Electronic Supplementary Material (ESI) for Chemical Communications

Pillar[5]arene-based polymeric architectures constructed by orthogonal supramolecular interactions

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Electronic Supplementary Information

(ESI)

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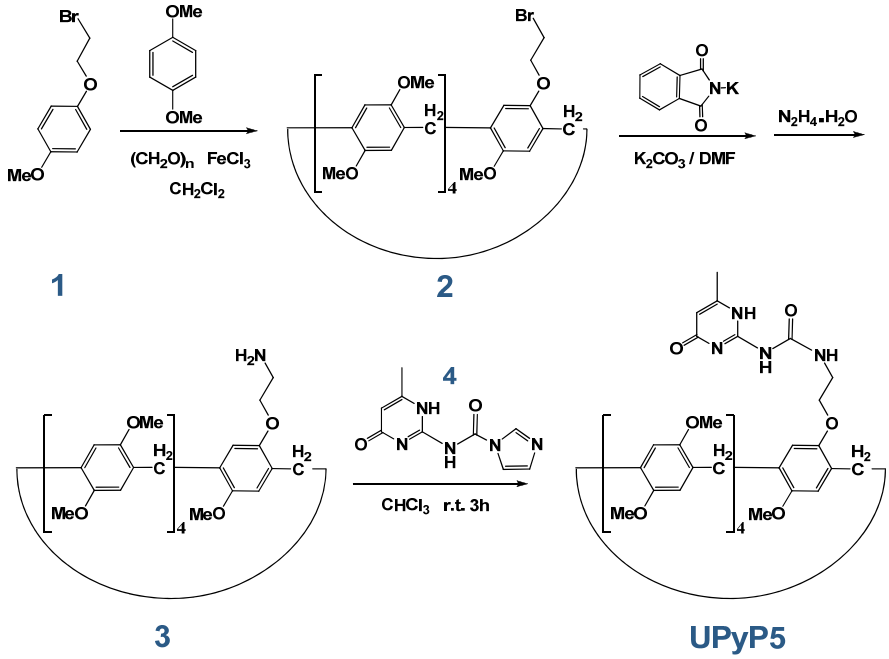
1. General methods

All solvents and reagents were used as supplied. The commercially available reagents and solvents were employed without further purification. All reactions were performed in atmosphere unless noted. Column chromatography was performed with silica gel (200-300 mesh) produced by Qingdao Marine Chemical Factory, Qingdao (China). All yields were given as isolated yields.

2. Measurements

Melting points (Mp) were determined using a Focus X-4 apparatus (made in China) and were not corrected. NMR spectra were recorded on a Bruker DPX 300 MHz spectrometer and Bruker DPX 400 MHz with internal standard tetramethylsilane (TMS) and solvent signals as internal references. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. Low-resolution electrospray ionization mass spectra (LR-ESI-MS) were obtained on Finnigan Mat TSQ 7000 instruments. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent 6540Q-TOF LCMS equipped with an electrospray ionization (ESI) probe operating in positive-ion mode with direct infusion. Viscosity measurements were carried out with Ubbelohde micro viscometers (Shanghai Liangjing Glass Instrument Factory, 0.40 mm inner diameter) at 298K in chloroform/acetonitrile. The UV-Vis absorption spectrum was measured on a Perkin Elmer Lambda 35 UV/Vis Spectrometer. The excitation and emission spectra were recorded on a Perkin Elmer LS55 Fluorescence Spectrometer. Cyclic voltammetric measurements were carried out in an electrolyte solution consisting of 0.02 M tetra-*n*-butylammonium hexafluorophosphate using a Pt working electrode, an auxiliary Pt electrode, and an Ag/AgCl reference electrode. Cyclic voltammograms were recorded on a CHI812B electrochemical station (made in China) controlled by a CHI812B electrochemical detector program at a rate of 0.100 V/s.

3. Synthesis of UPyP5



Scheme S1. Synthetic route of **UPyP5**

Preparation of compound **2**

Compound **2** was synthesized according to the method reported by Stoddart's group.[S1] ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm) = 6.81-6.78 (m, 9H, Ar*H*), 6.70 (s, 1H, Ar*H*), 4.04 (t, J = 6 Hz, 2H), 3.81-3.77 (m, 10H), 3.71-3.64 (m, 27H), 3.45 (t, J = 6 Hz, 2H), which is in accordance with the results reported by Stoddart's group [δ = 6.80-6.76 (m, 9H), 6.70 (s, 1H), 4.04 (t, J = 6 Hz, 2H), 3.80-3.75 (m, 10H), 3.68-3.64 (m, 27H), 3.44 (t, J = 6

Hz, 2H)].

Preparation of compound **3**

Phthalimide (0.184 g, 1.25 mmol) and K_2CO_3 (0.345 g, 2.5 mmol) was added to a solution of **2** (0.84 g, 1.00 mmol) in dry N,N-dimethylformamide (30 mL). The reaction mixture was stirred at ambient temperature for 12 h under the protection of nitrogen atmosphere. Then the DMF solvent was removed under vacuum to give buff solid. The buff solid was added into THF (20 mL) and hydrazine hydrate (10 mL). After 24 h reflux, the reaction solution was cooled to room temperature. THF was removed from the solution under vacuum. Then the solution was washed with 1 M NaOH aqueous solution (20 mL) and extracted with CH_2Cl_2 (50 mL), and dried (Na_2SO_4). The organic layer was removed under vacuum to give a white solid. Column chromatography was used in the final separation with 100:1 CH_2Cl_2/CH_3OH as the eluent, to give white solid **3 (**0.45 g, yield 77.2%). Mp 48.0-50.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm) = 6.80-6.76 (m, 8H), 6.69 (s, 2H), 3.79-3.78 (m, 12H), 3.66-3.63 (m, 27H), 2.89 (t, J = 5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ = 150.8, 128.5, 128.3, 128.2, 114.9, 114.4, 114.3, 114.2, 114.1, 70.6, 55.9, 41.7, 30.0, 29.7, 29.5. ESI-MS m/z: calcd. 779.4, found $[M+H]^+$ = 780.4, $[M+Na]^+$ = 802.4.

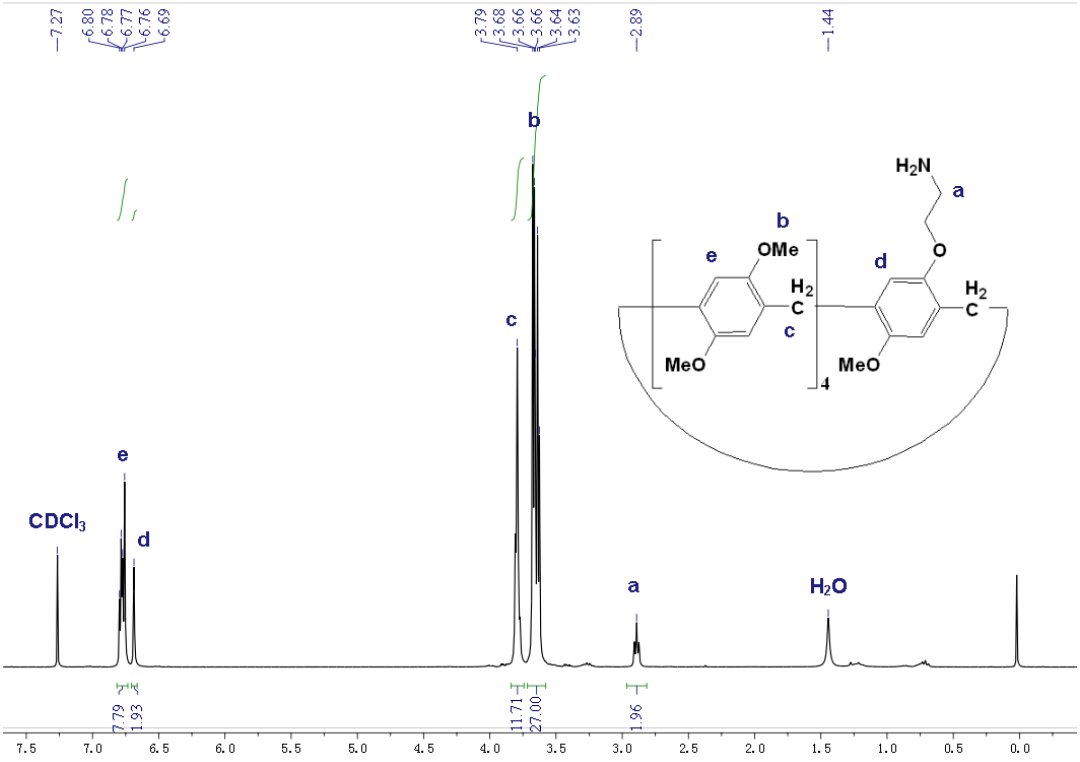


Figure S1. ^{1}H NMR spectrum (300 MHz) of **3** in $CDCl_3$

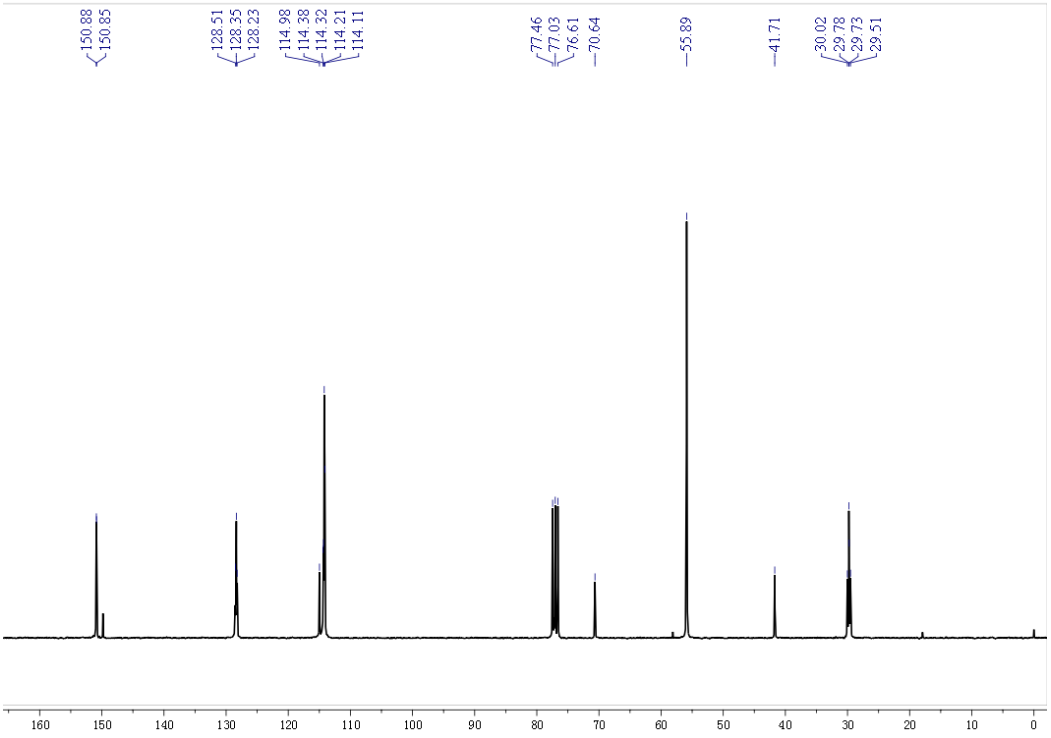


Figure S2. ^{13}C NMR spectrum (75 MHz) of **3** in $CDCl_3$

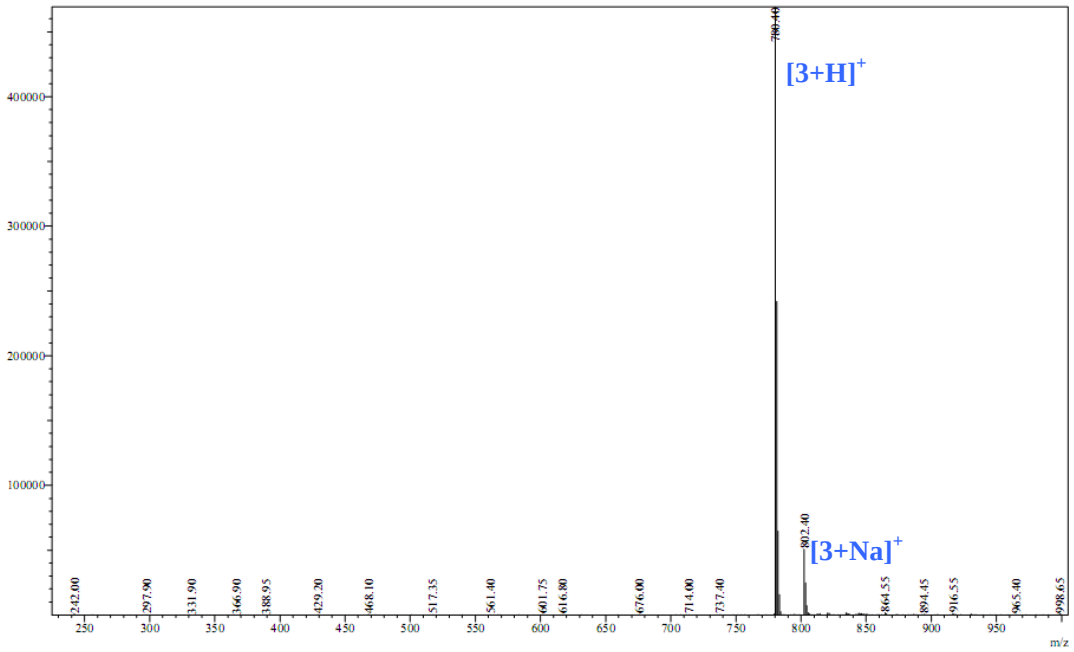


Figure S3. ESI-MS spectrum of **3** in methanol solution.

Preparation of compound **UPyP5**

The procedure for reacting imidazolides with amines is exemplified by the synthesis of mono-functional ureidopyrimidinone[S2]. 2-(1-Imidazolylcarbonylamino)-6-methyl-4(1H)-pyrimidinone (**4**) (0.238 g, 1.085 mmol) and **3** (0.423 g, 0.542 mmol) were dissolved in $CHCl_3$ (10 mL) and this solution was stirred overnight under nitrogen at ambient temperature. To the reaction mixture $CHCl_3$ (50 mL) was added and the organic layer was washed with 1M HCl (20 mL), saturated $NaHCO_3$ solution (20 mL) and brine (20 mL). After drying with Na_2SO_4 the organic layer was removed by evaporation in vacuo. Column chromatography was used in the final separation with 150:1 CH_2Cl_2/CH_3OH as the eluent, to give white solid **UPyP5** (0.258 g, yield 51.1%). Mp 134.0-137.0 °C.

^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm) = 12.97 (s, 1H), 11.96 (s, 1H), 10.62 (s, 1H), 6.90 (s, 1H), 6.82-6.74 (m, 9H), 5.78 (s, 1H), 4.03 (t, 2H), 3.80-3.76 (m, 10H), 3.68-3.64 (m, 27H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ = 172.9, 156.9, 154.5, 150.8, 150.7, 150.6, 149.7, 148.1, 128.7, 128.5, 128.4, 128.3, 128.1, 114.9, 114.3, 114.1, 114.0, 113.9, 113.8, 106.7, 67.3, 55.9, 55.8, 55.7, 55.6, 39.81, 29.7, 29.6, 29.2, 18.8 ppm. ESI-MS m/z: calcd. 930.4, found. $[M+H]^+$ = 931.4, $[M_2+H]^+$ = 1863.0 (dimer).

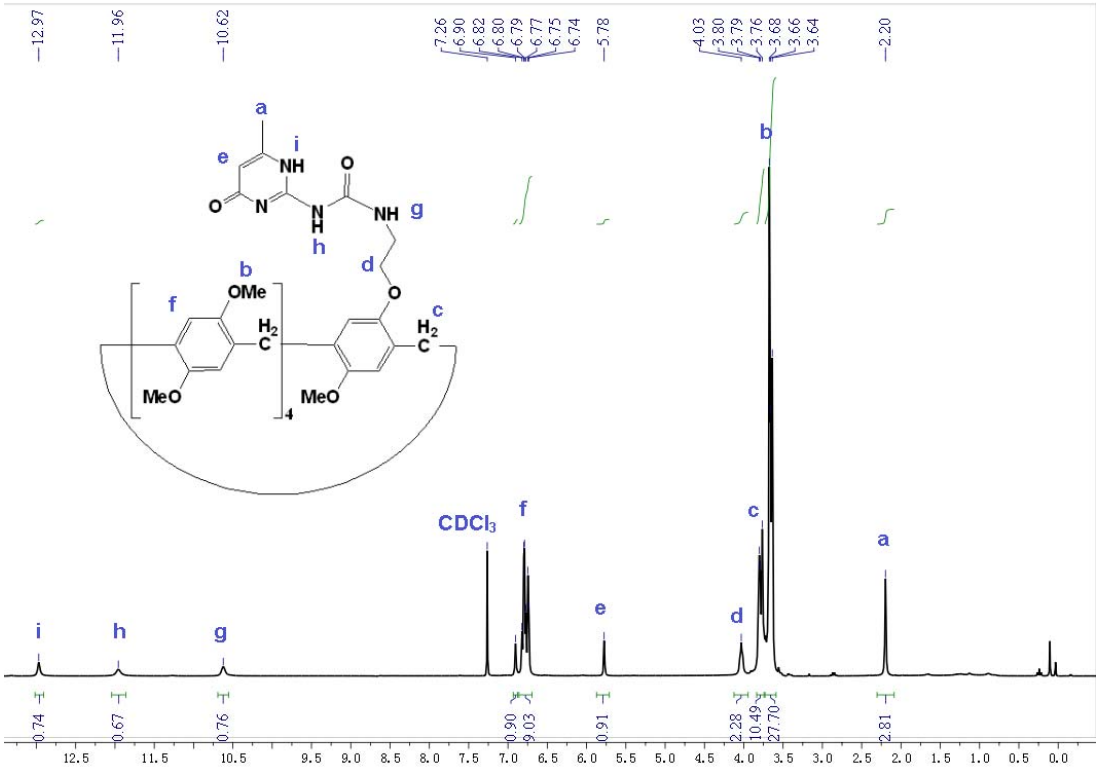


Figure S4. ^{1}H NMR spectrum (300 MHz) of **UPyP5** in $CDCl_3$

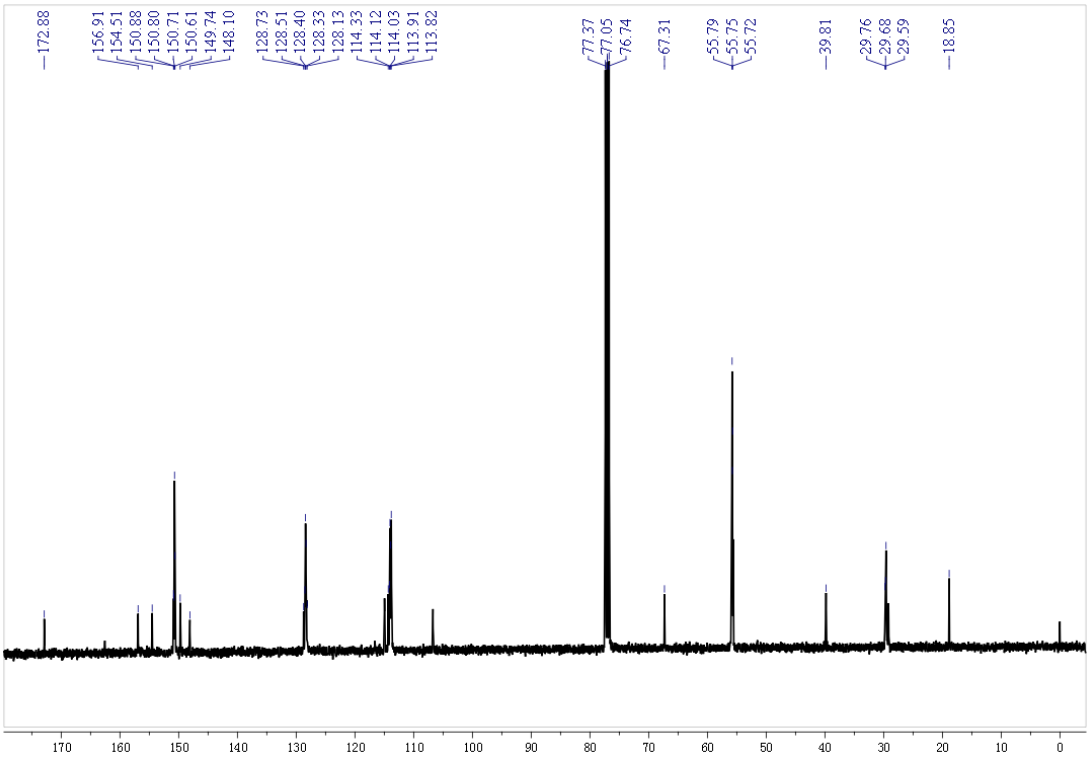


Figure S5. ^{13}C NMR spectrum (100 MHz) of **UPy-P5** in $CDCl_3$

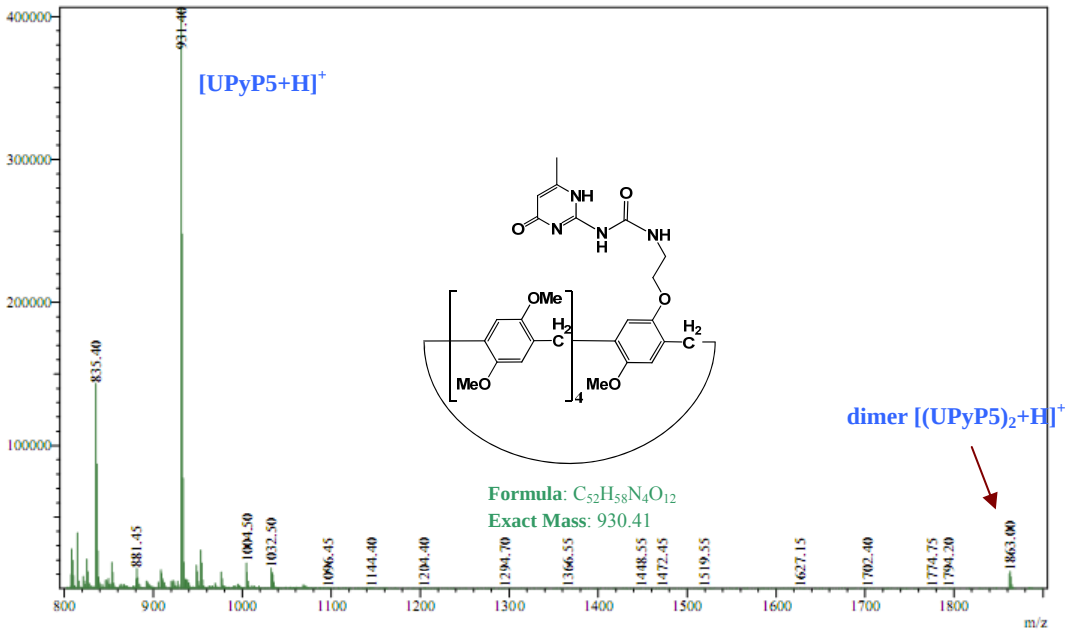
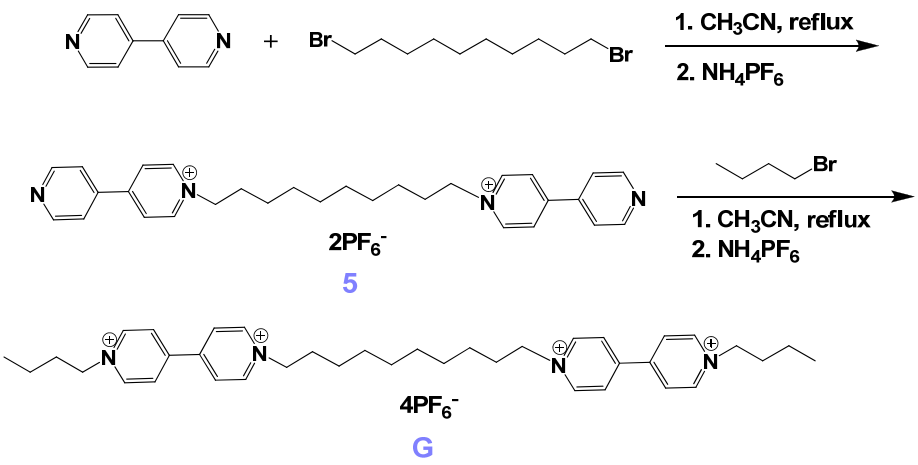


Figure S6. ESI-MS spectrum of **UPy-P5** in methanol solution.

4. Synthesis of G



Scheme S2. Synthetic route of **G**

Preparation of compound **5**

Compound **5** was prepared according to literature method.[S3] A solution of 1,10-dibromodecane (1.89 g, 6.3 mmol) in CH_3CN (60 mL) was added dropwise into a stirred solution of 4,4'-bipyridine (5.56 g, 35.7 mmol) in CH_3CN (60 mL) and refluxed over night. After it cooled, the suspension was filtered. The solid was washed with CH_3CN and then dried in an oven to afford a pale green solid. It was dissolved in minimum deionized water and aqueous NH_4PF_6 (5.0 g, 30.6 mmol) was added to precipitate a white solid. The resulting solid was filtered and washed with water to afford the desired product **5** (3.42 g, 73%). The ^{1}H NMR spectrum of **5** is shown in Figure S4. ^{1}H NMR (400 MHz, DMSO-d_6, room temperature) δ (ppm): 9.20 (d, J = 6.6 Hz, 4H), 8.86 (d, J = 6.8 Hz, 4H), 8.62 (d, J = 6.5 Hz, 4H), 8.03 (d, J = 6.0 Hz, 4H), 4.59 (t, J = 7.3 Hz, 4H), 1.93 (m, 4H), 1.28 (m, 12H).

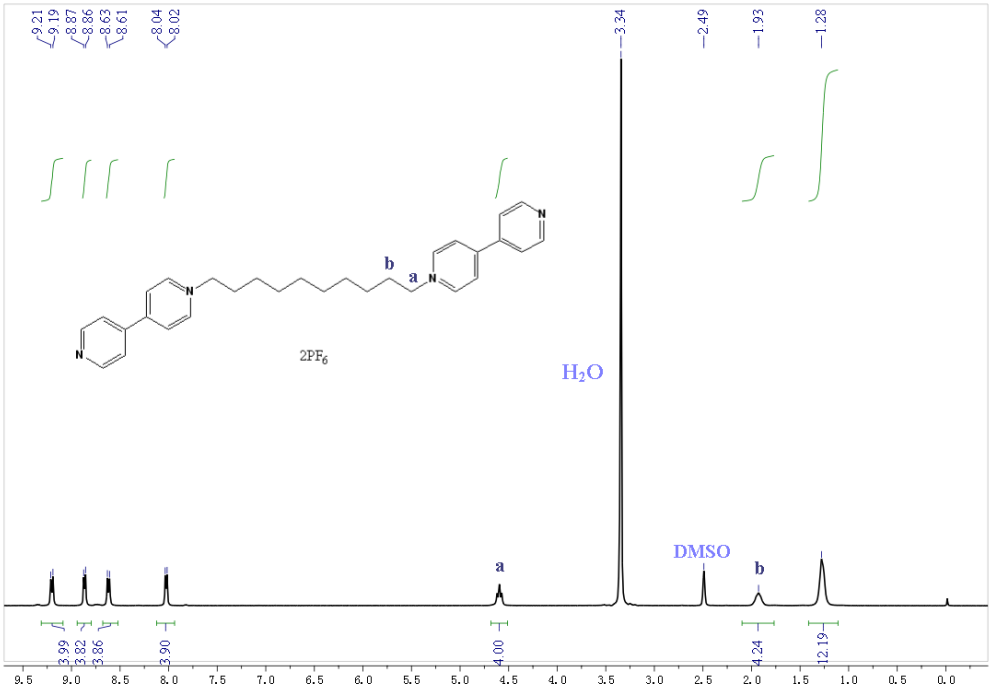


Figure S7. ^{1}H NMR spectrum (300 MHz) of **5** in DMSO-d_6

Preparation of compound **G**

A solution of compound **5** (1.00 g, 1.34 mmol) and 1-bromobutane (0.74 g, 5.39 mmol) in CH_3CN (100 mL) was refluxed overnight. After it cooled, the mixture was filtered. The solid was washed with CH_3CN and dried. Then excess aqueous NH_4PF_6 (0.44 g, 2.68 mmol) was added to the solution of this solid in minimal deionized

water. The suspension was heated at reflux for 0.5h. After it cooled, the mixture was filtered. The solid was washed with water and dried in an oven to afford a white solid (2.50 g, 26%). ^{1}H NMR (300 MHz, CD_3CN) δ 8.90 (d, J = 6.0 Hz, 8H), 8.39(d, J = 6.3 Hz, 8H), 4.62 (t, J = 6.7 Hz, 8H), 2.01 (t, J = 6.9 Hz, 8H), 1.49-1.34 (m, 16H), 0.99 (t, J = 7.3, 6H) ppm; ^{13}C NMR (75 MHz, CD_3CN) δ 149.9, 145.5, 127.2, 117.4, 62.1, 31.0, 28.9, 28.6, 25.6, 18.9, 12.7; ESI-MS m/z 169.50 $[M]^{4+}$ 141.70, $[M+PF_6]^{3+}$, 237.29, $[M+2PF_6]^{2+}$ 428.18, $[M+3PF_6]^{+}$ 1001.33.

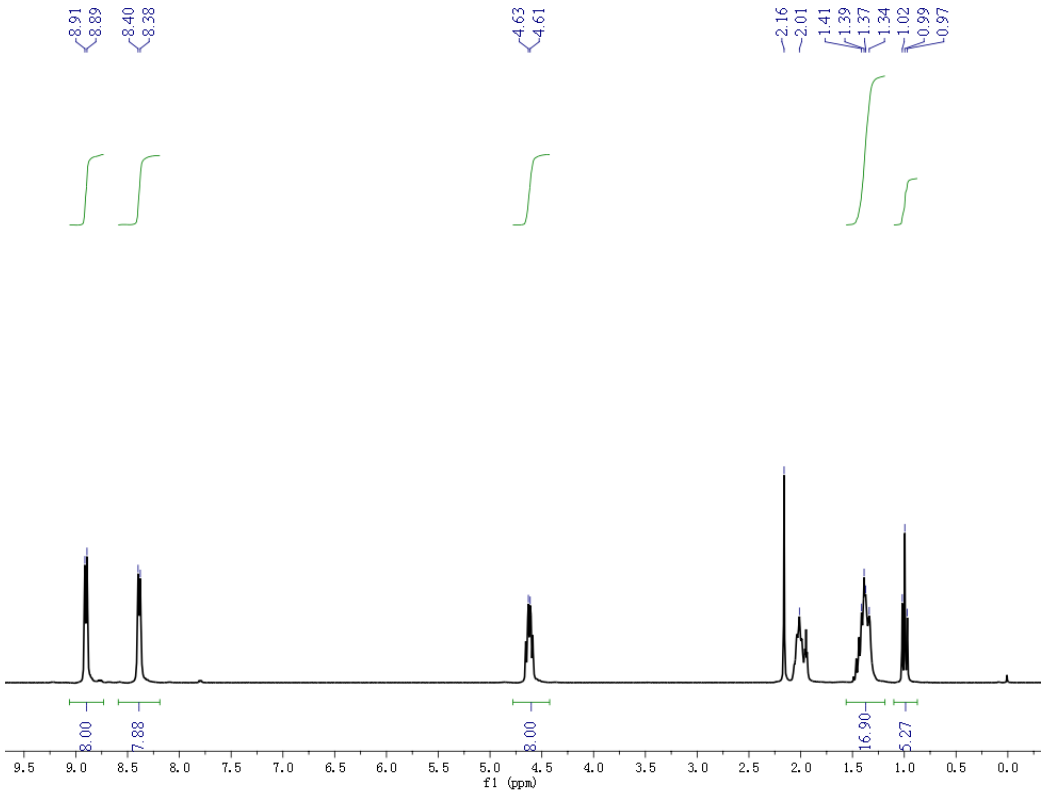


Figure S8. ^{1}H NMR spectrum (300 MHz) of **G** in acetonitrile-d_6

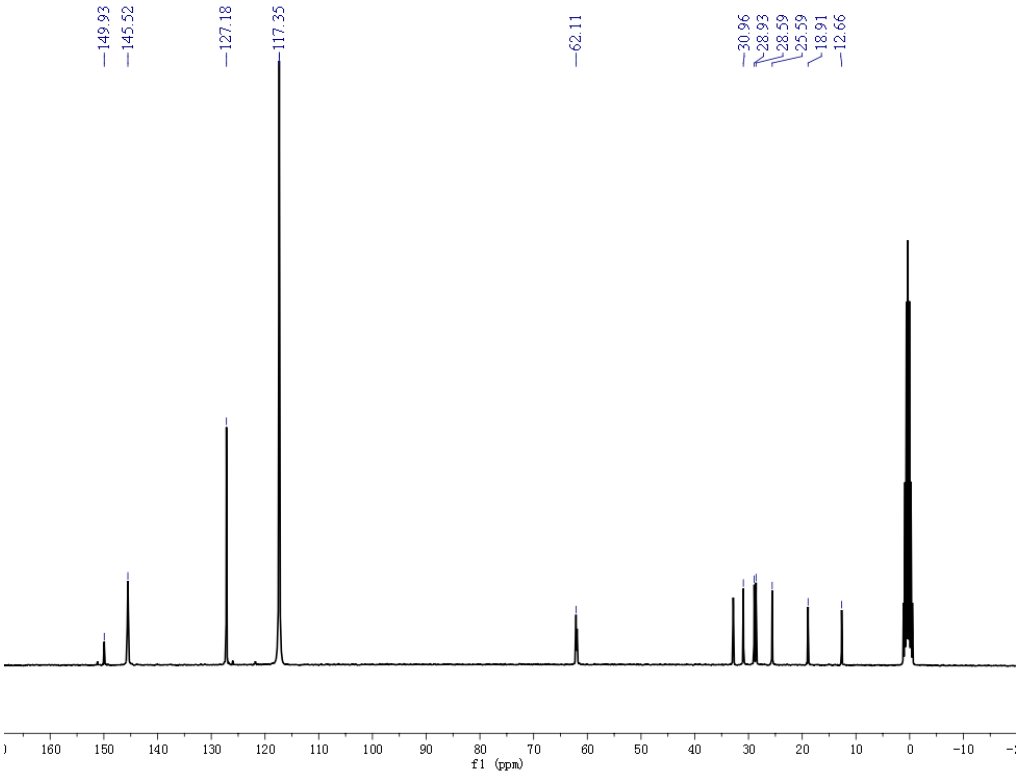


Figure S9. ^{13}C NMR spectrum (75 MHz) of **G** in acetonitrile-d_6

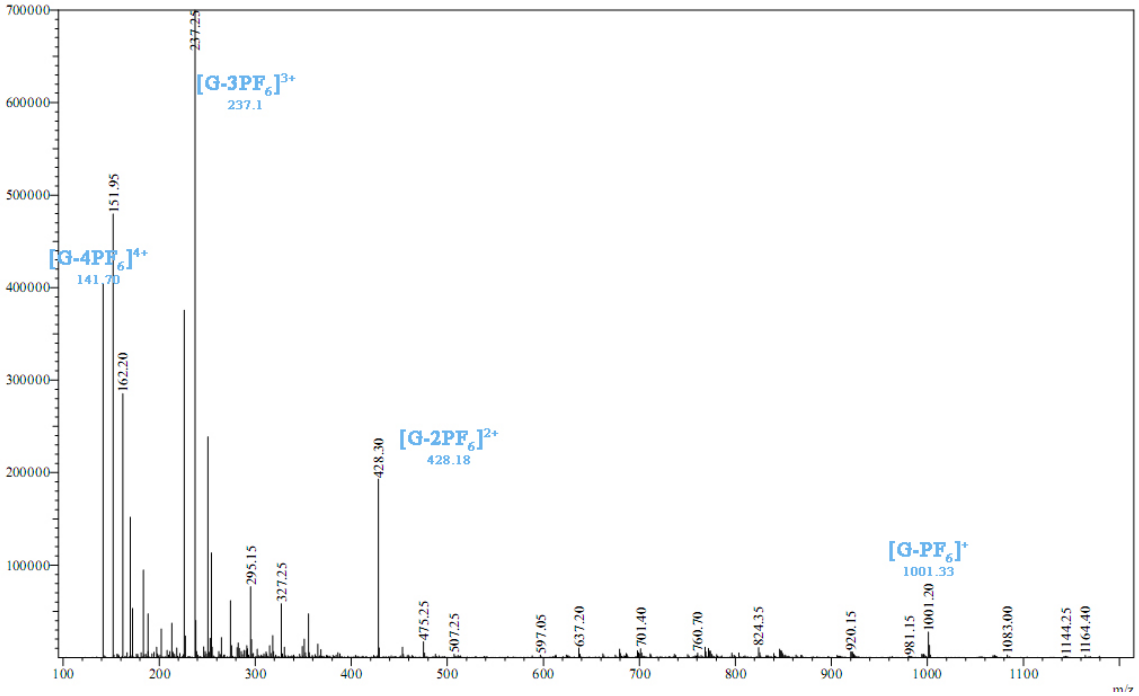


Figure S10. ESI-MS spectrum of **G** in methanol solution.

5. ESI-MS spectrum of the complexation between UPyP5 and G

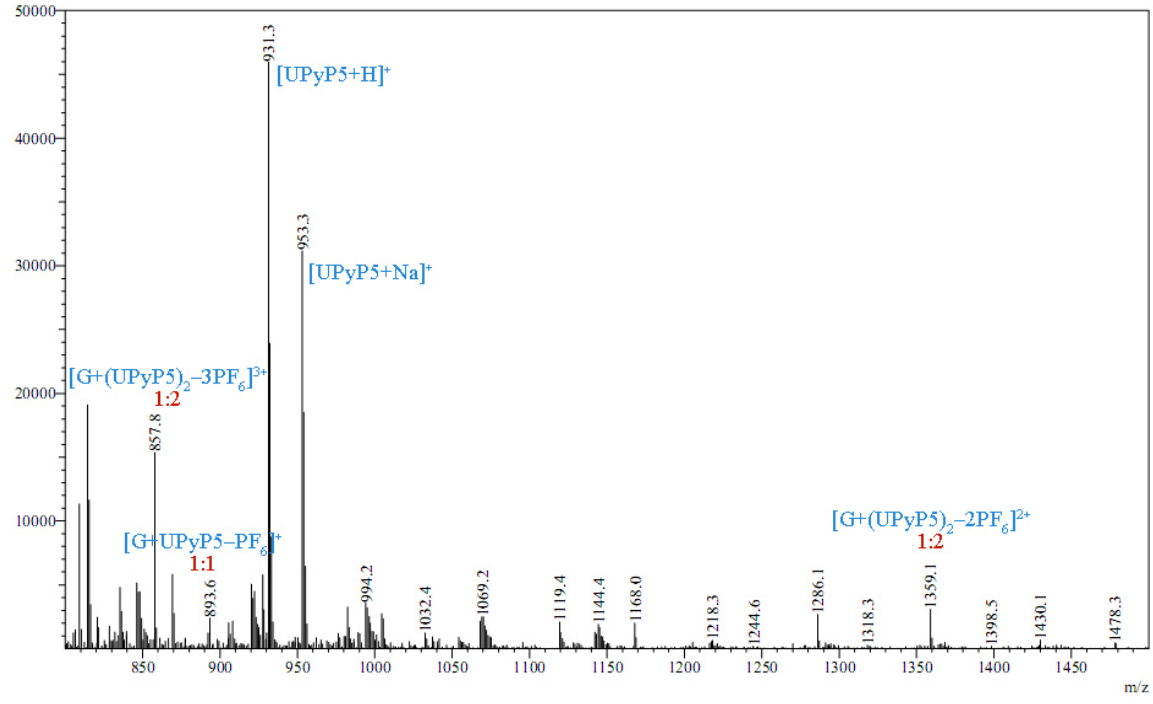


Figure S11. ESI-mass spectrum of **G** in the presence of equimolar **UPyP5** in methanol solution.

6. UV-Vis spectroscopy & fluorescent titration experiment

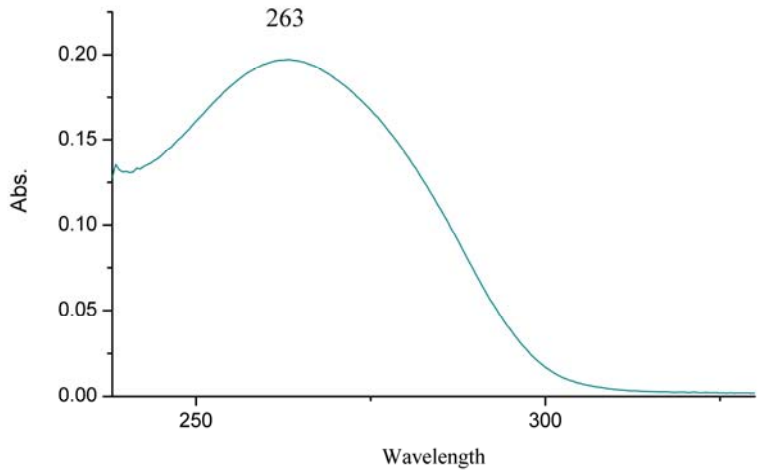


Figure S12. UV-vis spectrum of **G** (1×10^{-5} M) in $CHCl_3/CH_3CN$ (1/1, *v/v*) solution

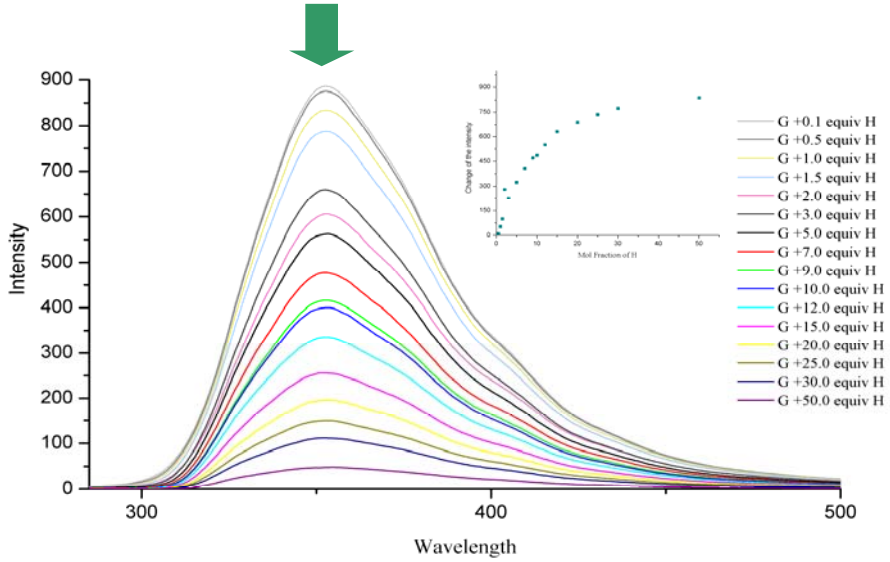
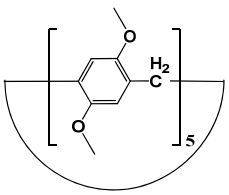
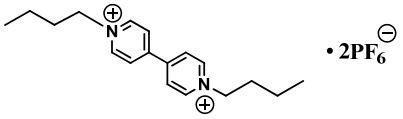


Figure S13. Fluorescent titration of **G** (1×10^{-5} M) in $CHCl_3/CH_3CN$ (1/1, *v/v*) solution with various equivalence of **UPyP5**. Inset: titration profile of the absorption changes upon the addition of **1**. Changes in the fluorescence intensities at 353 nm from **G** upon the addition of **UPyP5** were plotted

7. Determination of K_a value and complex stoichiometry



DMpillar[5]arene (**DMP5**)



G2

To estimate the binding ability of **UPyP5** and **G**, **DMP5** (host) and **G2** (guest) were chosen as the model compounds and their association constant of our supramolecular polymer. The Job plot from ^{1}H NMR data indicates a 1:1 binding between the host and guest.

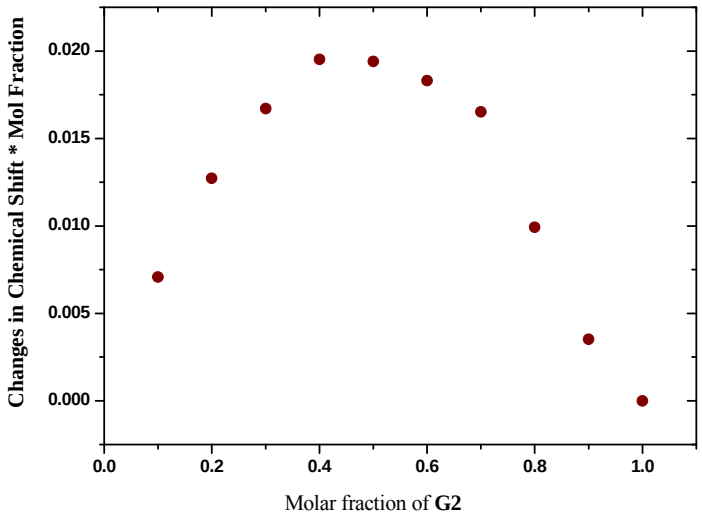


Figure S14. Job Plot of the complex formed between **DMP5** (host) and **G2** (guest) showing a 1:1 stoichiometry. The job plot was conducted by varying the mole fractions of the guest and host. Concentration: [Host] + [Guest] = 10 mM.

Then ^{1}H NMR titrations were performed with a constant concentration of **G2** (2.00 mM) and varying concentrations of **DMP5** (0.20 to 20.0 mM). However, the chemical shift change of α-H in **G2** is too small ($\Delta\delta$ < 0.3 ppm) in $CDCl_3/CD_3CN$ (1/1, *v/v*) solvent, thus the average association constants can't be calculated accurately.

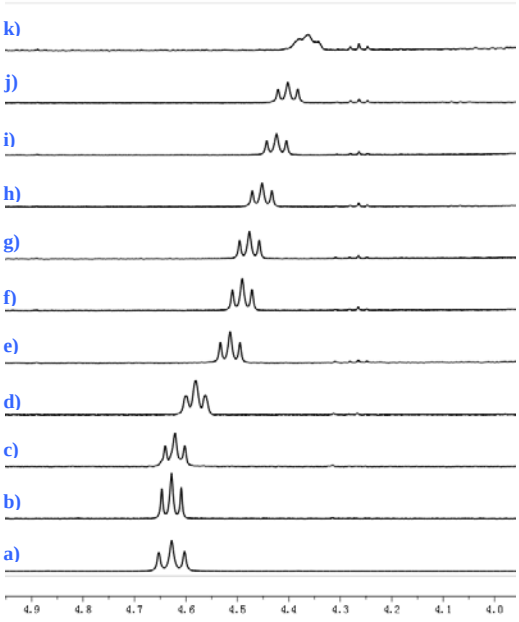


Figure S15. Partial ^{1}H NMR titration spectra of 2.00 mM **G2** solution with (a) 0 (b) 0.1(c) 0.5 (d) 3 (e) 8 (f) 10 (g) 11 (h) 13 (i) 15 (j) 17 (k) 20 equiv of **DMP5**.

From the fluorescent spectroscopy titration experiment, we found that the emission spectrum of the viologen derivatives can be quenched by the **UPy-P5**, thus the association constant (K_a) between **DMP5** and **G2** was determined through fluorescence quenching titration experiment according to the reported method[S4]. With a constant concentration of **G2** (2.00 mM) and varying concentrations of **DMP5** (0.20 to 20.0 mM) in $CHCl_3/CH_3CN$ (1/1, *v/v*) solution, a gradual quenching was also observed.

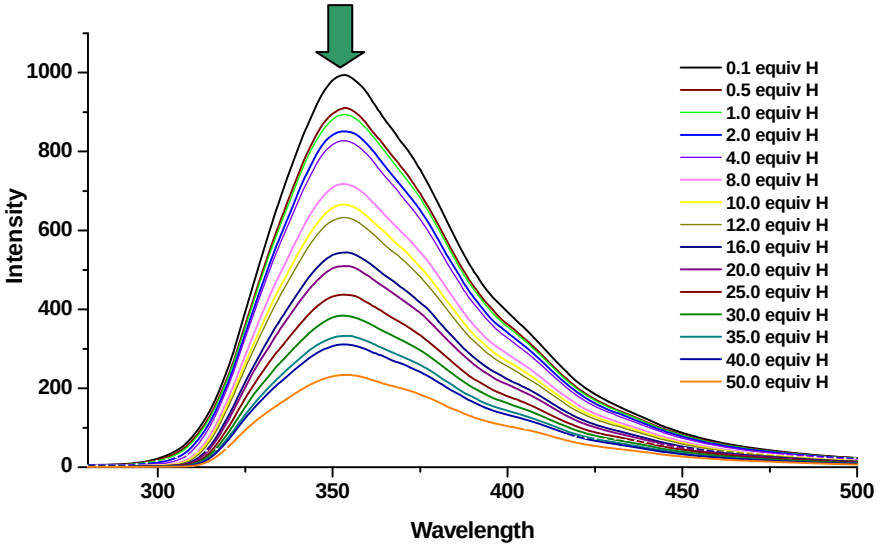


Figure S16. Fluorescent titration of **G2** (1×10^{-5} M) in $CHCl_3/CH_3CN$ (1/1, *v/v*) solution with various equivalence of **DMP5**.

Changes in the ratios (I/I_0) of the fluorescence intensities at 353 nm from **G2** upon addition of **DMP5** were plotted and the association constant was calculated from Eq.1, where "a" is a constant, K_a stands for the association constant.

$$\mathbf{I / I_0 = \frac{1 + aK_aC_{host}}{1 + K_aC_{host}}} \qquad \text{(Eq.1)}$$

By fitting the above spectrum data with Eq. 1, the K_a values was determined to be $(4.46 \pm 0.09)\times 10^3$ M^{-1} for **G2-DMP5** complex and approximated as the K_a value between **UPyP5** and **G**. This value is less than the complex between pillar[5]arene and **C8BpyC8** ($1.2 \pm 0.2 \times 10^4$ M^{-1})[S4], and less than the binding constant of monofunctional pillar[5]arene and alkanediamines (about $1.0\text{-}3.6 \times 10^4$ M^{-1})[S1], indicating weak interactions between **DMP5** and **G2**.

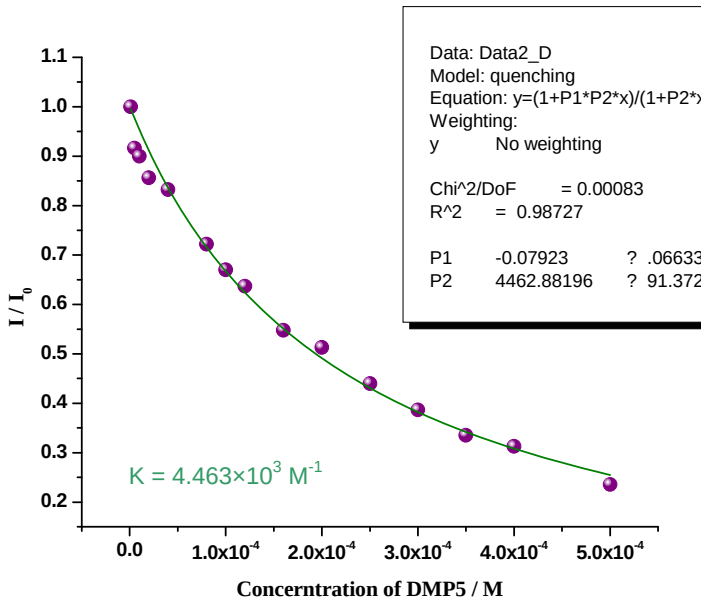
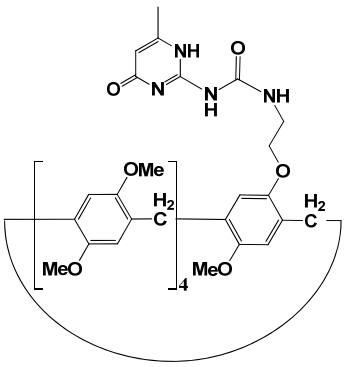
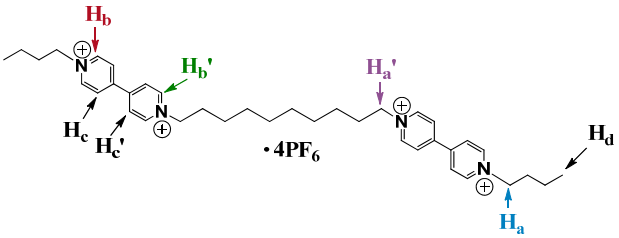


Figure S17. Plot of the changes in the ratios (I/I_0) of the fluorescence intensities at 353 nm from **G2** upon addition of host **DMP5**.

8. ^{1}H NMR spectra of UPyP5 and G solutions and the calculation of polymerization degrees at different concentrations



UPyP5



G

Figure S18. Naked-eye observation of the color change of **UPyP5** and **G** complex at different **G** concentrations (a) blank solvent (b) 0.5 mM (c) 1 mM (d) 2 mM (e) 5 mM (f) 10 mM (g) 20 mM (h) 40 mM (i) 70 mM **G** concentrations.

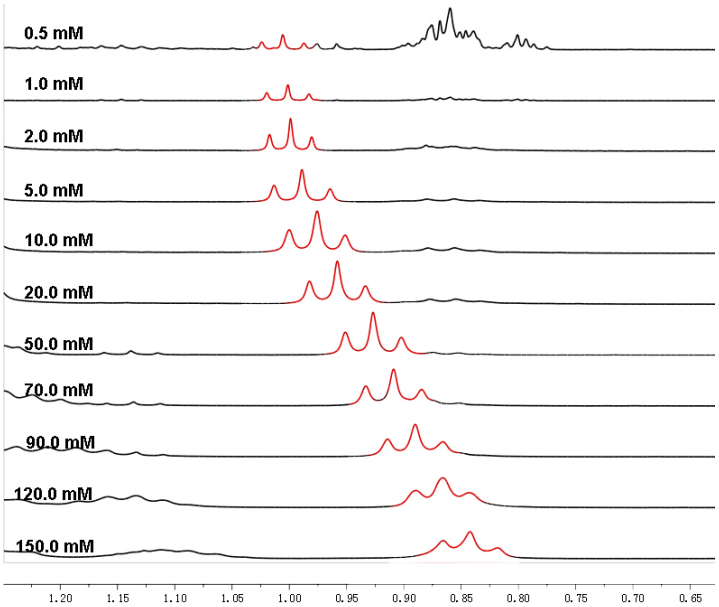


Figure S19. Partial ^{1}H NMR spectra at various **G** concentrations showing upfield shifts of the terminal protons H_d

With the increasing of the initial concentration of **UPyP5** or **G** separately in $CDCl_3/CD_3CN$ (1/1, *v/v*) solvent, the solution remains colorless and turns buff, respectively. When mixing them together, the solution turns into brick red due to the charge transfer interaction from the π-electron rich pillar[5]arene cavity and the π-electron poor viologen unit. With the increasing of both **UPyP5** and **G** concentration, the red color became darker and darker.

The chemical shift of the H_b located on **G** was relative with the monomer **G** concentration (Figure 2a). It was

observed that when the initial concentrations increased, the calculated chemical shift change of H_b increased sharply at first and then gradually slowly. It is indicated that the percentage of complexed viologen moieties increased with increasing concentration, suggesting the formation of linear supramolecular daisy.

On the basis of the chemical shift change of H_b, the fractions of the complexed viologen moieties (p) and the degree of polymerization (n) at different initial concentrations of **UPyP5** and **G** were estimated[S5], with the hypothesis that the UPy dissociation was negligible in the solution for its strong binding ability. The value of the maximum chemical shift change $\Delta_0 = 1/2.261 = 0.442$ ppm, was determined by extrapolation of a plot of $\Delta = \delta - \delta_u$ vs. $1/[G]_0$ in high initial concentration range.

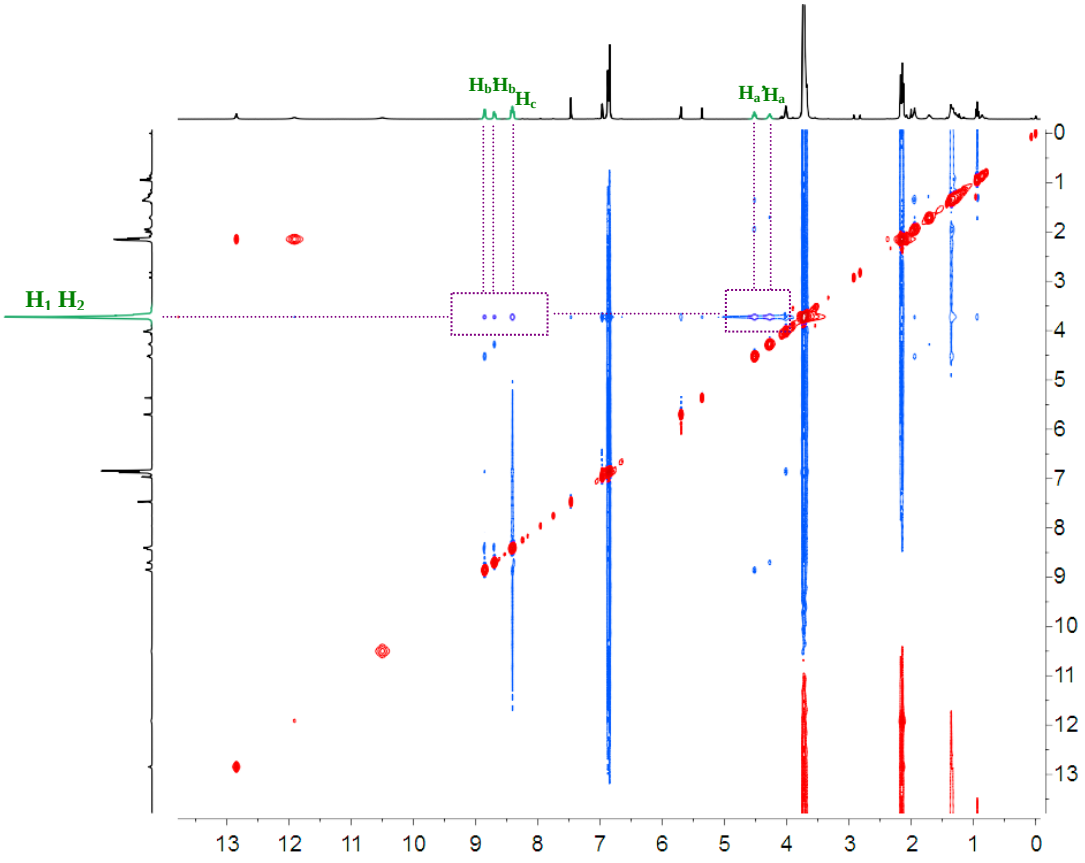
Table S1. Calculated values of p and n at different initial **G** concentrations

$[G]_0$ (mM)	Chemical Shift changes	P[a]	n[b]
1	0.0246	0.05566	1.05894
2	0.0352	0.07964	1.08653
5	0.0503	0.1138	1.12841
10	0.0845	0.19118	1.23636
20	0.126	0.28507	1.39873
50	0.2117	0.47896	1.91924
70	0.2571	0.58167	2.39048
90	0.3038	0.68733	3.19826
120	0.3657	0.82738	5.79292
150	0.4188	0.94751	19.05172

[a] Calculated from $p = \Delta / \Delta_0$; [b] Calculated from $n = 1/(1-p)$.

9. 2D NOESY spectrum of the complexation between UPyP5 and G

(a)



(b)

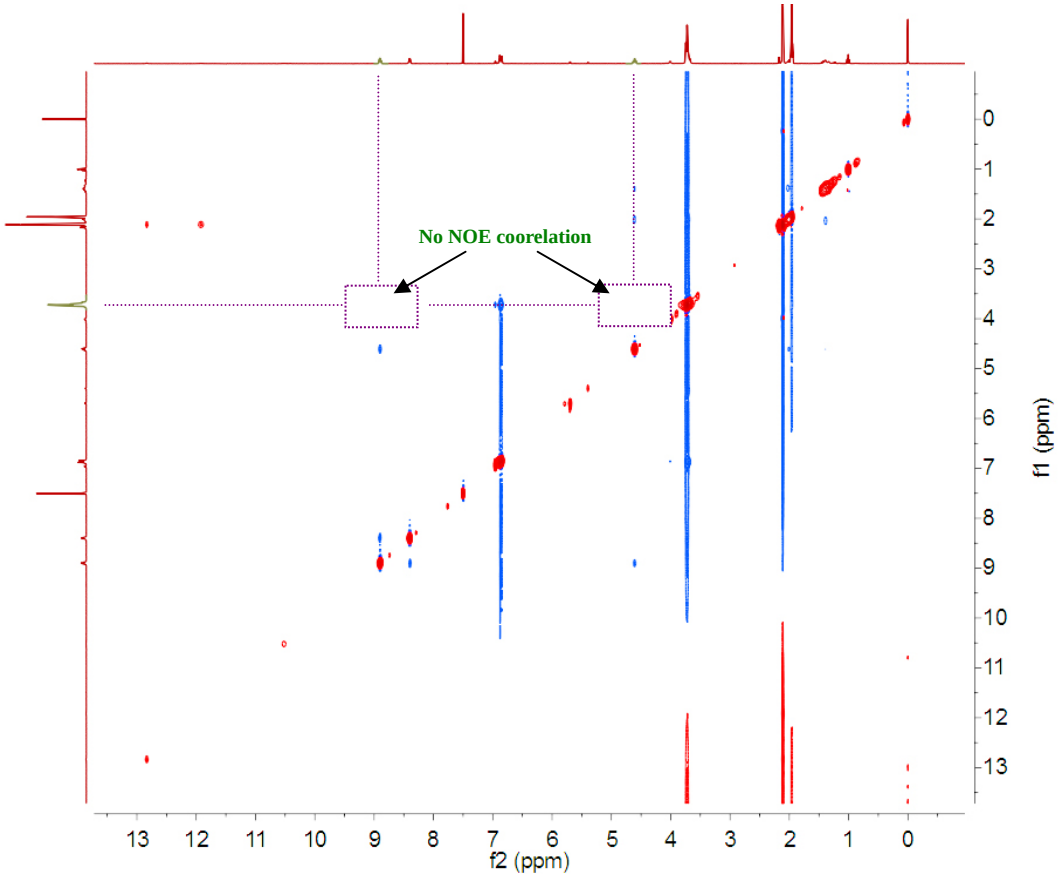
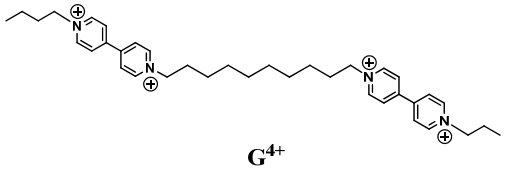


Figure S20. Partial NOESY NMR spectra (400 MHz, $CDCl_3/CD_3CN$ = 1/1 (*v/v*), 293 K) of **UPyP5** and **G** in 2:1 molar ratio at **G** concentration of (a)20 mM (b) 1 mM with a mixing time of 300 ms.

As seen from the NOESY spectrum of **UPyP5** and **G** in 2:1 molar ratio at relatively high concentration (Fig. S20a, G conc. = 20 mM), the intensities of the NOE peaks between H_1, H_2 and H_b, $H_{b'}$, H_1, H_2 and H_a, $H_{a'}$ indicates the weak interactions between **UPyP5** and **G**. While these correlations could not be observed in low concentration spectrum (Fig. S20b, G conc. = 1 mM), indicating the low fraction of the complexed **G** and the formation of oligomers at low concentration.

10. A comment on the cyclic voltammetric measurements

The influence of the complexation of **UPyP5** and **G** on the electrochemical properties of solutions was analyzed through cyclic voltammetry (CV) performed at various concentrations (Fig. 4b). The electrochemistry reduction process shows two clear reversible reduction processes of viologen groups corresponding to the following 2-electron reactions.[S6]



$\mathbf{G^{4+}}$

$$\mathbf{G^{4+}} + 2e^- \rightleftharpoons \mathbf{G^{2+}}$$

$$\mathbf{G^{2+}} + 2e^- \rightleftharpoons \mathbf{G}$$

Upon concentration increasing the reduction processes become more energetic with both of the first and second reduction potentials of the viologen shifting toward more negative values. These indicated that the percentage of encircled viologen units by pillar[5]arene units becomes larger as the concentration increases.

From the fluorescent titration, we know that the fluorescence intensity of viologen decreased with increasing fraction of threaded **G** due to the inhibition of the electron transfer process. So logically, when a reduction potential is applied to the solution of **UPyP5** and **G**, $\mathbf{G}^{4+}$ would undergo reduction process to $\mathbf{G}^{2+}$ and eventually **G**, which would further lead to the de-threading of the paraquat moieties and the recovery of its fluorescence. Subsequently, when a high voltage potential is applied to the same solution, the oxidation would occur in a short time, and then the quenching of the fluorescence would happen again. On the basis of this pillararene-bisparaquat system, a fast and reversible redox-fluorescence switch might be established, and this part of research is ongoing in our lab.

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