Supporting Information for

# Fluorescent cross-linked supramolecular polymers constructed from a novel self-complementary AABB-type heteromultitopic monomer

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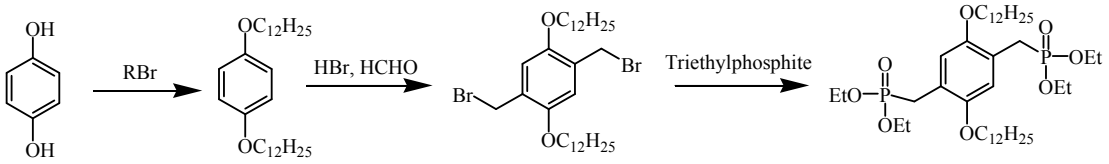
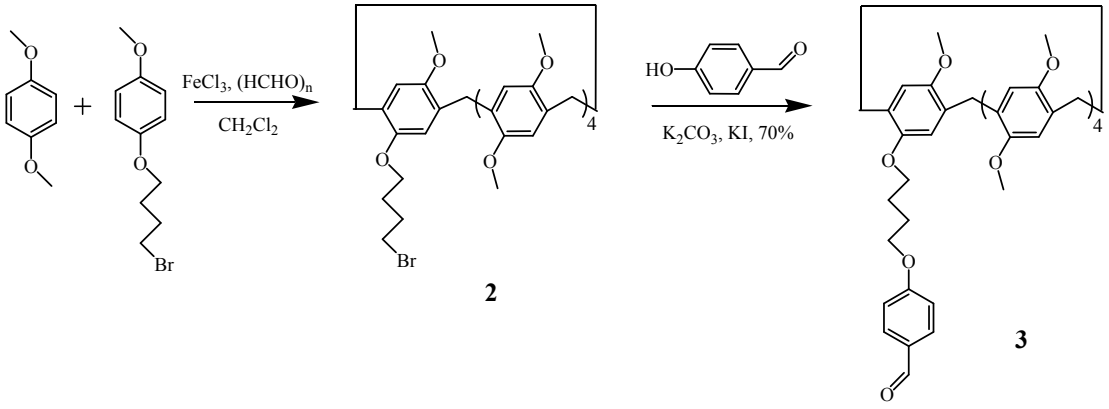
## 1. Synthesis procedure.




**1**

***Scheme. S1*** Synthetic route for compound **1**.

Compound **1** and compound **2** were synthesized according to the procedures reported before.[S1-S3]




**2** **3**

***Scheme. S2*** Synthetic route for compound **3**

Synthesis of compound **3**

To a solution of p-hydroxybenzaldehyde (0.35 g, 2.87 mmol) in DMF (20 mL) was added $K_2CO_3$ (0.60 g, 4.3 mmol) and KI (0.07 g, 0.43 mmol). After stirring for 0.5 hour under 80℃, compound **2** (2.5 g, 2.87 mmol) in DMF (10 mL) was added dropwise. The reaction mixture was stirred at 80℃ for another 10 hours. After cooling to room temperature,

the mixture was filtered through celite and DMF was evaporated under vacuum. Then the residue was dissolved in $CH_2Cl_2$ (100 mL), washed with $H_2O$ (2×100 mL) and brine (2×100 mL), and dried over anhydrous $MgSO_4$. The organic layer was evaporated under vacuum and subjected to column chromatography on silica gel using $CH_2Cl_2$ as the eluent. Compound **3** was obtained as a white solid (1.85 g, 70%). $^1$H NMR (400 MHz, $CDCl_3$, 298 K) δ 9.89 (s, 1H), 7.82 (d, J = 8.1 Hz, 2H), 6.94 (d, J = 8.2 Hz, 2H), 6.82 – 6.69 (m, 10H), 3.99 (t, J = 5.4 Hz, 2H), 3.91 (d, J = 5.6 Hz, 2H), 3.77 (d, J = 5.1 Hz, 10H), 3.63 (d, J = 15.4 Hz, 27H), 1.92 (m, 4H). $^{13}$C NMR (126 MHz, $CDCl_3$, 298K) δ 190.8 (s), 164.1 (s), 150.9-150.6 (m), 149.8 (s), 132.0 (s), 129.9 (s), 128.5 – 128.1 (m), 115.0 (s), 114.8 (s), 114.2-113.8 (m), 77.3 (s), 77.0 (s), 76.8 (s), 67.9 (d, J = 6.3 Hz), 56.0-55.6 (m), 52.9 (s), 29.9-29.3 (m), 26.2 (s), 26.0 (s). MS (MALDI-TOF) calcd for $C_{55}H_{60}O_{12}$, *m/z* = 912.4085 [M]+, Found: *m/z* = 912.4112.

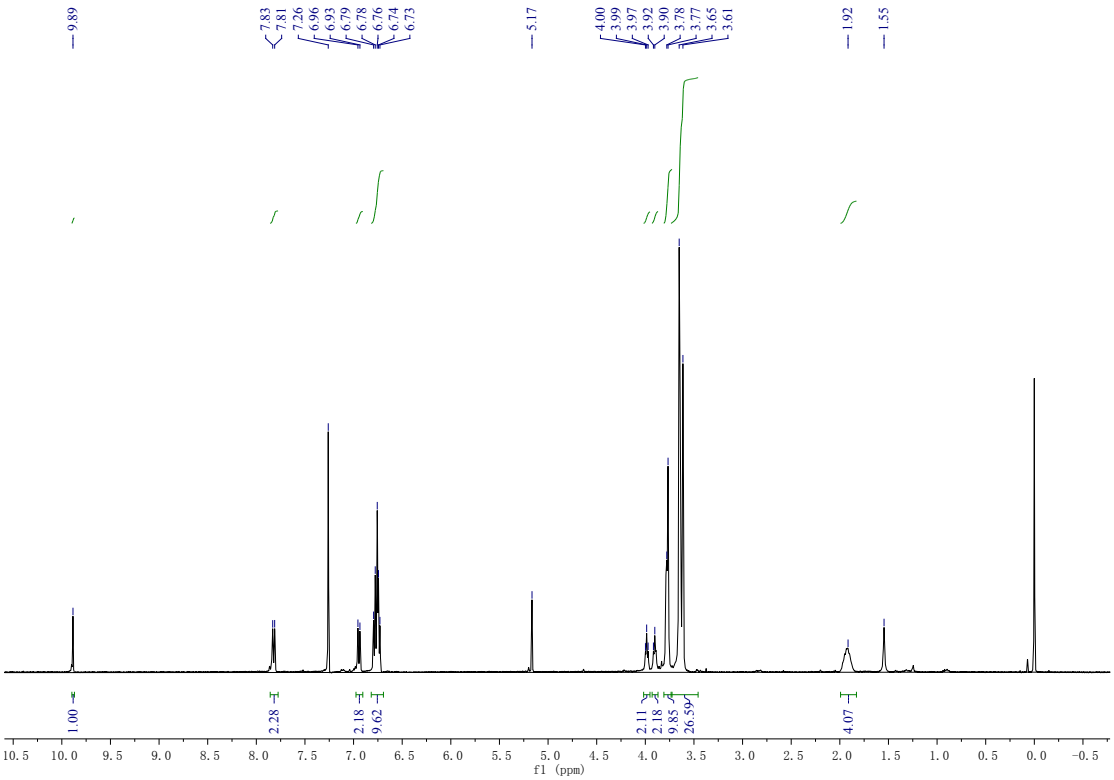



*Fig. S1* $^{1}$H NMR (400 MHz, $CDCl_3$, 298 K) of **3**.

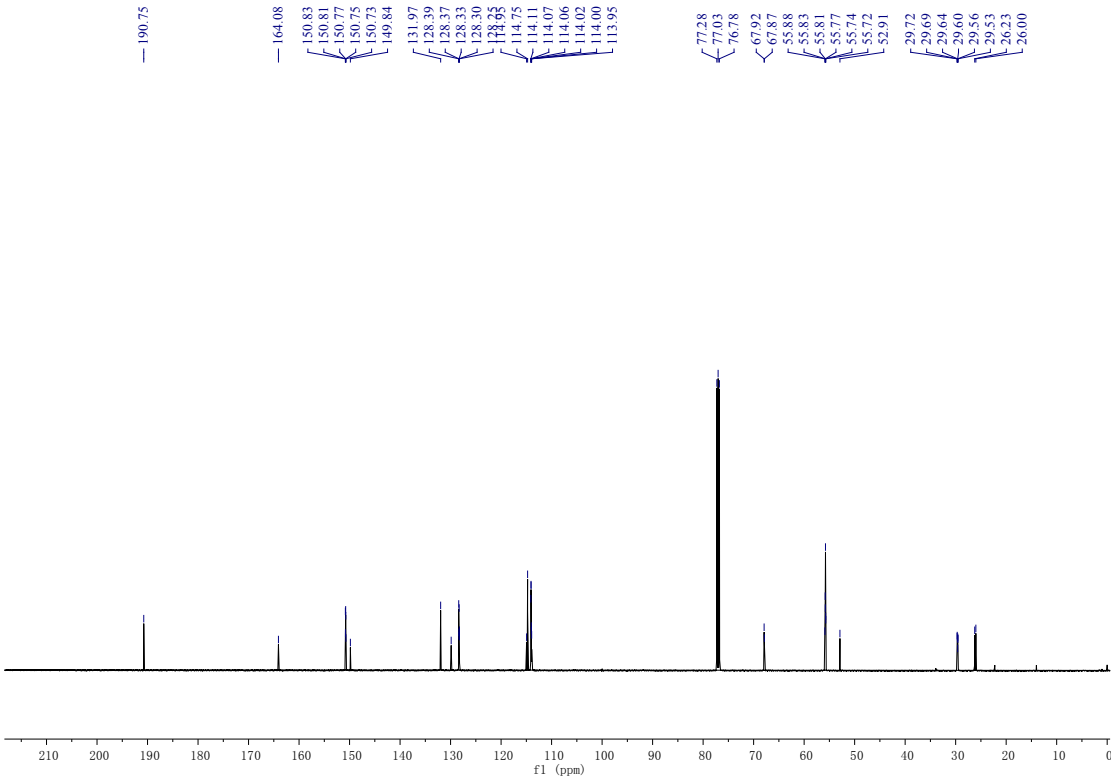



*Fig. S2* $^{13}$C NMR (126 MHz, $CDCl_3$, 298 K) of **3**.

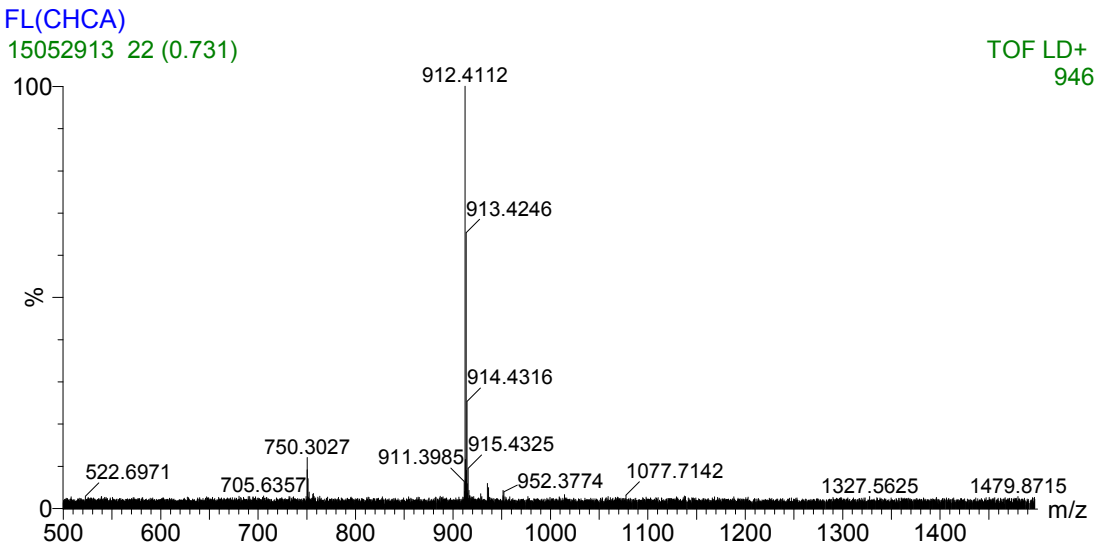



*Fig. S3* MALDI-TOF MS spectrum of **3**.

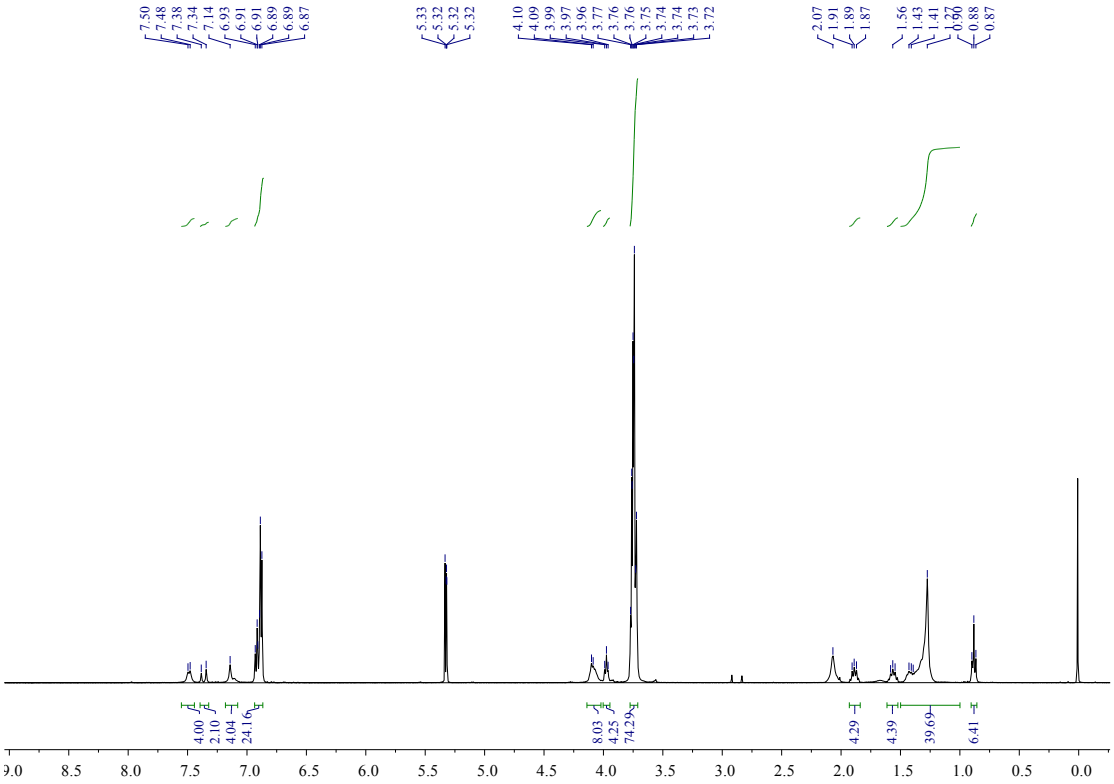



*Fig. S4* $^{1}$H NMR (400 MHz, $CD_2Cl_2$, 298 K) of **APOPV**.

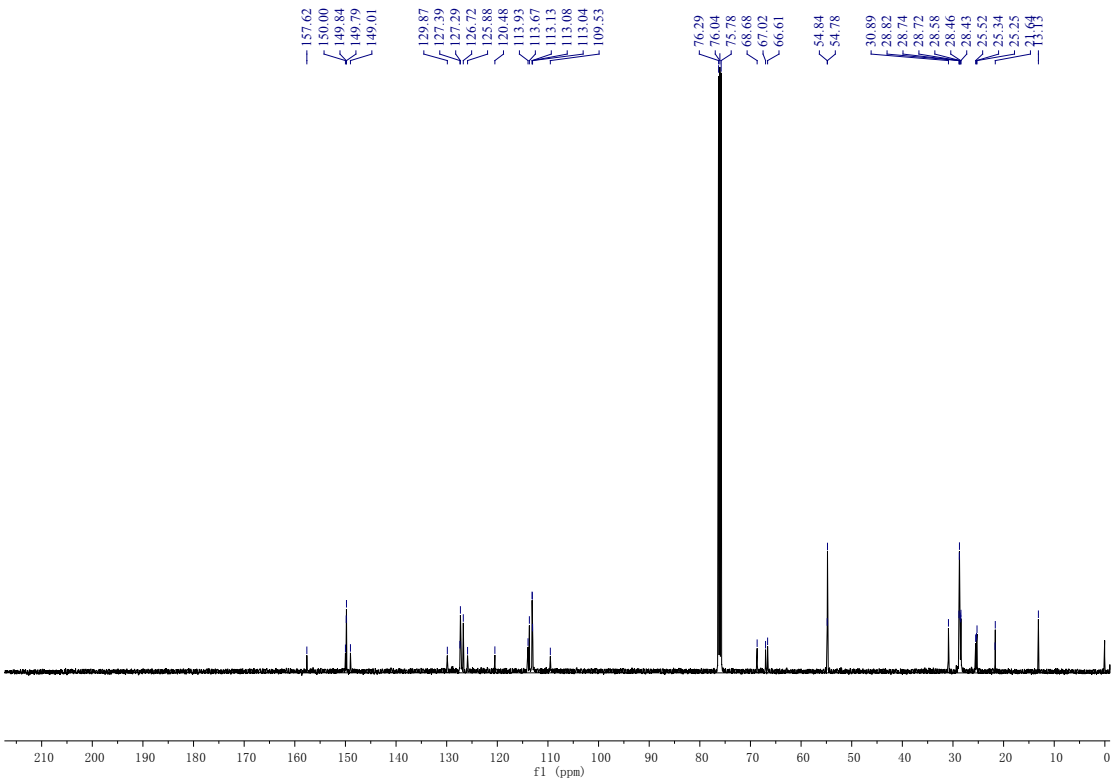



*Fig. S5* $^{13}$C NMR (126 MHz, $CDCl_3$, 298 K) of **APOPV**.

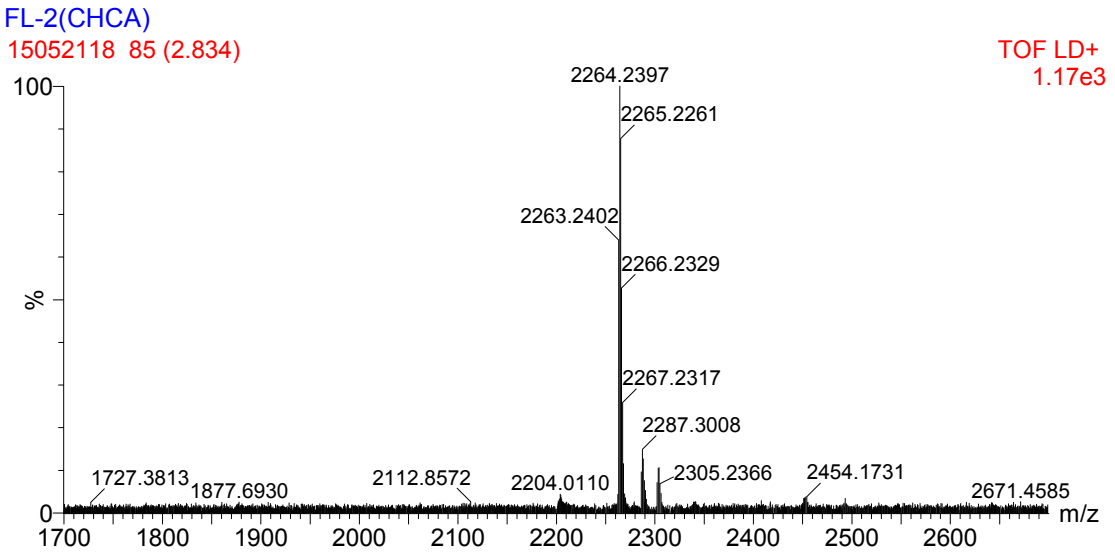



*Fig. S6* MALDI-TOF MS spectrum of **APOPV**.

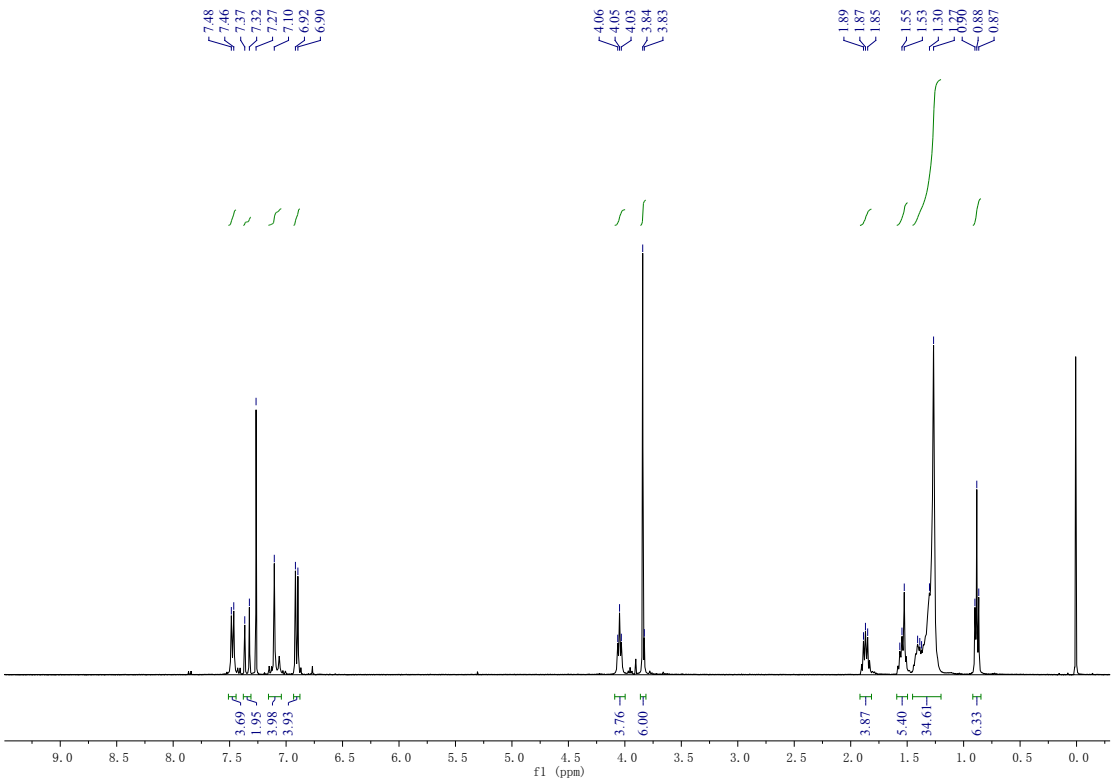



*Fig. S7* $^{1}$H NMR (400 MHz, $CDCl_3$, 298K) of **AOPV**.

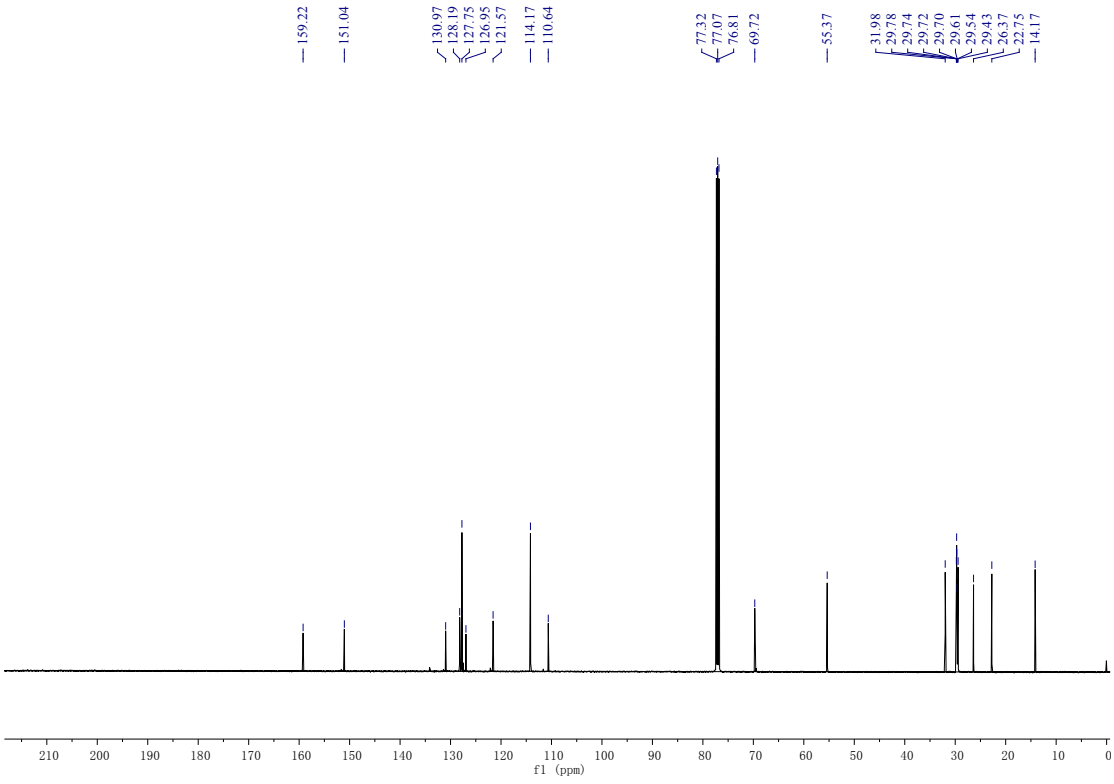



*Fig. S8* $^{13}$C NMR (126 MHz, $CDCl_3$, 298 K) of **AOPV**.

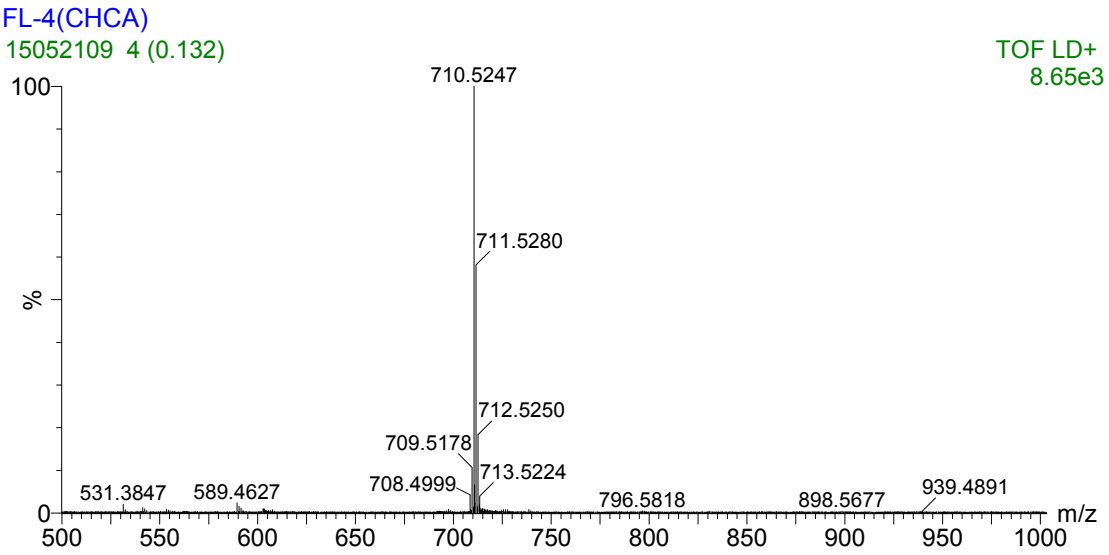
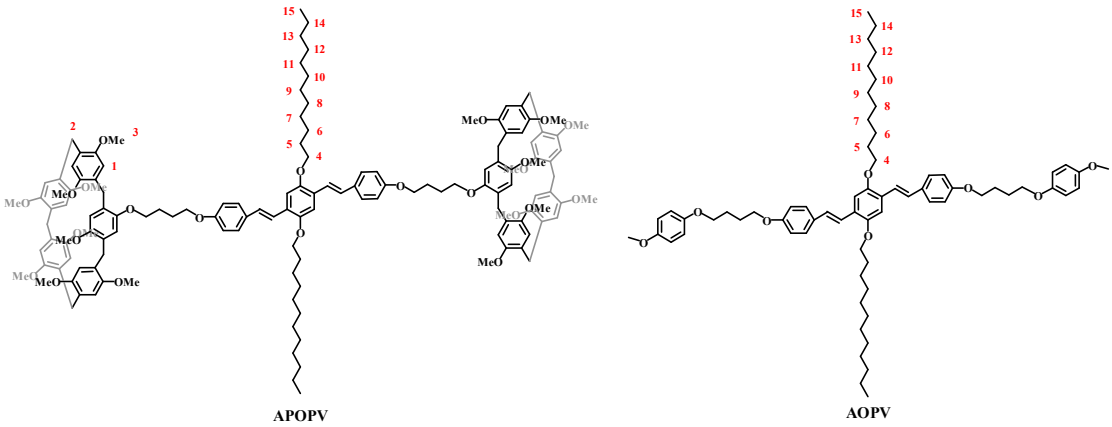



*Fig. S9* MALDI-TOF MS spectrum of **AOPV**.

## 2. Supplementary data




***Scheme. S3*** The structures of **APOPV** and **AOPV**.

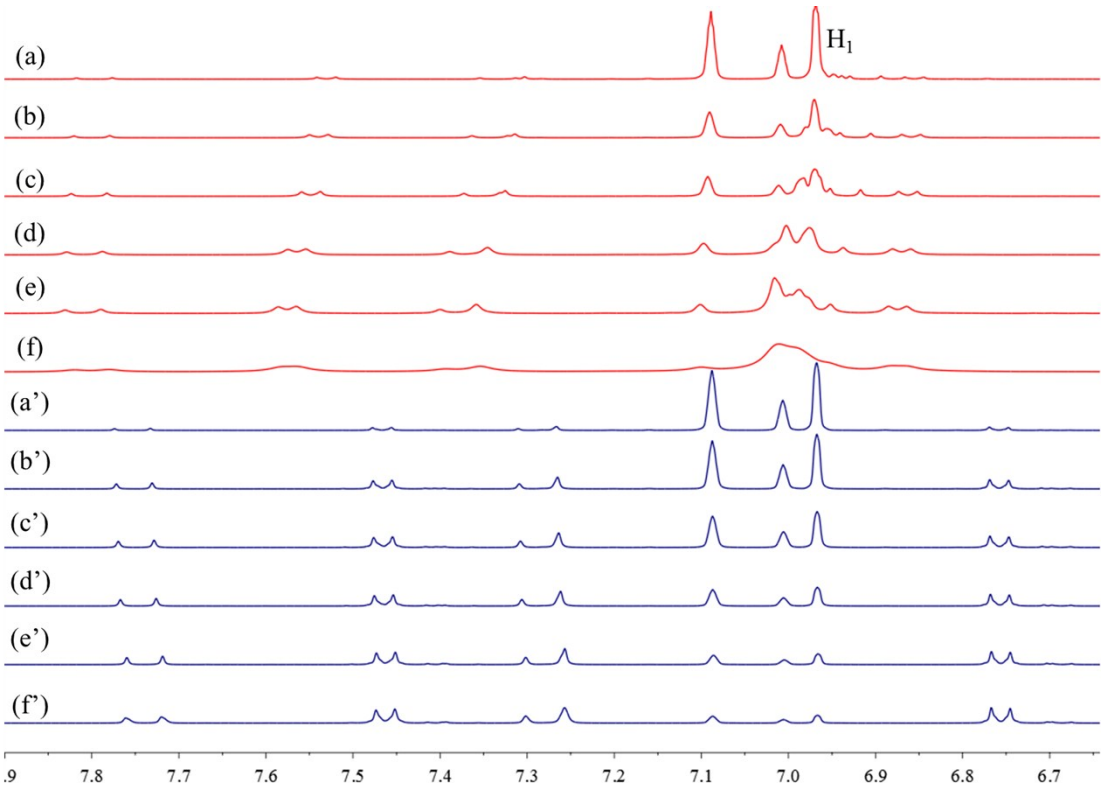



*Fig. S10* Partial $^{1}$H NMR spectra (toluene-$d_8$, 400MHz, 298K) of **APOPV** and **AOPV** at different concentrations. **APOPV**: (a) 1.00, (b) 5.00, (c) 10.0, (d) 20.0, (e) 40.0, (f) 60 mM; **AOPV**: (a') 1.00, (b') 5.00, (c') 10.0, (d') 20.0, (e') 40.0, (f') 60 mM.

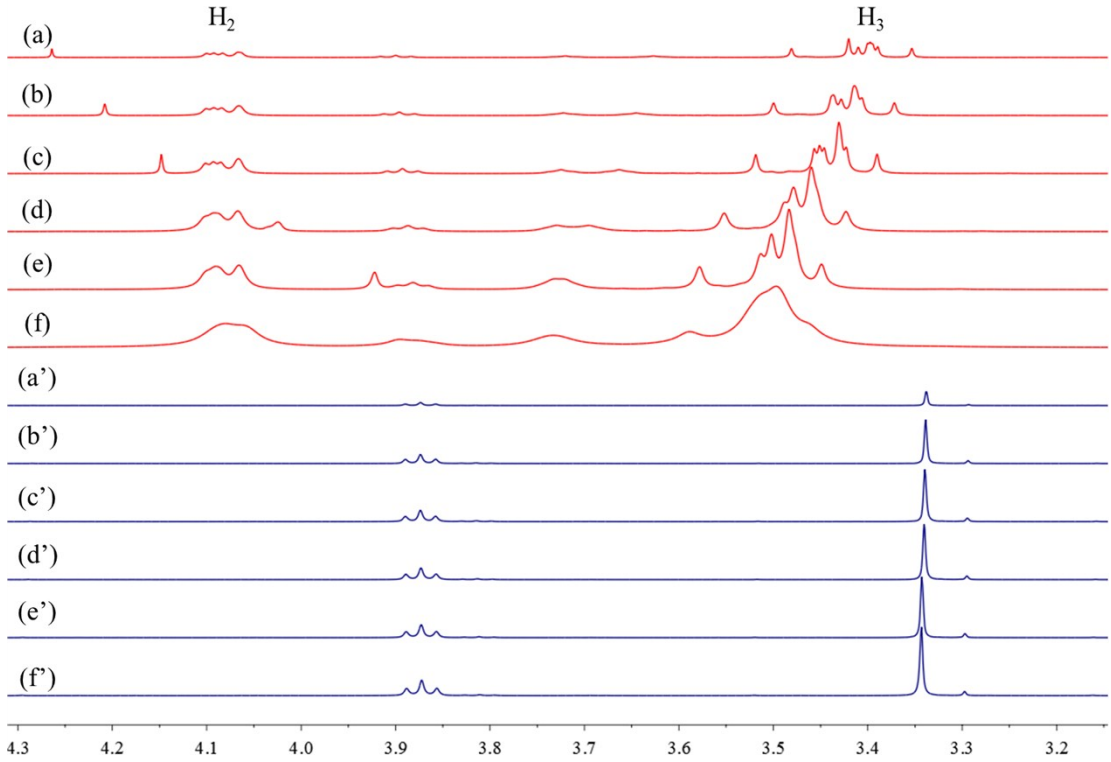



*Fig. S11* Partial $^{1}$H NMR spectra (toluene-$d_8$, 400MHz, 298K) of **APOPV** and **AOPV** at different concentrations. **APOPV**: (a) 1.00, (b) 5.00, (c) 10.0, (d) 20.0, (e) 40.0, (f) 60 mM; **AOPV**: (a') 1.00, (b') 5.00, (c') 10.0, (d') 20.0, (e') 40.0, (f') 60 mM.

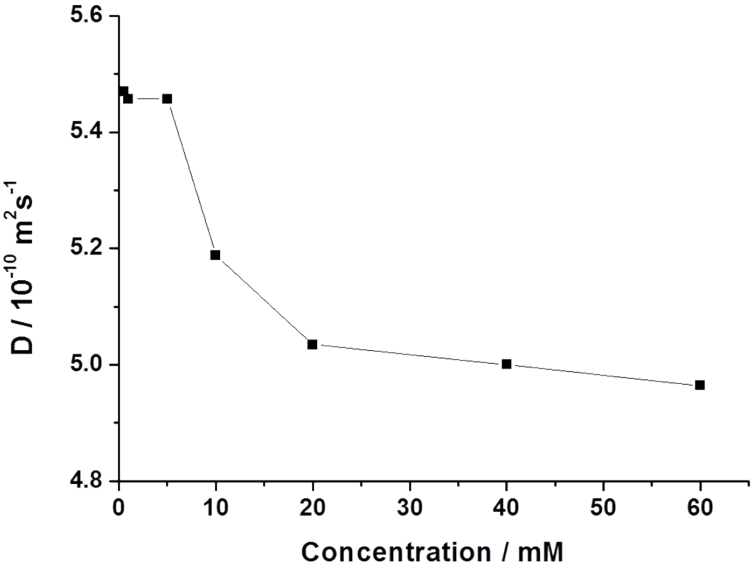



*Fig. S12* Diffusion coefficient of **AOPV** with different concentrations recorded in toluene-d8 at 25 ℃.

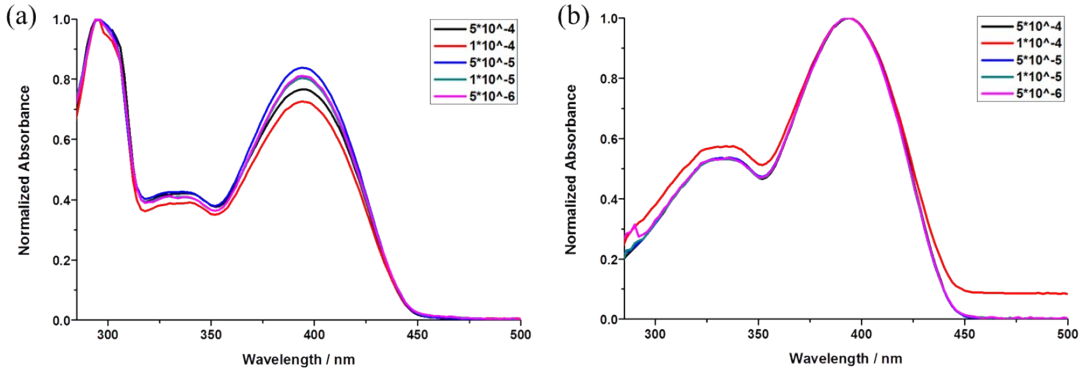



*Fig. S13* UV-Vis spectra of **APOPV** (a) and **AOPV** (b) at different concentration.

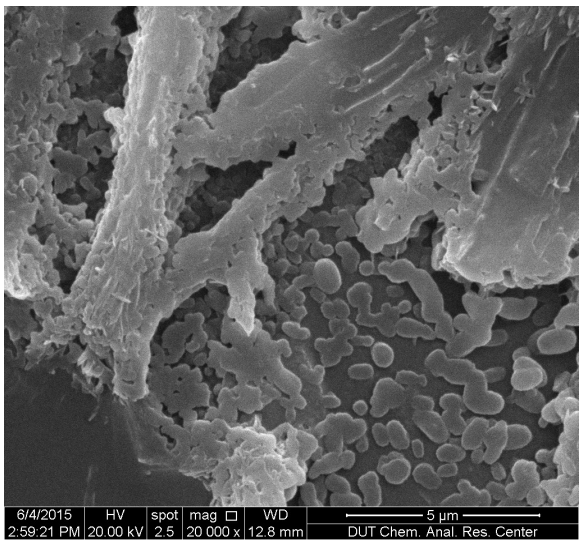
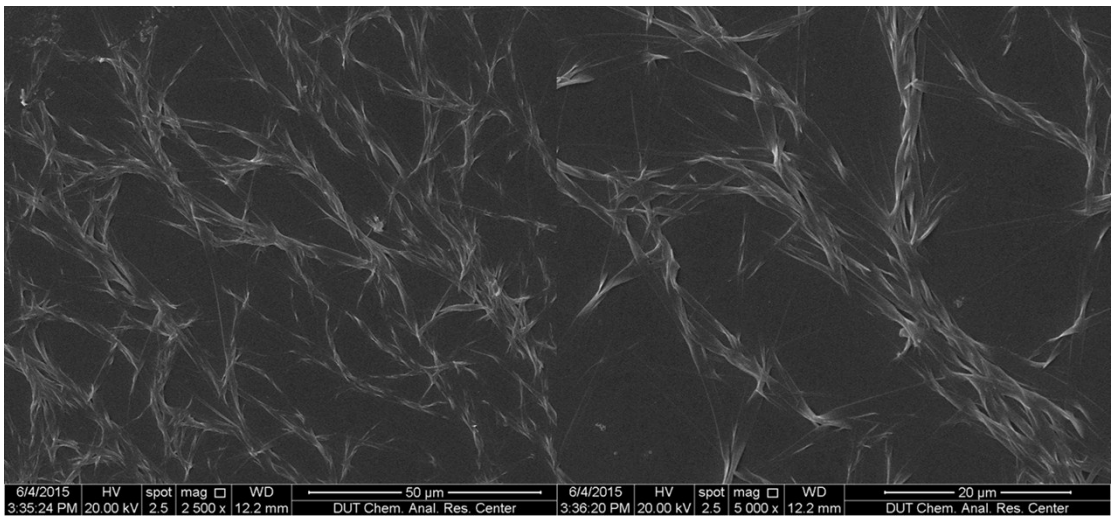



*Fig. S14* The SEM images of **APOPV** solvent in $10^{-3}$ M.




*Fig, S15* The SEM images of **AOPV** solvent in $10^{-3}$ M.

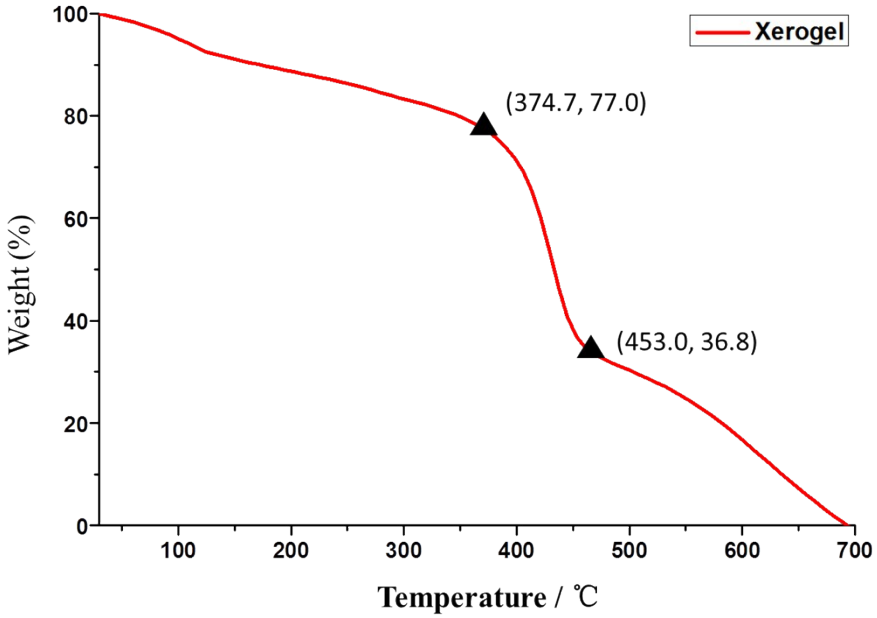



*Fig. S16* Thermogravimetric analysis (TGA) of the supramolecular xerogels of **APOPV**.

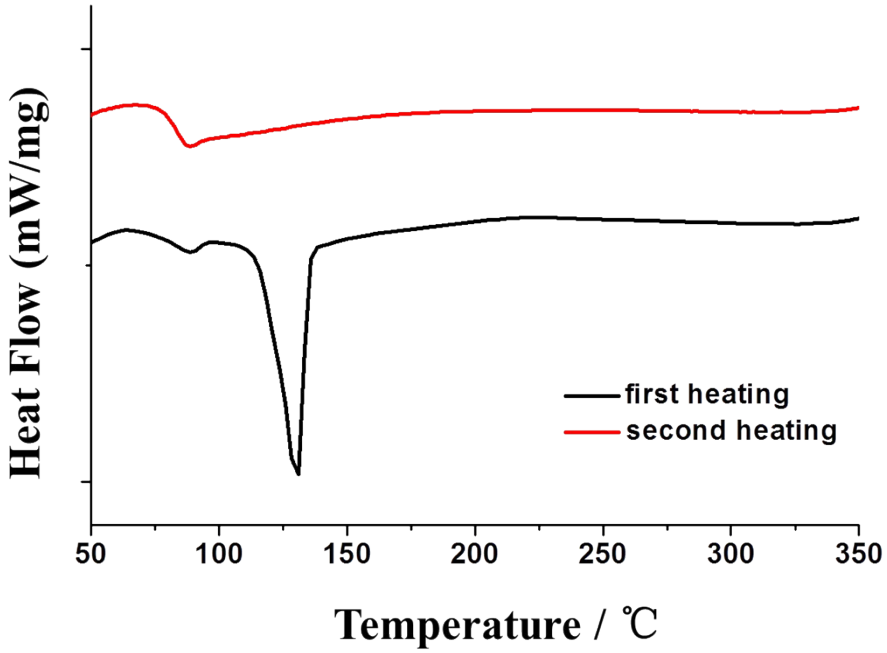



*Fig. S17* Differential scanning calorimetry (DSC) of the supramolecular xerogels of **APOPV**.

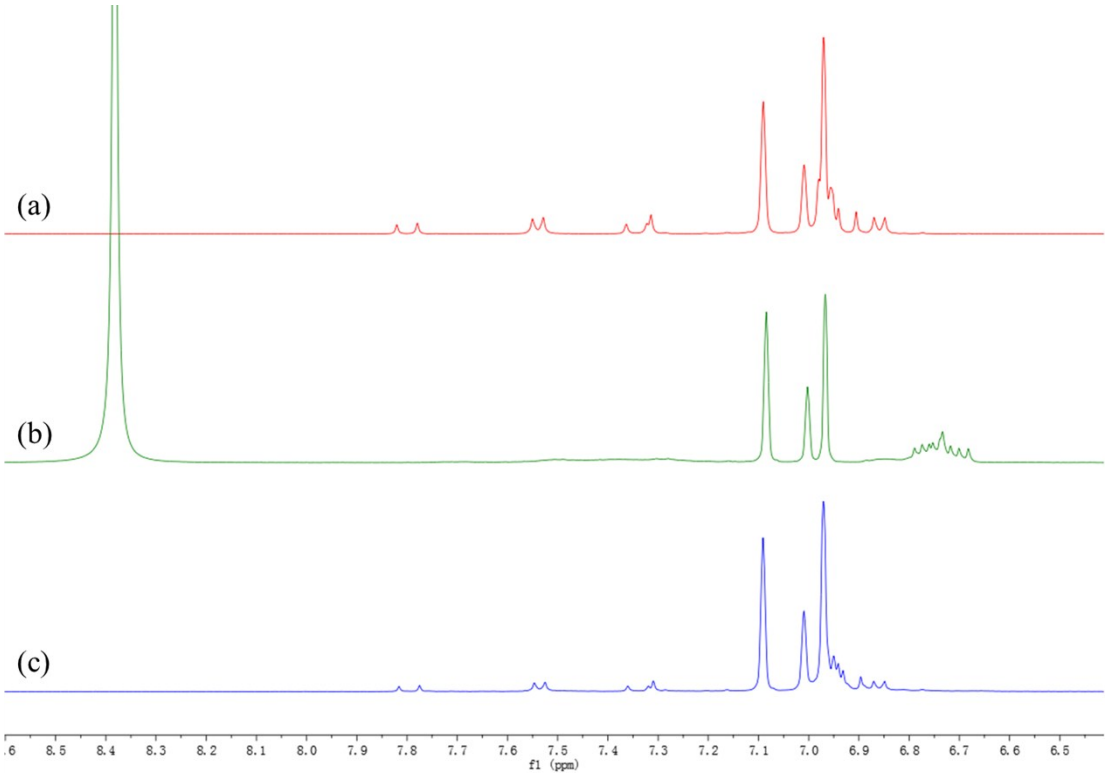



*Fig. S18* Partial $^{1}$H NMR spectra (toluene-$d_8$, 400MHz, 298K) of **APOPV**: (a) pure **APOPV** (5 mM); (b) after addition of 5 μL (25 equiv.) of TFA to a; (c) after addition of 20 μL (55 equiv.) of TEA to b.

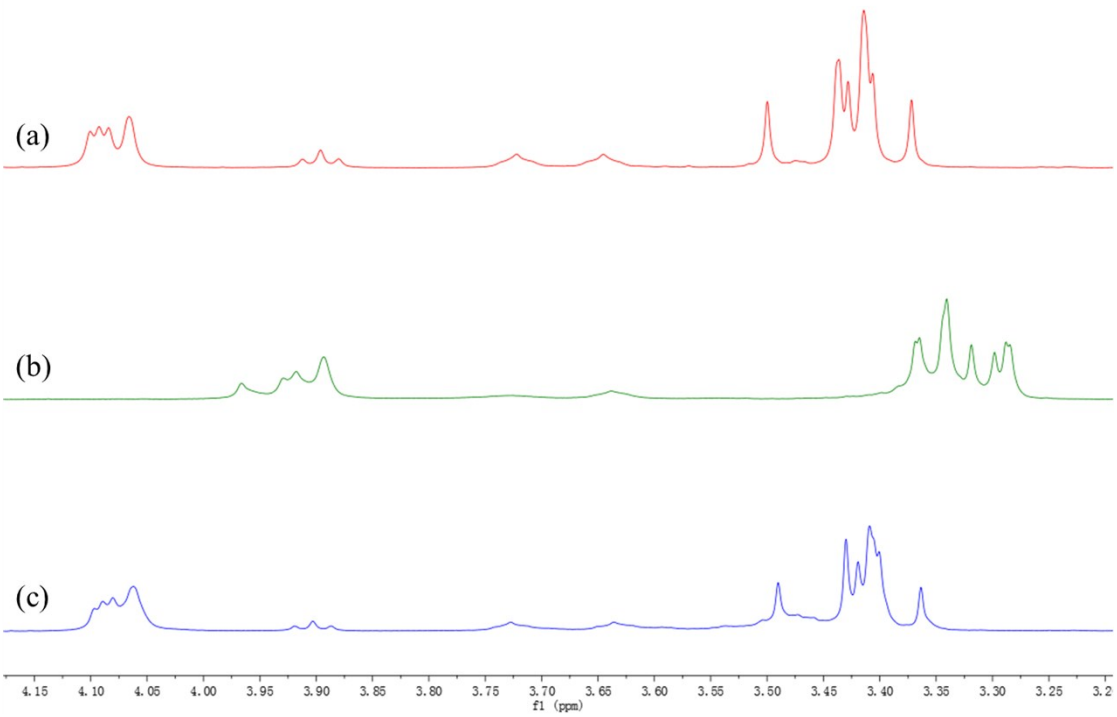



*Fig. S19* Partial $^{1}$H NMR spectra (toluene-$d_8$, 400MHz, 298K) of **APOPV**: (a) pure **APOPV** (5 mM); (b) after addition of 5 μL (25 equiv.) of TFA to a; (c) after addition of 20 μL (55 equiv.) of TEA to b.

## 3. Determination of the associate constants

NMR titrations were performed to determinate the binding constants ($K_a$) between pillar[5]arene (**P5A**) and alkyl chain (**G**) in toluene. Therefor we used dimethylpillar[5]arene as host and the concentration of **P5A** was constant. The 1-dodecyloxy-4-methoxy benzene was synthesized as guest and its concentration was varied. Using the nonlinear curve-fitting method,[S4] the associate constants can be obtained from the following equation:

$$A = (A_\infty/[P5A])*(0.5[G]+0.5([P5A]+1/K_a)-(0.5*([G]^2+(2[G](1/K_a-[P5A]))+(1/K_a+[P5A])^2)^{0.5}))$$

Where $A$ is the chemical shift change of H3 on the pillar[5]arene, $A_\infty$ is the chemical shift change of H3 when the host is completely complexed, [P5A] is the fixed concentration of the host, and [G] is the concentration of the guest 1-dodecyloxy-4-methoxy benzene.

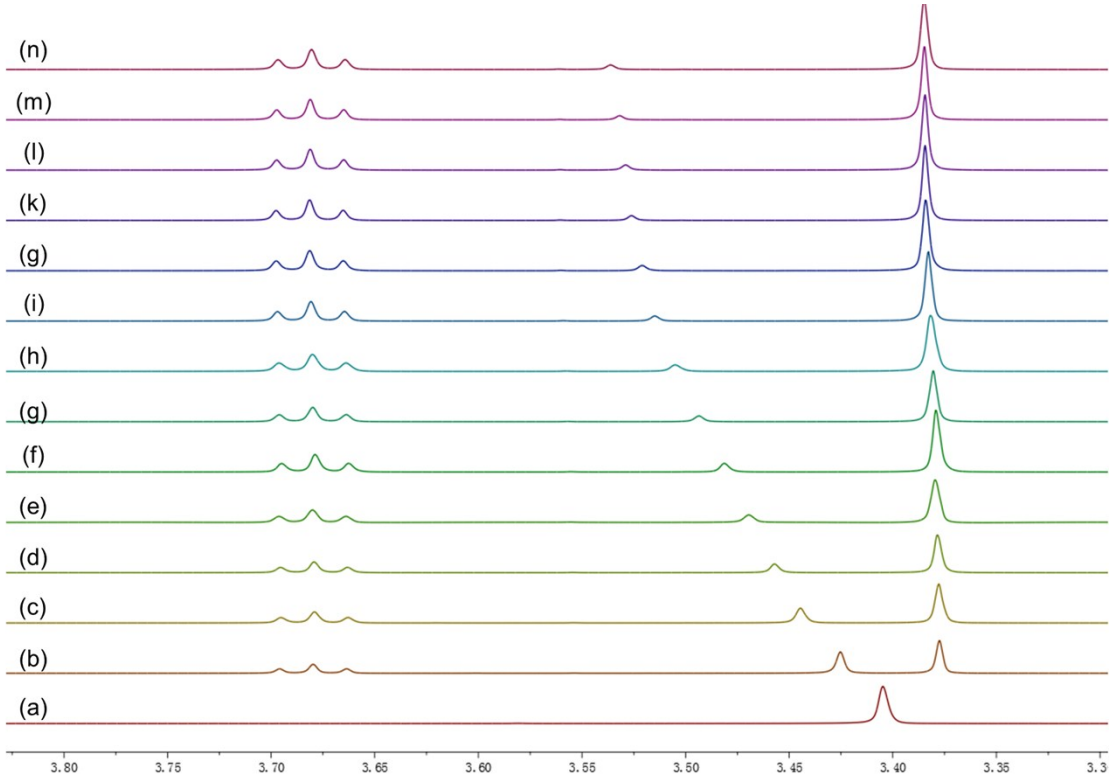



*Fig. S20* Partial $^1$H NMR spectra (toluene-$d_8$, 400MHz, 298K) of **P5A** at a concentration of 2 mM upon addition of the guest 1-dodecyloxy-4-methoxy benzene: (a) 0 mM; (b) 10 mM; (c) 20 mM; (d) 30 mM; (e) 40 mM; (f) 50 mM; (g) 60 mM; (h) 70 mM; (i) 80 mM; (j) 90 mM; (k) 100 mM; (l) 110 Mm; (m) 120 mM; (n) 150 mM.

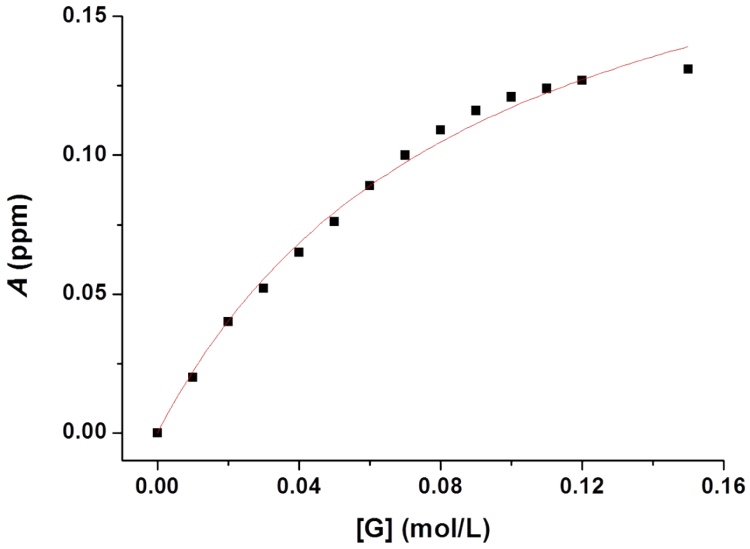



*Fig. S21* The non-linear curve-fitting for the complexation of P5A host (2 mM) with guest 1-dodecyloxy-4-methoxy benzene at different concentration.

S1 M. A. Mezour, I. I. Perepichka, J. Zhu, R. B. Lennox and D. F. Perepichka, *ACS nano*, 2014, 8, 2214-2222.
S2 B. Narayan, S. P. Senanayak, A. Jain, K. S. Narayan, and S. J. George, *Adv. Funct. Mater.*, 2013, 23, 3053–3060.
S3 L. Liu, D. Cao, Y. Jin, H. Tao, and H. Meier, *Org. Biomol. Chem.*, 2011, 9, 7007-7010.
S4 C. Li, L. Zhao, J. Li, X. Ding, S. Chen, Q. Zhang, Y. Yu and X. Jia, *Chem. Commun.*, 2010, 46, 9016-9018.