Supporting Information for

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

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Scheme. S1 Synthetic route for compound 1.

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

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 K₂CO₃ (0.60 g, 4.3 mmol) and KI (0.07 g, 0.43 mmol). After stirring for 0.5 hour under 80°C, compound 2 (2.5 g, 2.87 mmol) in DMF (10 mL) was added dropwise. The reaction mixture was stirred at 80°C 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$_2$Cl$_2$ (100 mL), washed with H$_2$O (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$_2$Cl$_2$ as the eluent. Compound 3 was obtained as a white solid (1.85 g, 70%). $^1$H NMR (400 MHz, CDCl$_3$, 298 K) $\delta$ 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) $\delta$ 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 ¹H NMR (400 MHz, CD₂Cl₂, 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 °C.

**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.

![TGA graph]

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

![DSC graph]
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 determine the binding constants ($K_a$) between pillar[5]arene (P5A) and alkyl chain (G) in toluene. Therefore 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:
\[ A = \left( A_\infty / [P5A] \right)^* \left( 0.5[G] + 0.5([P5A] + 1/K_a) - (0.5\cdot [G]^2 + 2[G](1/K_a-[P5A]) + (1/K_a + [P5A])^2)^{0.5} \right) \]

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.