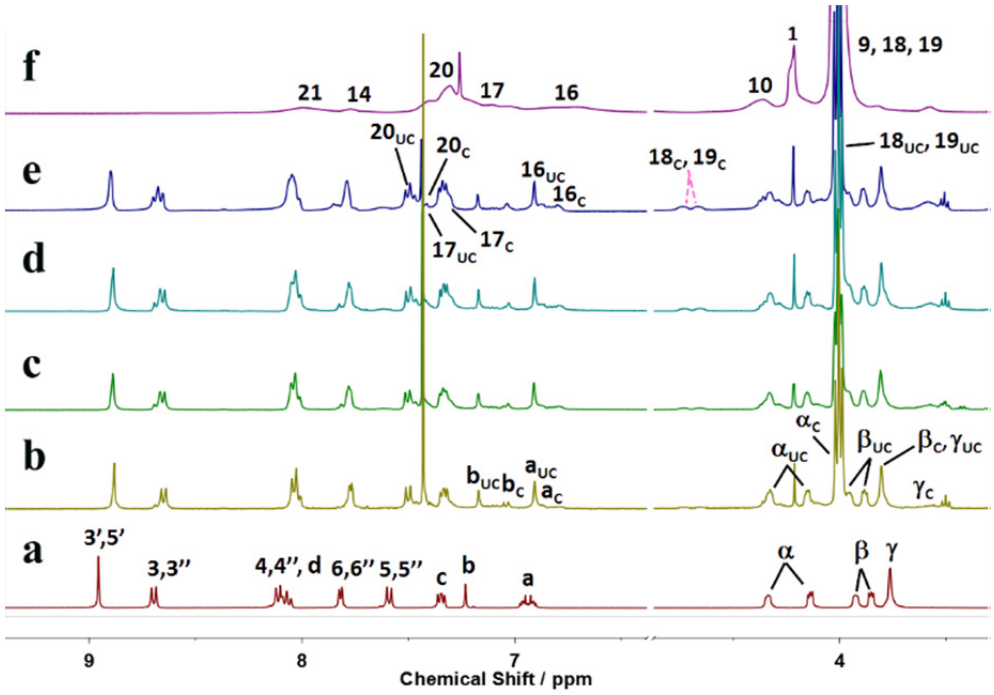
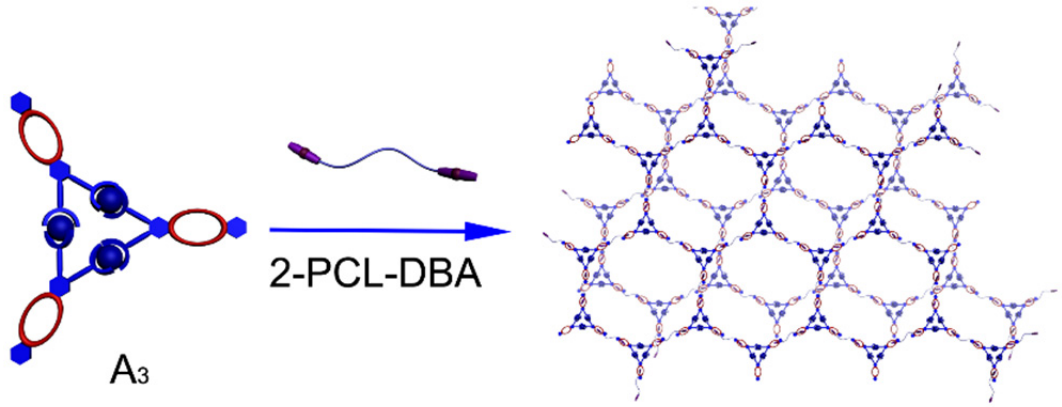



**Fig. S15** Partial $^1$H NMR spectra (400 MHz) of (a) **A$_3$** in $CD_3CN$, (b-e) the mixture of **A$_3$** and 1.5 equivalent of **2-PCL-DBA** of in $CDCl_3/CD_3CN$ (v/v = 3/2). The molar ratio of DB24C8 and DBA was 1:1 and the concentration of **A$_3$** was 0.5 mM (b), (c) 1.0 mM, (d) 2.0 mM, (e) 5.0 mM and (f) **2-PCL-DBA** in $CDCl_3$. Here ‘‘U’’ and ‘‘C’’ denote uncomplexed and complexed moieties, respectively.




**Scheme S3** Cartoon representation of $\mathbf{A_3}$ and 1.50 equivalents of **2-PCL-DBA** formation of a supramolecular network.

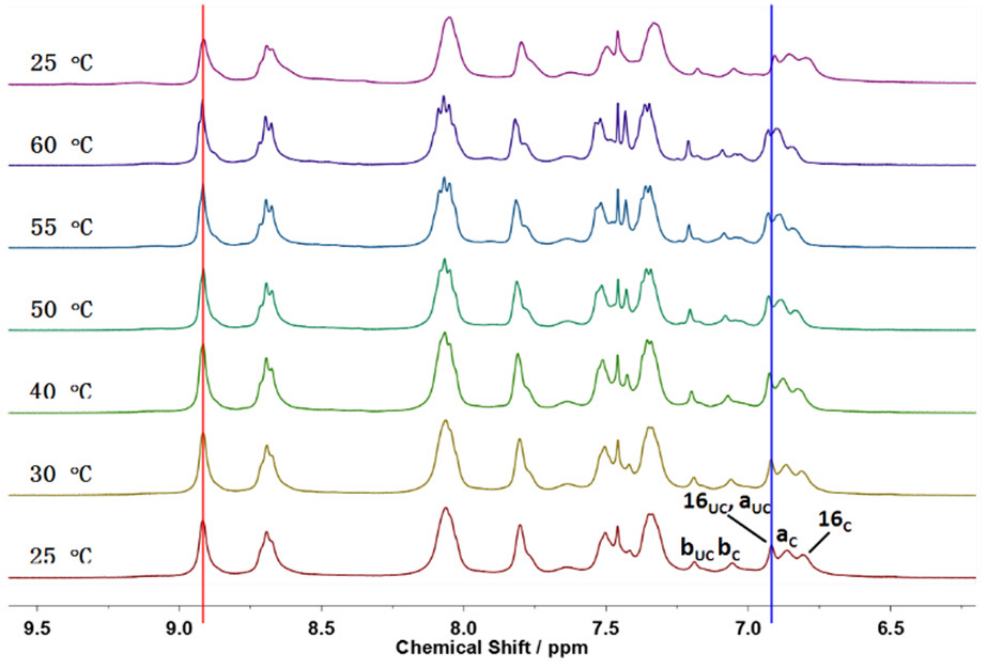



**Fig. S16.** Variable temperature NMR of the mixture of $\mathbf{A_3}$ and 0.75 equivalent of **4-PCL-DBA** in $CDCl_3/CD_3CN$ (v/v = 3/2). The molar ratio of DB24C8 and DBA was 1:1 and the concentration of $\mathbf{A_3}$ was 10 mM.

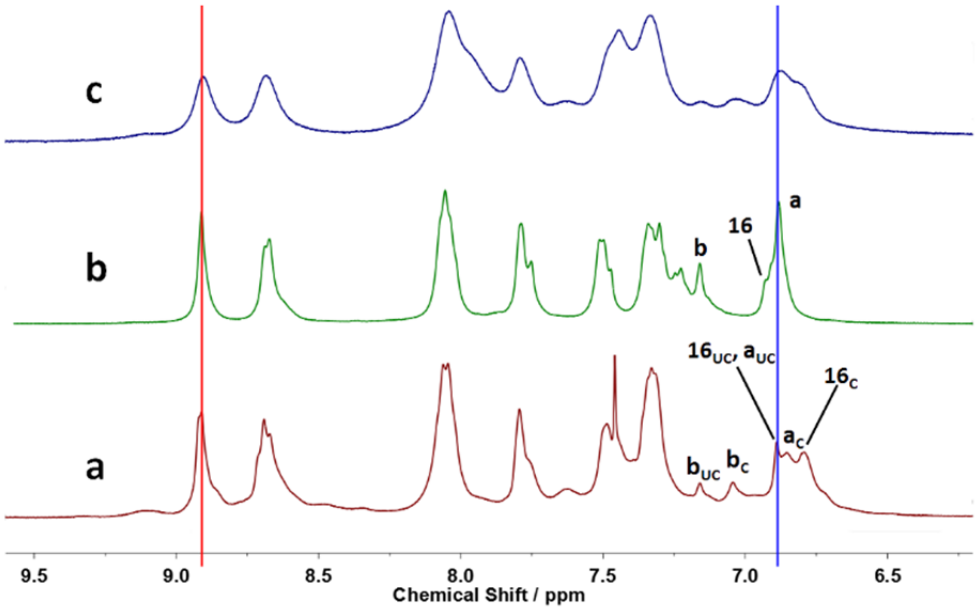



**Fig. S17** Partial $^{1}$H NMR spectra (400 MHz) of (a) the mixture of $\mathbf{A_3}$ and 0.75 equivalent of **4-PCL-DBA** in $CDCl_3/CD_3CN$ (v/v = 3/2). The molar ratio of DB24C8 and DBA was 1:1 and the concentration of $\mathbf{A_3}$ was 10 mM, (b) obtained by adding 3.0 equivalents of TEA to (a), (c) obtained by adding 3.6 equivalents of $HPF_6$ to (b). Here ‘‘U’’ and ‘‘C’’ denote uncomplexed and complexed moieties, respectively.

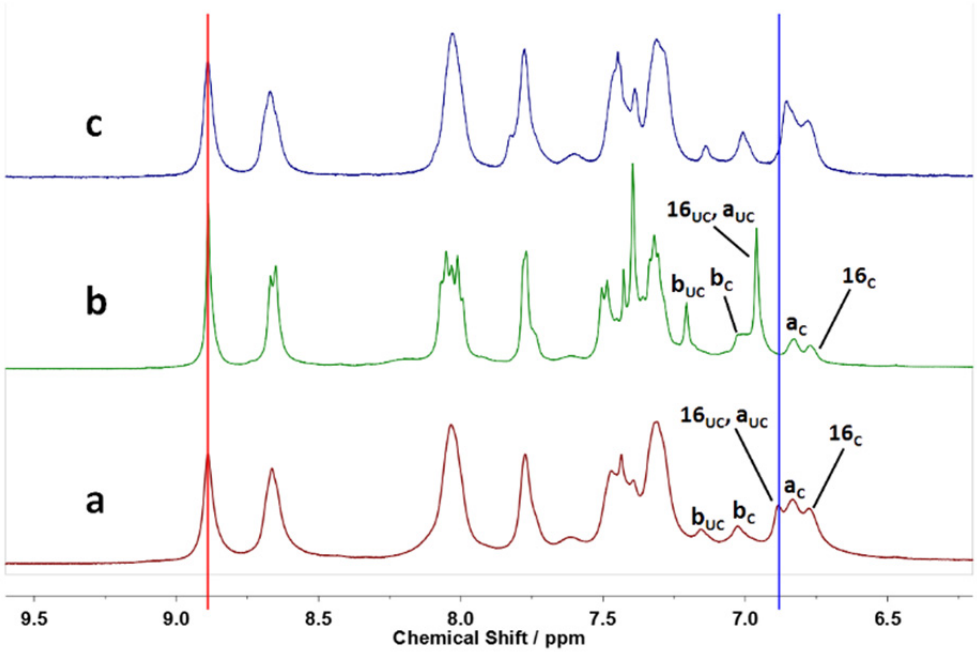



**Fig. S18** Partial $^{1}$H NMR spectra (400 MHz) of (a) the mixture of $\mathbf{A_3}$ and 0.75 equivalent of **4-PCL-DBA** in $CDCl_3/CD_3CN$ (v/v = 3/2), the molar ration of DB24C8 and DBA was 1:1, the concentration of $\mathbf{A_3}$ was 10 mM, (b) obtained by adding 3.0 equivalents of $KPF_6$ to (a), (c) obtained by adding 6.0 equivalents of 18C6 to (b). Here ‘‘U’’ and ‘‘C’’ denote uncomplexed and complexed moieties, respectively.

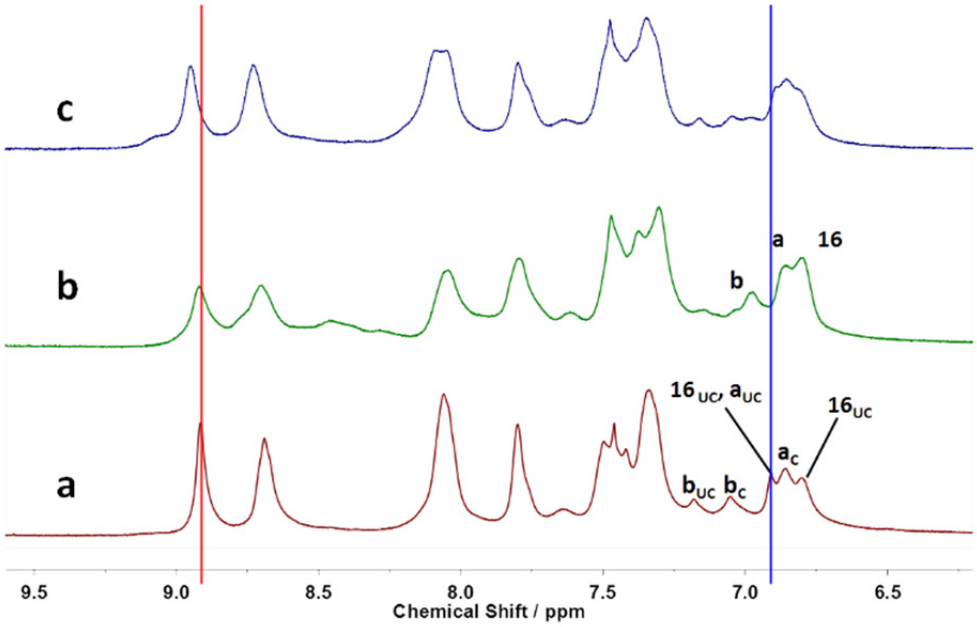
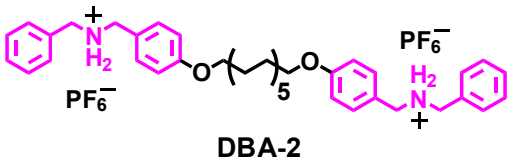



**Fig. S19** Partial $^{1}$H NMR spectra (400 MHz) of (a) the mixture of $\mathbf{A}_3$ and 0.75 equivalent of **4-PCL-DBA** in $CDCl_3/CD_3CN$ (v/v = 3/2). The molar ratio of DB24C8 and DBA was 1:1 and the concentration of $\mathbf{A_3}$ was 10 mM, (b) obtained by adding 3.0 equivalents of tetrabutylammonium chloride to (a), (c) obtained by adding 3.0 equivalents of AgOTf to (b). Here ‘‘U’’ and ‘‘C’’ denote uncomplexed and complexed moieties, respectively.



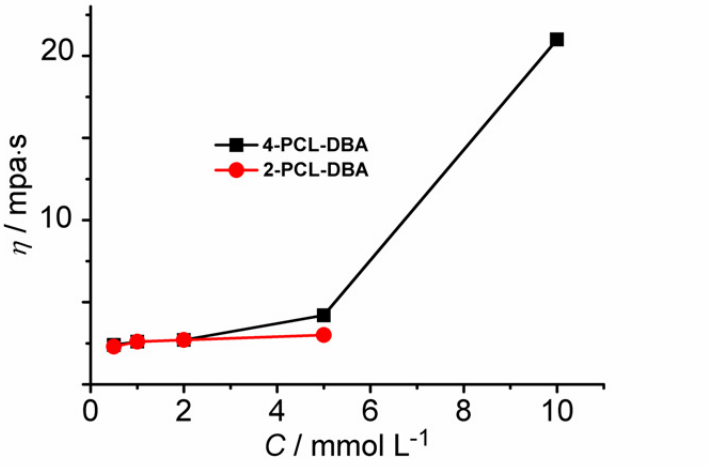




**Fig. S20** (Top) The chemical structure of small molecule DBA. (Bottom) The dynamic viscosities increase with the concentration of complex systems.

**Additional Discussion**

The treatment of $\mathbf{A_3}$ with **DBA-2** in the $CHCl_3$/MeCN mixture solvent (v/v = 3/2) leads to the formation of precipitate immediately at a concentration of 10 mM. Therefore, the corresponding viscosity cannot be measured reasonably. We did measure the dynamic viscosities of the supramolecular networks (Fig. S20). As expected, the dynamic viscosity increased remarkably at the concentration of 10 mM in the case of **4-PCL-DBA/$\mathbf{A_3}$**, where the gel formed at this concentration.

## Supplementary References


S1. L. He, L. Li, X. Liu, J. Wang, H. Huang and W. Bu, *Polym. Chem*., 2016, **7**, 3722.
S2. P. Jarosz, K. Lotito, J. Schneider, D. Kumaresan, R. Schmehl, R. Eisenberg, *Inorg. Chem*. 2009, **48**, 2420.
S3. Z. Ge, J. Hu, F. Huang, S. Liu, *Angew. Chem. Int. Ed*, 2009, **48**, 1798.
S4. C. G. Palivan, R. Goers, A. Najer, X. Zhang, A. Car and W. Meier, *Chem. Soc. Rev.*, 2016, **45**, 377.
S5. (*a*) Y. Xu, L. Wang, X. Zhu and C. Wang, *RSC Adv.*, 2016, **6**, 31053; (*b*) C. O. González, F. D. Meo, A. G. Campo, D. Beljonne, P. Norman, M. S. Sorbed, M. Linares and D. B. Amabilino, *J. Am. Chem. Soc.*, 2015, **137**, 15795.
S6. (*a*) W.-Y. Zhang, Y.-J. Lin, Y.-F. Han and G.-X. Jin, *J. Am. Chem. Soc.*, 2016, **138**, 10700; (*b*) K. Wu, K. Li, Y. J. Hou, M. Pan, L. Y. Zhang, L. Chen and C. Y. Su, *Nat. Commun*, 2016, **7**, 10487; (*c*) Y. Shi, M. Wang, C. Ma, Y. Wang, X. Li and G. Yu, *Nano. Lett*, 2015, **15**, 6276.
S7. (*a*) G. R. Newkome, E. He and L. A. Goínez, *Macromolecules*, 1998, **31**, 4382; (*b*) J. M. Ludlow III, M. Tominaga, Y. Chujo, A. Schultz, X. Lu, T. Xie, K. Guo, C. N. Moorefield, C. Wesdemiotis and G. R. Newkome, *Dalton Trans.*, 2014, **43**, 9604; (*c*) D. Liu, Z. Jiang, M. Wang, X. Yang, H. Liu, M. Chen, C. N. Moorefield, G. R. Newkome, X. Li and P. Wang, *Chem. Commun.*, 2016, **52**, 9773.