Electronic Supplementary Information (23 pages)

A pillar[5]arene-based hydrogel adsorbent in aqueous environment for organic micropollutants

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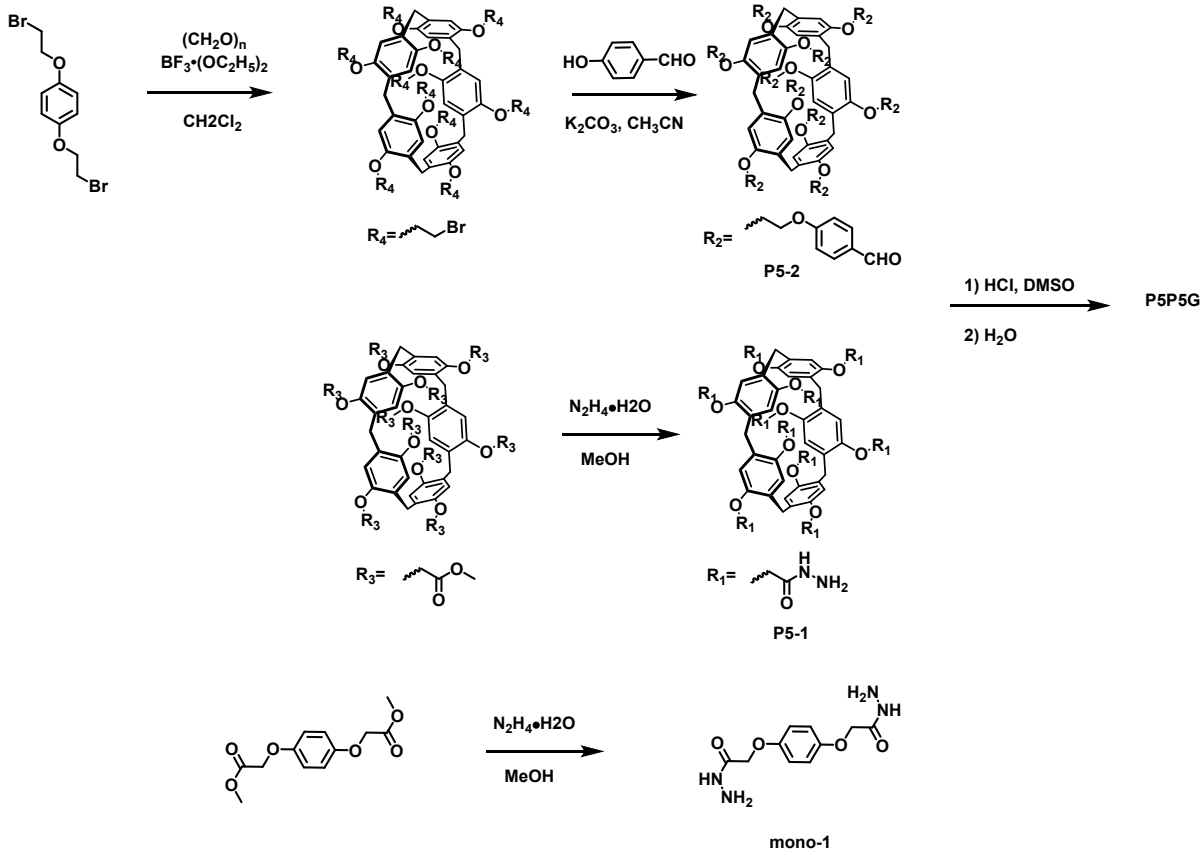
1. Synthetic route of P5P5G



Scheme S1 The synthetic route to **P5P5G**.

*Systhesis of hydrazide-functionalized pillar[5]arene **P5-1***

Hydrazide-functionalized pillar[5]arene **P5-1** was synthesized according to the published procedures.[S1]

*Systhesis of **mono-1***

Compound **mono-1** was synthesized according to the published procedures.[S1]

*Systhesis of 4-aldehydephenyl-functionalized pillar[5]arene **P5-2***[S2]

2-bromoethyl functionalized pillar[5]arene (**BrP5**) was synthesized according to the published procedures.[S3] **BrP5** (2.00 g, 0.600 mmol) and *p*-hydroxybenzaldehyde (2.18 g, 8.90 mmol) were mixed in acetonitrile (150 mL). K_2CO_3 (3.28 g, 11.9 mmol) was added and the mixture was stirred at 85 °C for 24 h and cooled to room temperature. After the reaction, the solid was removed and the solution was washed twice by water and evaporated. The residue was purified through flash column chromatography on silica gel (DCM/EA, *v*/*v*

3:1) to give a white solid **P5-2** (1.9 g 76%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 9.80 (s, 10H), 7.73 (d, J = 8.6 Hz, 20H), 6.85 (d, J = 8.6 Hz, 20H), 6.68 (s, 10H), 3.99 (d, J = 4.7 Hz, 20H), 3.88 (d, J = 4.2 Hz, 20H), 3.78 (s, 10H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 190.6, 163.7, 150.1, 132.0, 130.3, 129.4, 116.4, 114.9, 67.6, 67.5, 29.4. MS (MALDI-TOF): m/z 2091.2 $[M + H]^+$.

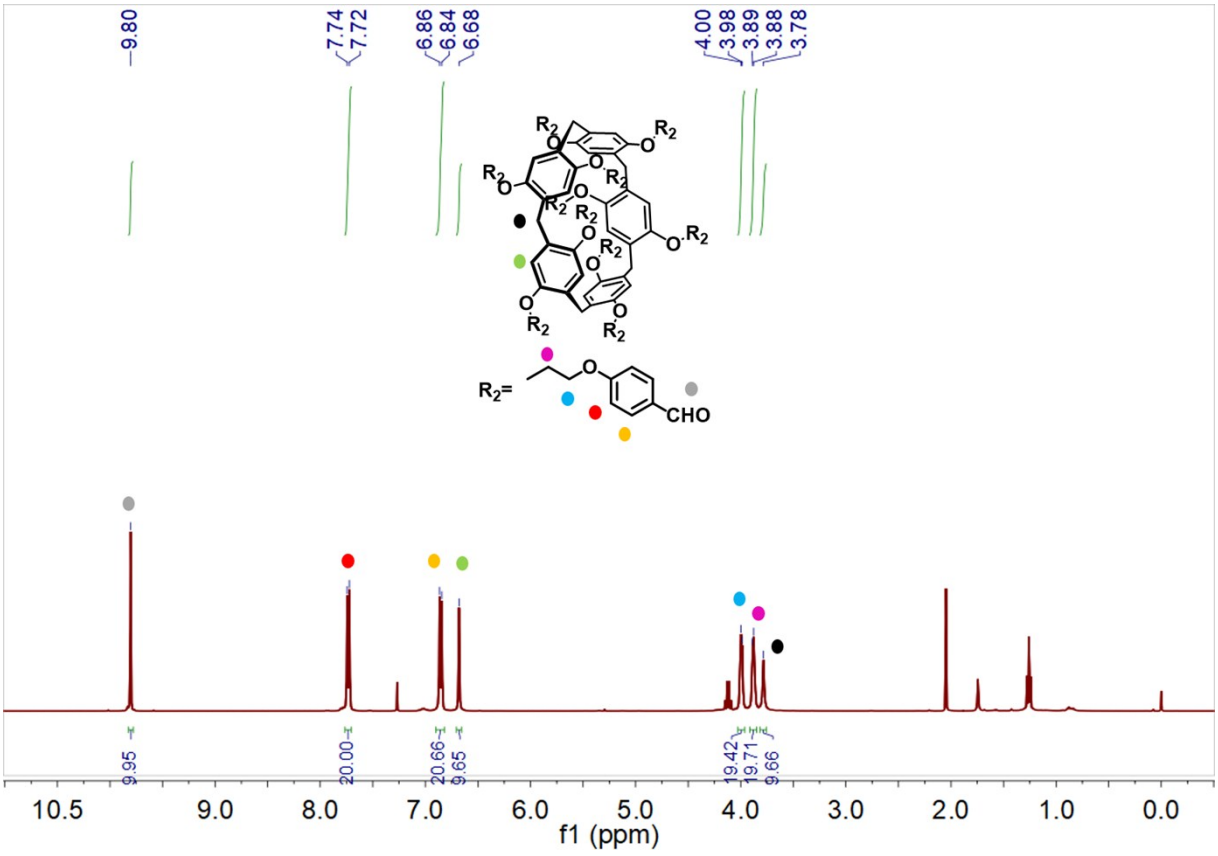


Fig. S1 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **P5-2**.

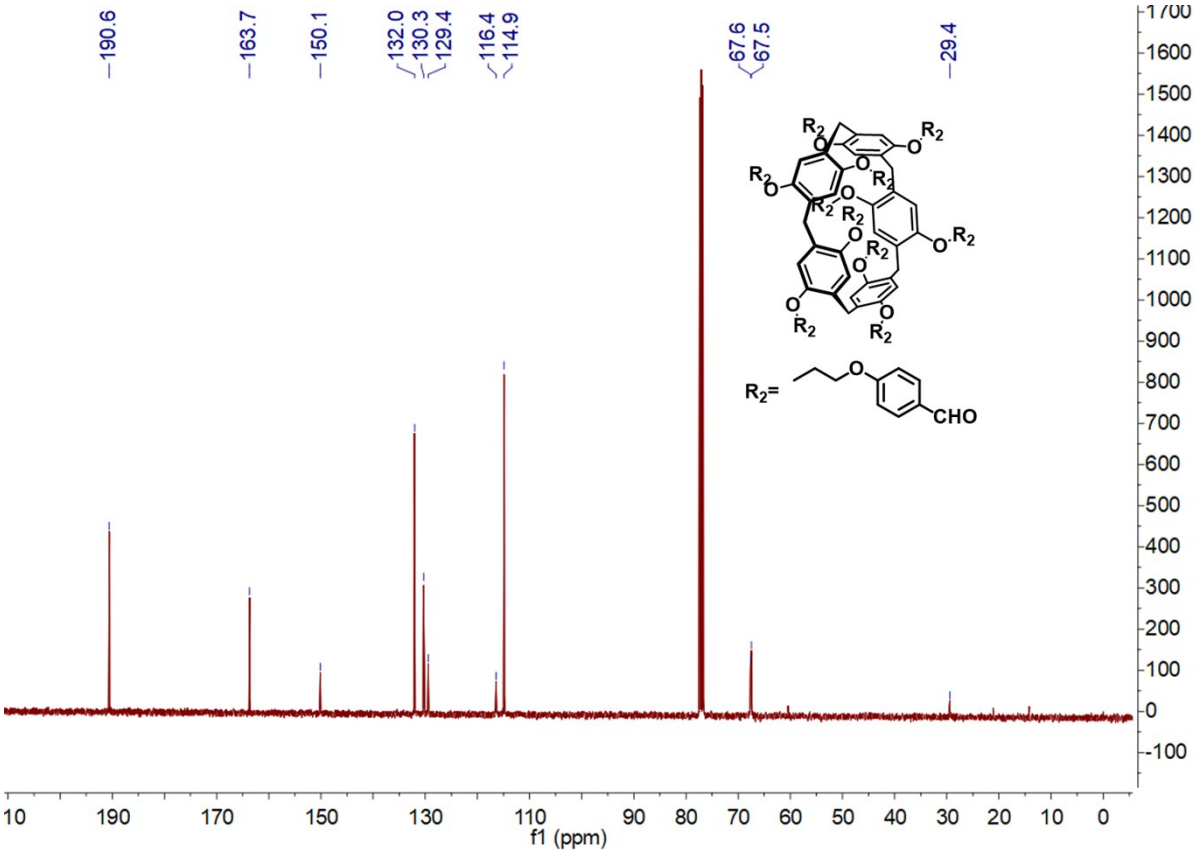


Fig. S2 ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298 K) of **P5-2**.

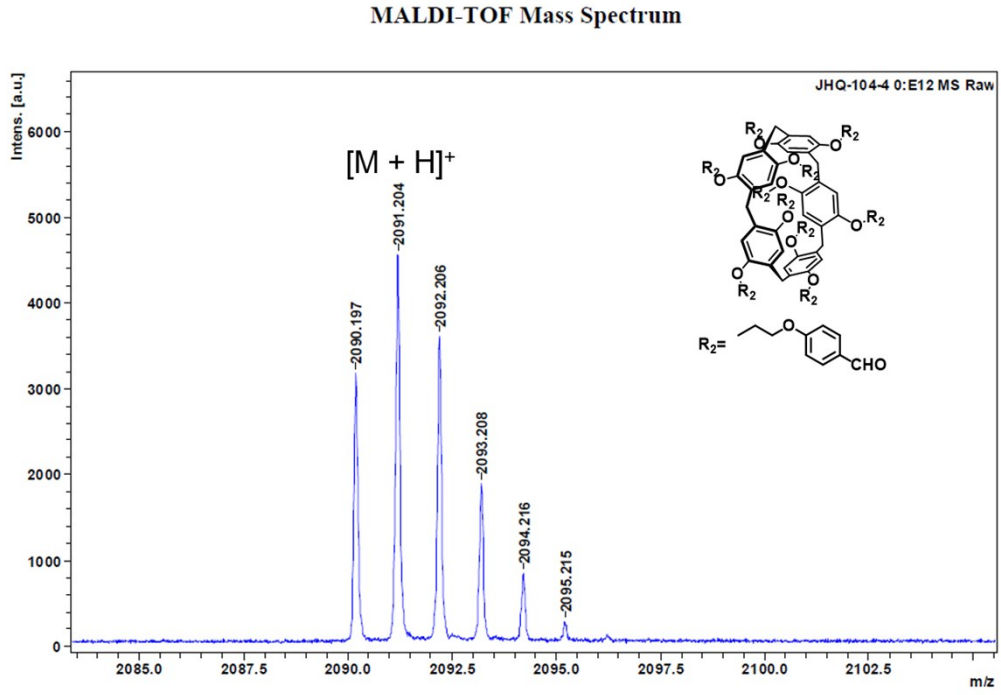


Fig. S3 MALDI TOF mass spectrum of **P5-2**.

2. The solid-state ^{13}C NMR spectra of P5-1 and P5-2

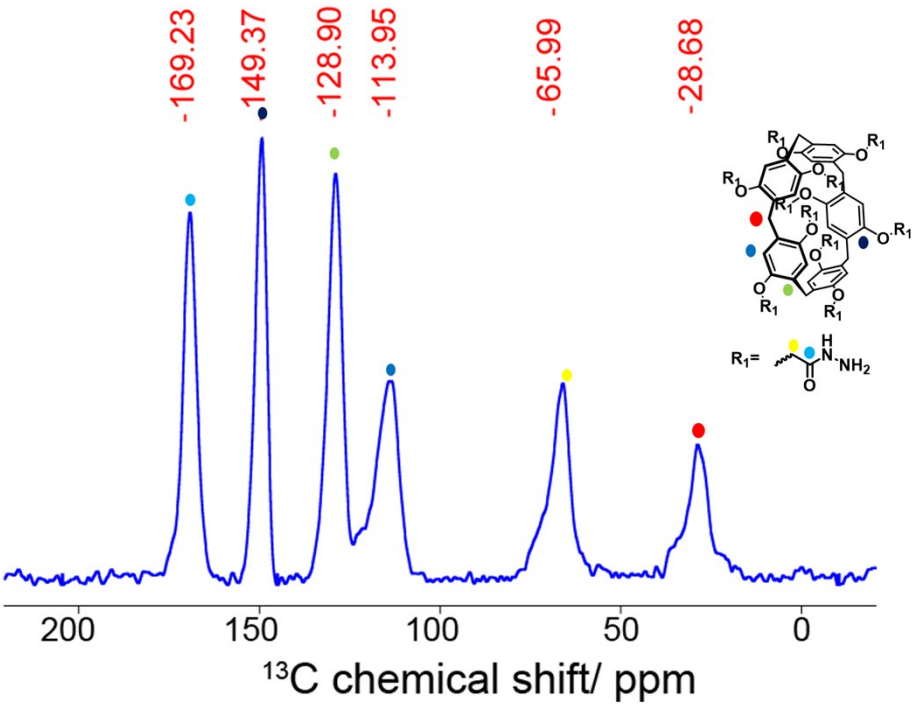


Fig. S4 ^{13}C CPMAS NMR spectrum of **P5-1**.

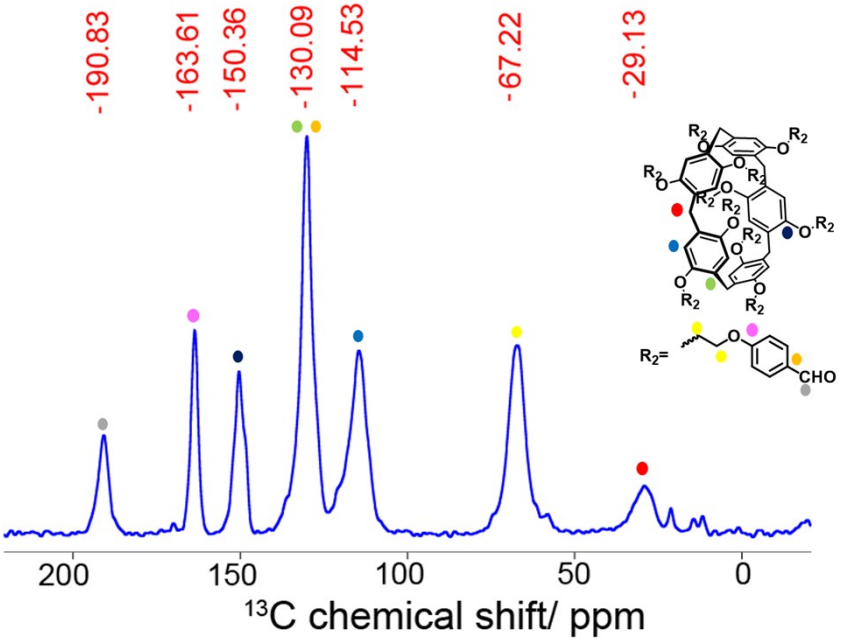


Fig. S5 ^{13}C CPMAS NMR spectrum of **P5-2**.

3. SEM sample preparation

The SEM sample was prepared by surface-blotting 5.00 mg of **P5P5G** with a filter paper and then freeze-drying.

4. Solvent content analysis

w_d (mg)	w_s (mg)	Solvent content
5.77	19.23	70.0%
4.63	16.39	71.8%
3.58	11.93	70.0%
5.13	17.17	70.1%

Table S1 Solvent content (water content) analysis of **P5P5G**. The solvent content (expressed as weight percent) of **P5P5G** was determined from the average (70.4%) of four measurements above.

5. Adsorption of different pollutants

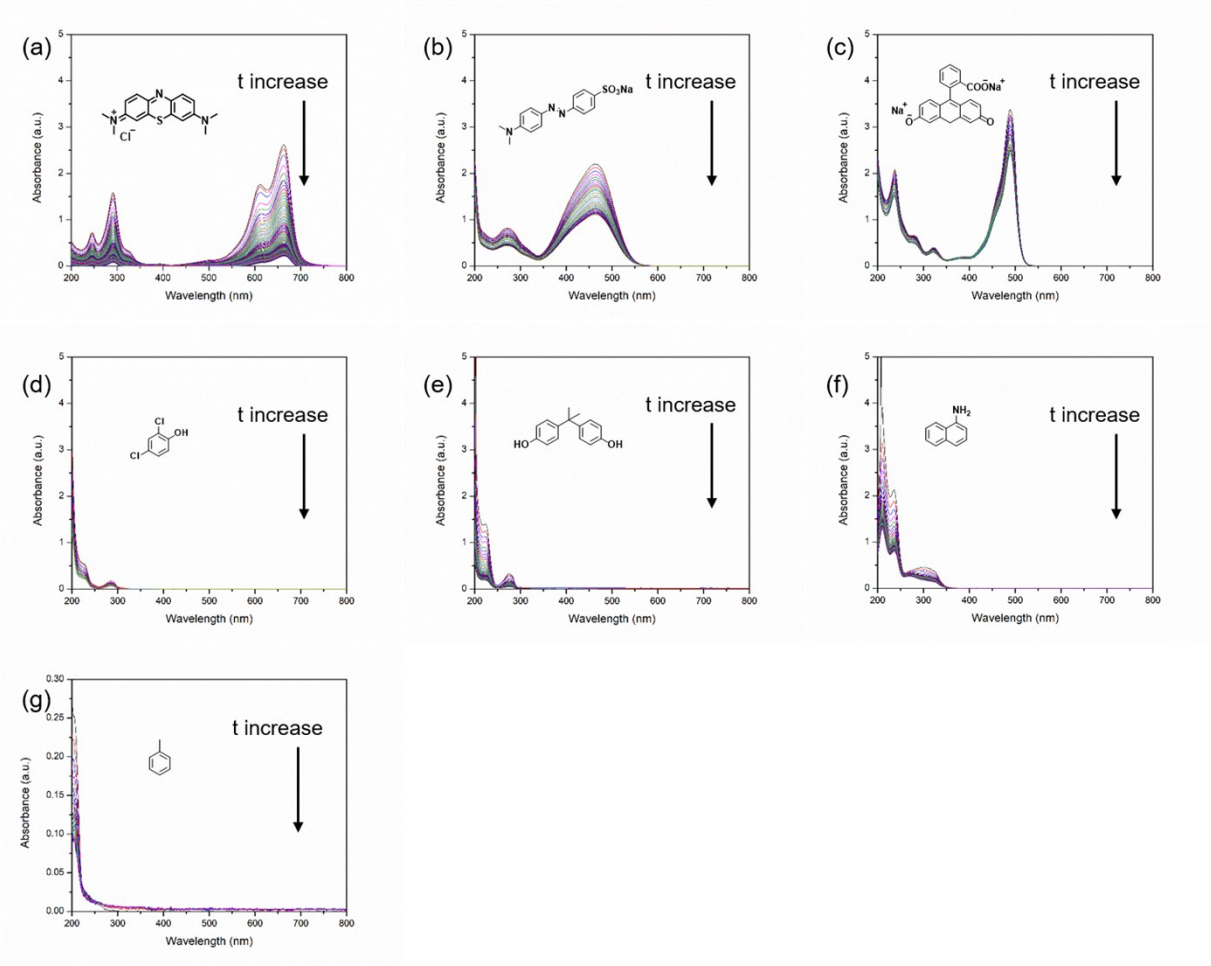


Fig. S6 UV-vis spectra recorded as a function of the contact time with **P5P5G** (1.00 mg/mL): (a) methylene blue; (b) methyl orange; (c) fluorescein sodium; (d)2,4-dichlorophenol; (e) bisphenol A; (f) 1-naphthyl amine; (g) toluene. c = 0.100 mM.

6. The pseudo-first-order model

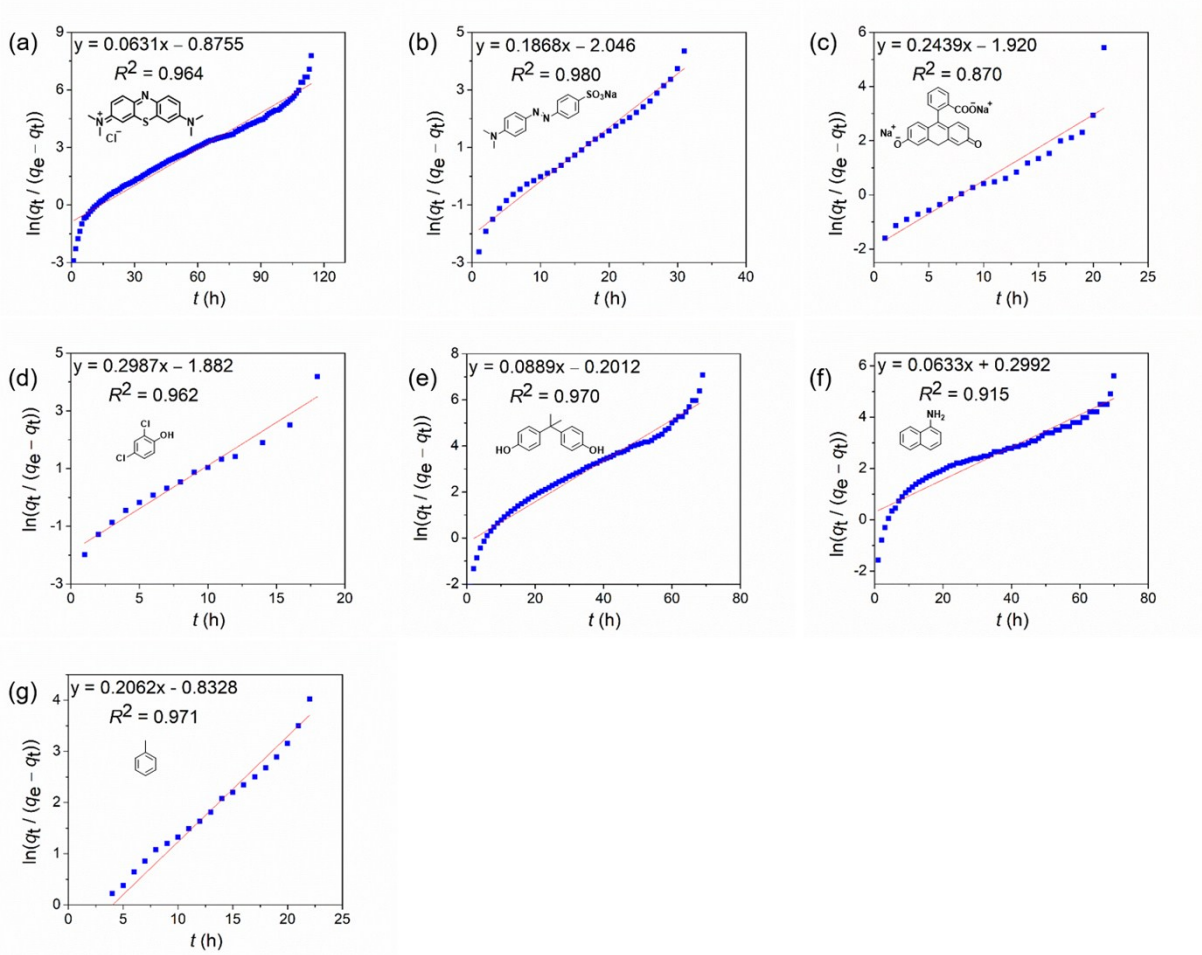


Fig. S7 The pseudo-first-order plots for **P5P5G** with (a) methylene blue, (b) methyl orange, (c) fluorescein sodium, (d) 2,4-dichlorophenol, (e) bisphenol A, (f) 1-naphthyl amine, and (g) toluene. Here t (in hour) is the contact time of each pollutant solution with **P5P5G** and q_t (in mg/g) is the amount of each pollutant adsorbed by a gram of **P5P5G**.

7. The pseudo-second-order model

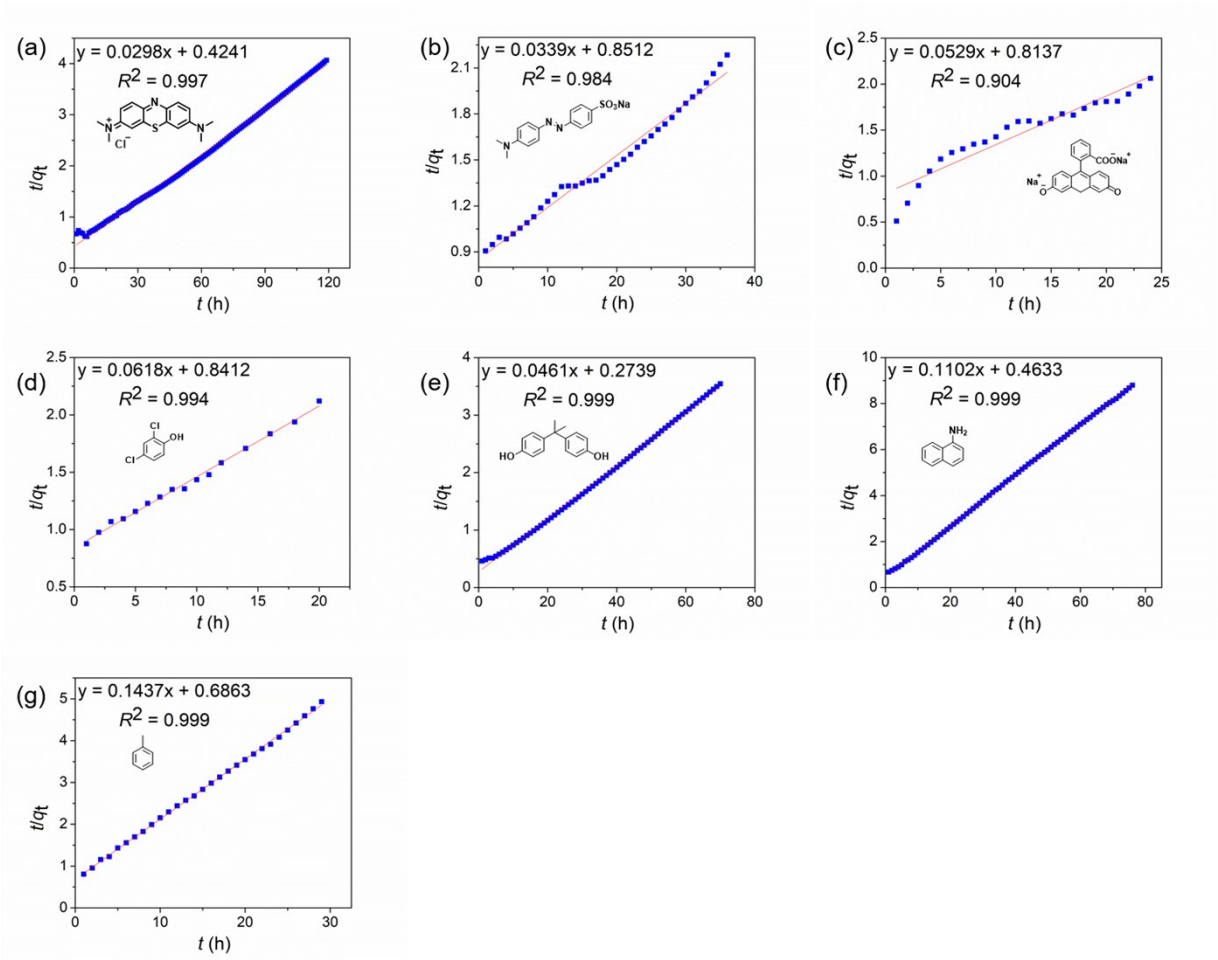


Fig. S8 The pseudo-second-order plots for **P5P5G** with (a) methylene blue, (b) methyl orange, (c) fluorescein sodium, (d) 2,4-dichlorophenol, (e) bisphenol A, (f) 1-naphthyl amine, and (g) toluene. Here t (in hour) is the contact time of each pollutant solution with **P5P5G** and q_t (in mg/g) is the amount of each pollutant adsorbed by a gram of **P5P5G**.

8. The Weber and Morris model

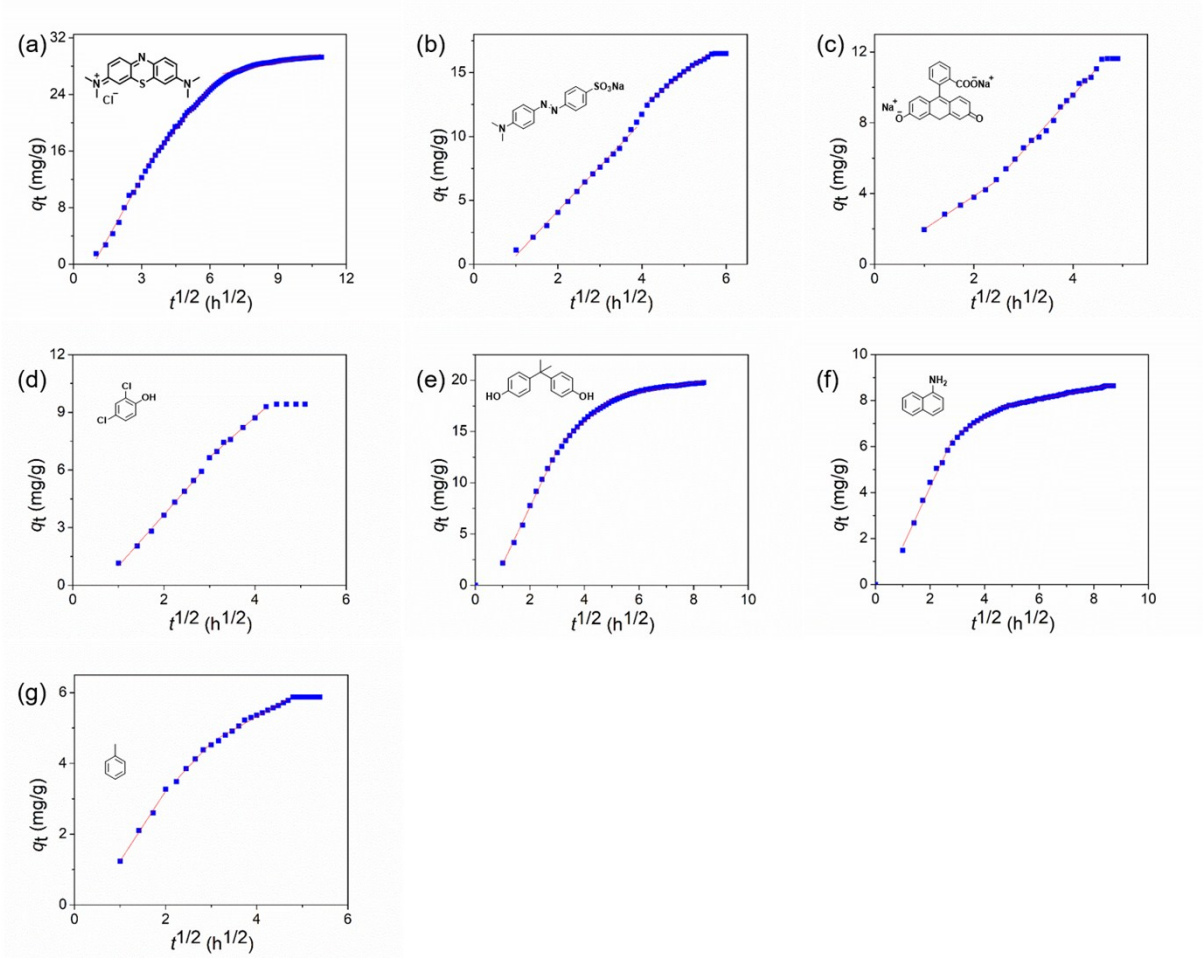


Fig. S9 The Weber and Morris plots for **P5P5G** with (a) methylene blue, (b) methyl orange, (c) fluorescein sodium, (d) 2,4-dichlorophenol, (e) bisphenol A, (f) 1-naphthyl amine, and (g) toluene. Here t (in hour) is the contact time of each pollutant solution with **P5P5G** and q_t (in mg/g) is the amount of each pollutant adsorbed by a gram of **P5P5G**.

9. The Langmuir adsorption isotherm model

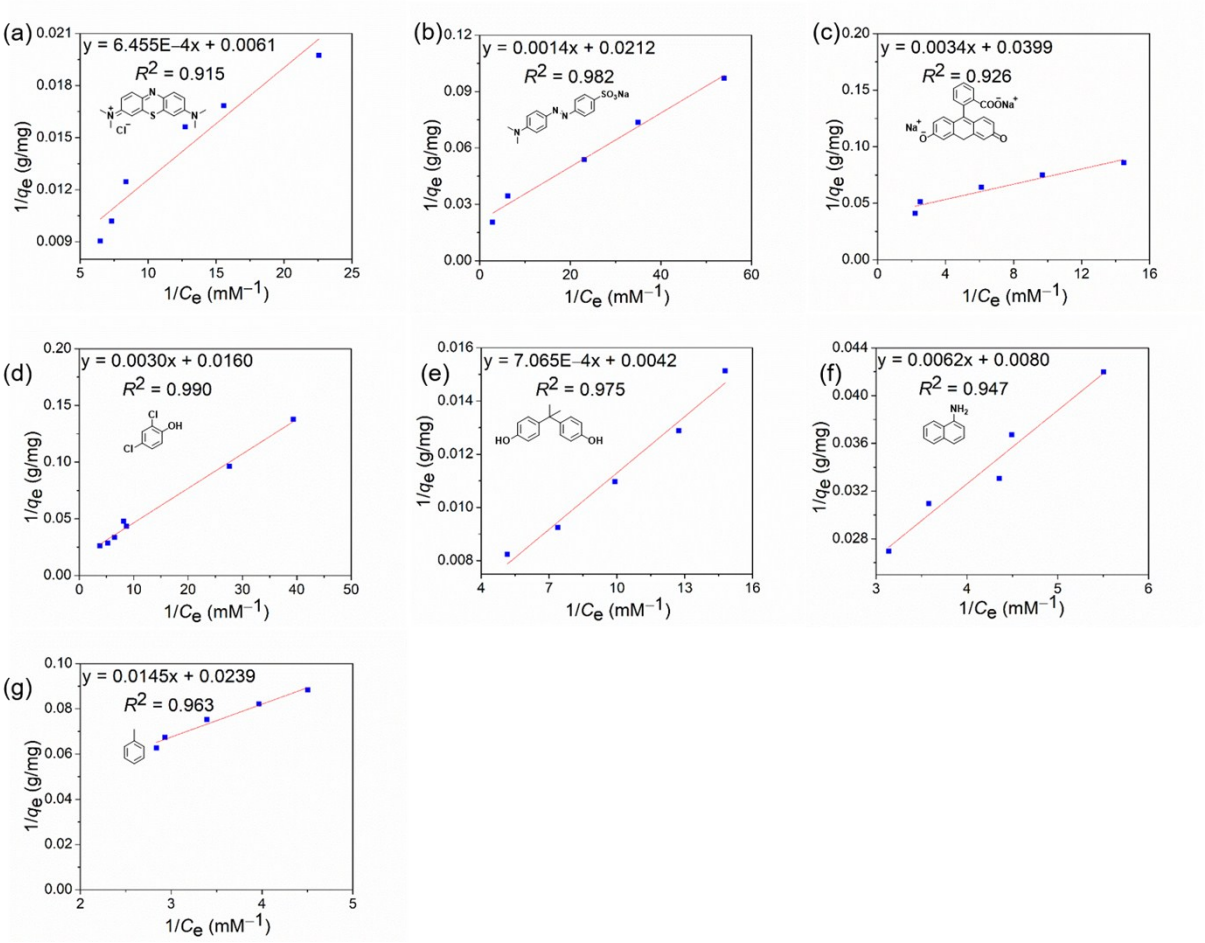


Fig. S10 The Langmuir model plots for **P5P5G** with (a) methylene blue, (b) methyl orange, (c) fluorescein sodium, (d) 2,4-dichlorophenol, (e) bisphenol A, (f) 1-naphthyl amine, and (g) toluene. The concentration of each pollutant used in this study is 0.500 mM.

10. The Freundlich adsorption isotherm model

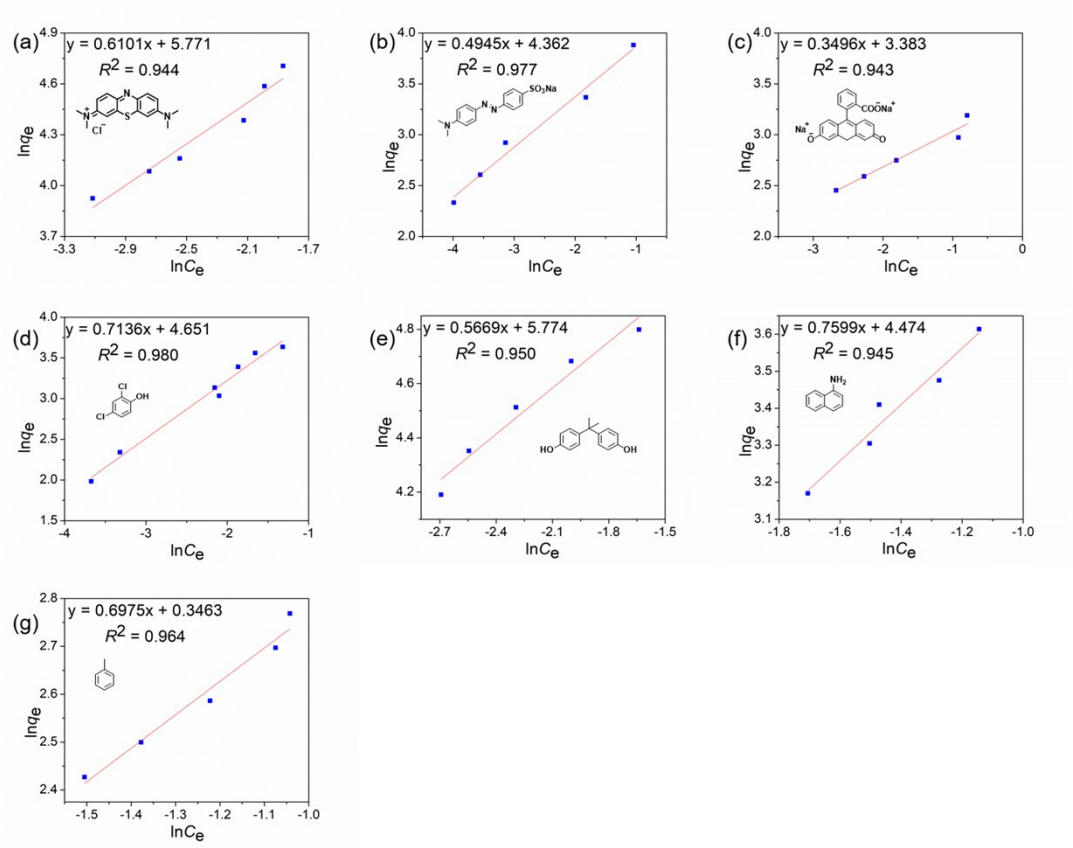


Fig. S11 The Freundlich model plots for **P5P5G** with (a) methylene blue, (b) methyl orange, (c) fluorescein sodium, (d) 2,4-dichlorophenol, (e) bisphenol A, (f) 1-naphthyl amine, and (g) toluene. The concentration of each pollutant used in this study is 0.500 mM.

11. Solid-state 2D ^{13}C–^{1}H HETCOR MAS result

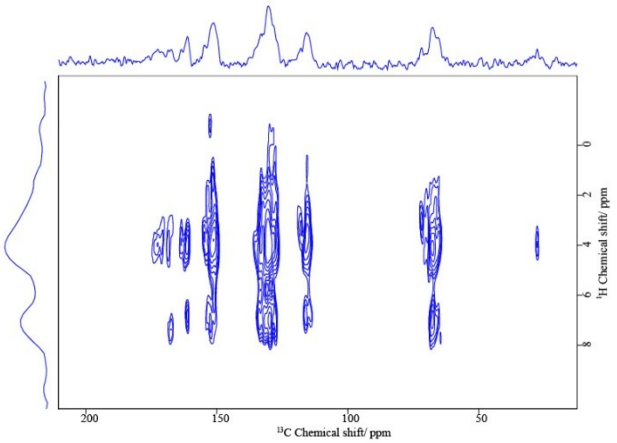


Fig. S12 Solid-state 2D ^{13}C–^{1}H HETCOR MAS spectrum of **P5P5G**. The spectrum exhibits that the characteristic proton signals of the $–CH_2$ unit at 4 ppm and the benzene group at 7 ppm are too broad to identify for the adsorption mechanism study.

12. Host-guest interactions between P5-1 and different pollutant molecules

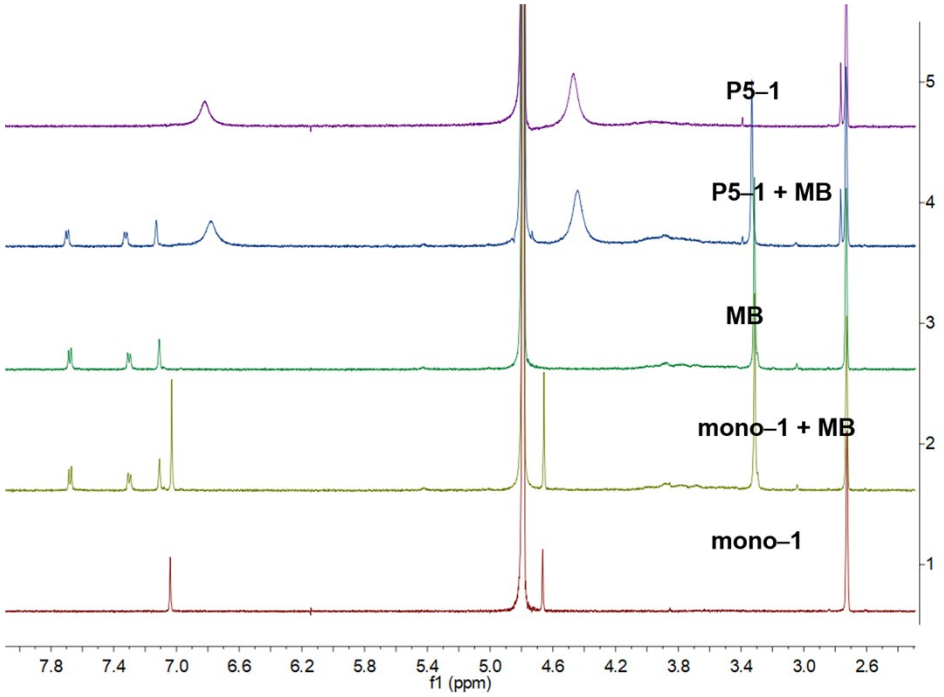


Fig. S13 ^{1}H NMR spectra (600 MHz, D_2O/DMSO-d_6, 10/1, 298 K) of **P5-1**, **P5-1** + methylene blue, methylene blue, **mono-1**, and methylene blue + **mono-1**. The host and guest molar ratio is 1:1 and the concentration is 2.00 mM.

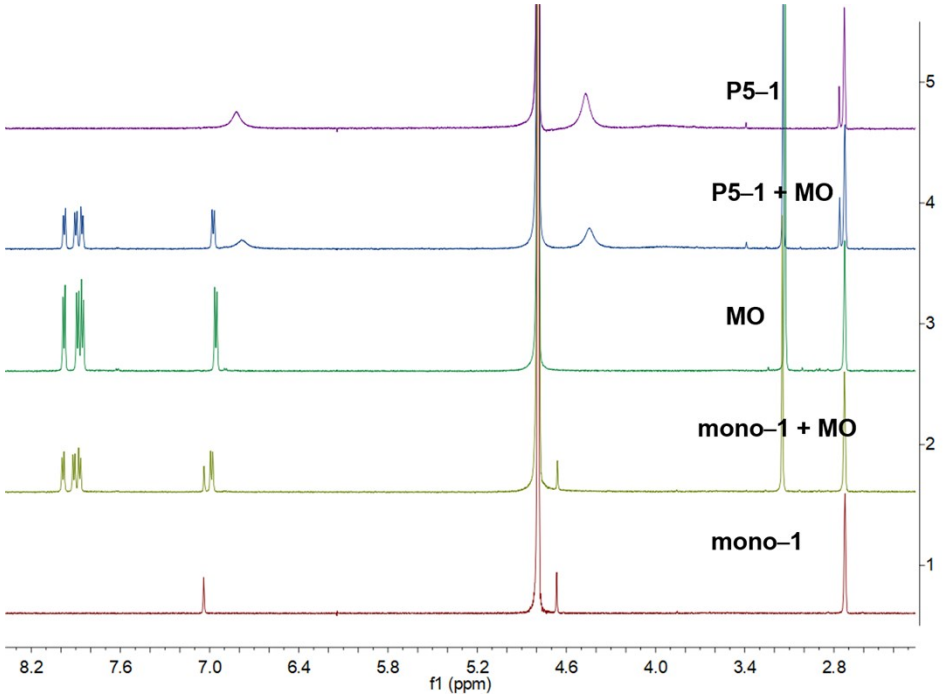


Fig. S14 ^{1}H NMR spectra (600 MHz, D_2O/DMSO-d_6, 10/1, 298 K) of **P5-1**, **P5-1** + methyl orange, methyl orange, **mono-1**, and methyl orange + **mono-1**. The host and guest molar ratio is 1:1 and the concentration is 2.00 mM.

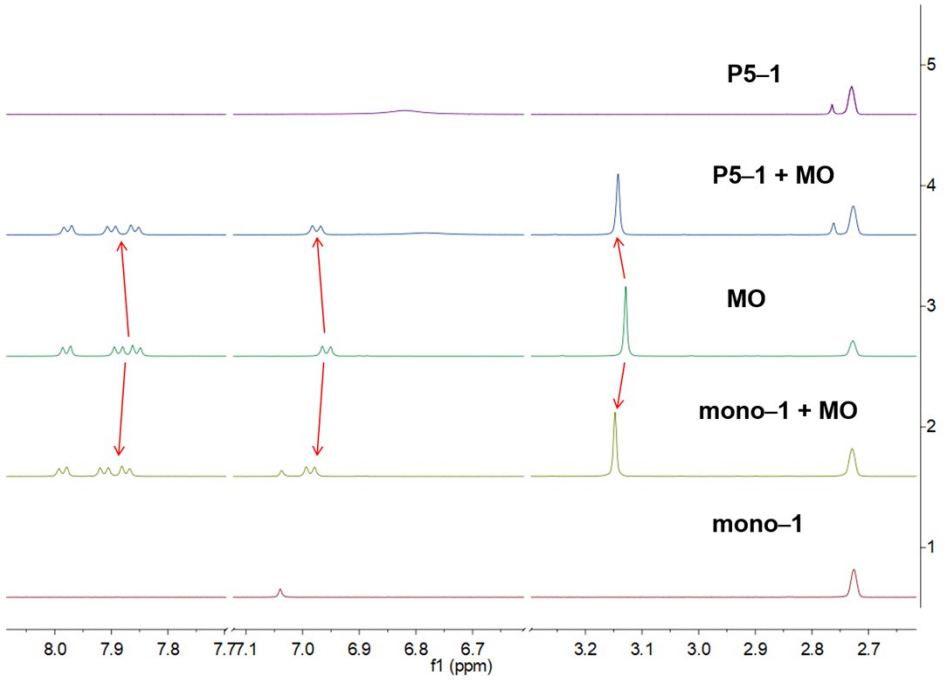


Fig. S15 Partial ^{1}H NMR spectra (600 MHz, D_2O/DMSO-d_6, 10/1, 298 K) of **P5-1**, **P5-1** + methyl orange, methyl orange, **mono-1**, and methyl orange + **mono-1**. The host and guest molar ratio is 1:1 and the concentration is 2.00 mM.

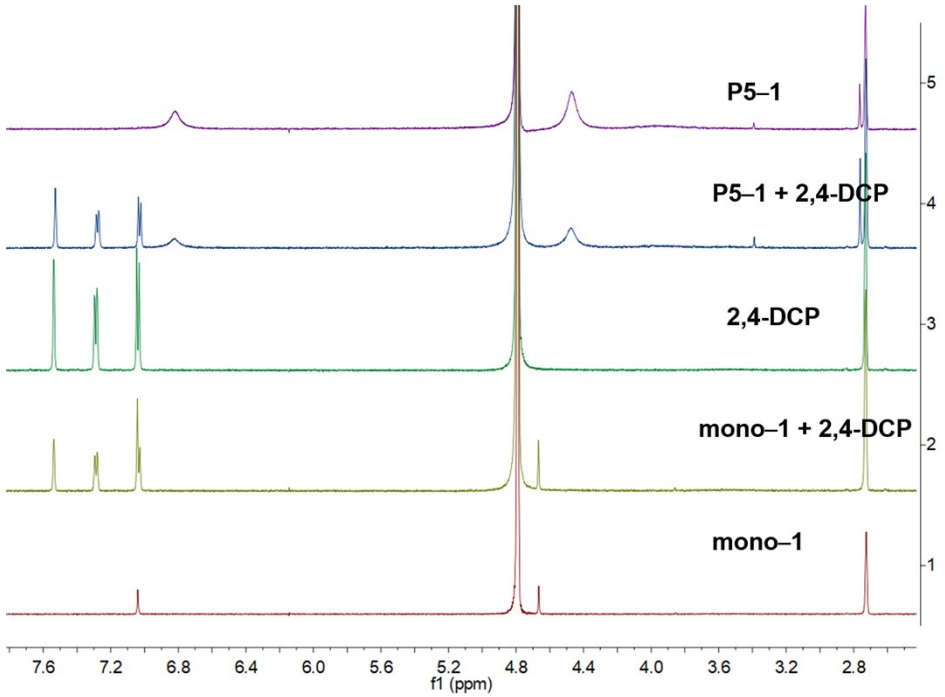


Fig. S16 ^{1}H NMR spectra (600 MHz, D_2O/DMSO-d_6, 10/1, 298 K) of **P5-1**, **P5-1** + 2,4-DCP, 2,4-DCP, **mono-1**, and 2,4-DCP + **mono-1**. The host and guest molar ratio is 1:1 and the concentration is 2.00 mM.

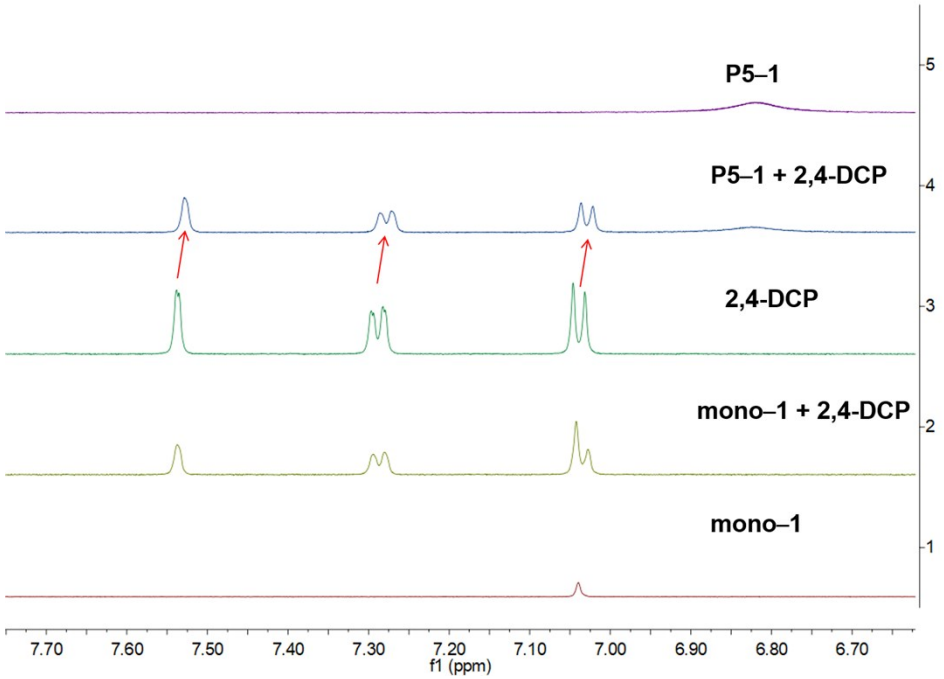


Fig. S17 Partial ^{1}H NMR spectra (600 MHz, D_2O/DMSO-d_6, 10/1, 298 K) of **P5-1**, **P5-1** + 2,4-DCP, 2,4-DCP, **mono-1**, and 2,4-DCP + **mono-1**. The host and guest molar ratio is 1:1 and the concentration is 2.00 mM.

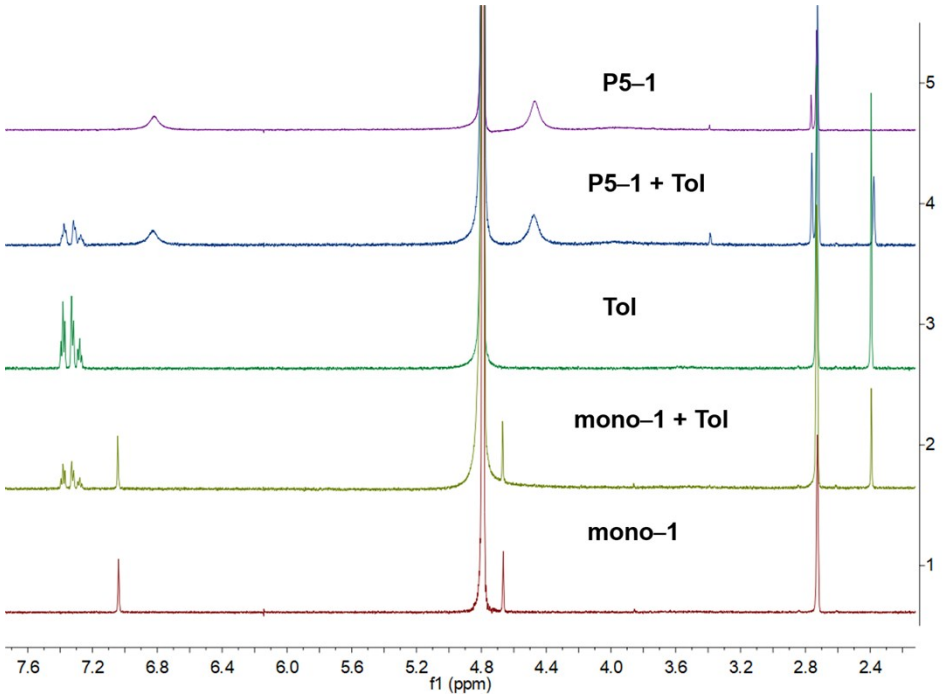


Fig. S18 ^{1}H NMR spectra (600 MHz, D_2O/DMSO-d_6, 10/1, 298 K) of **P5-1**, **P5-1** + toluene, toluene, **mono-1**, and toluene + **mono-1**. The host and guest molar ratio is 1:1 and the concentratoin is 2.00 mM.

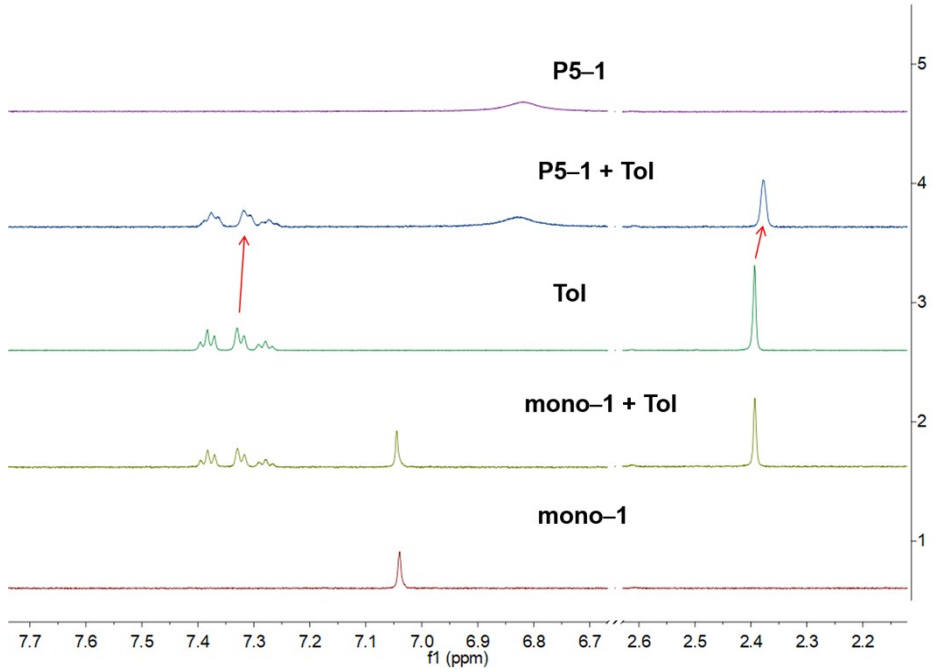


Fig. S19 Partial ^{1}H NMR spectra (600 MHz, D_2O/DMSO-d_6, 10/1, 298 K) of **P5-1**, **P5-1** + toluene, toluene, **mono-1**, and toluene + **mono-1**. The host and guest molar ratio is 1:1 and the concentration is 2.00 mM.

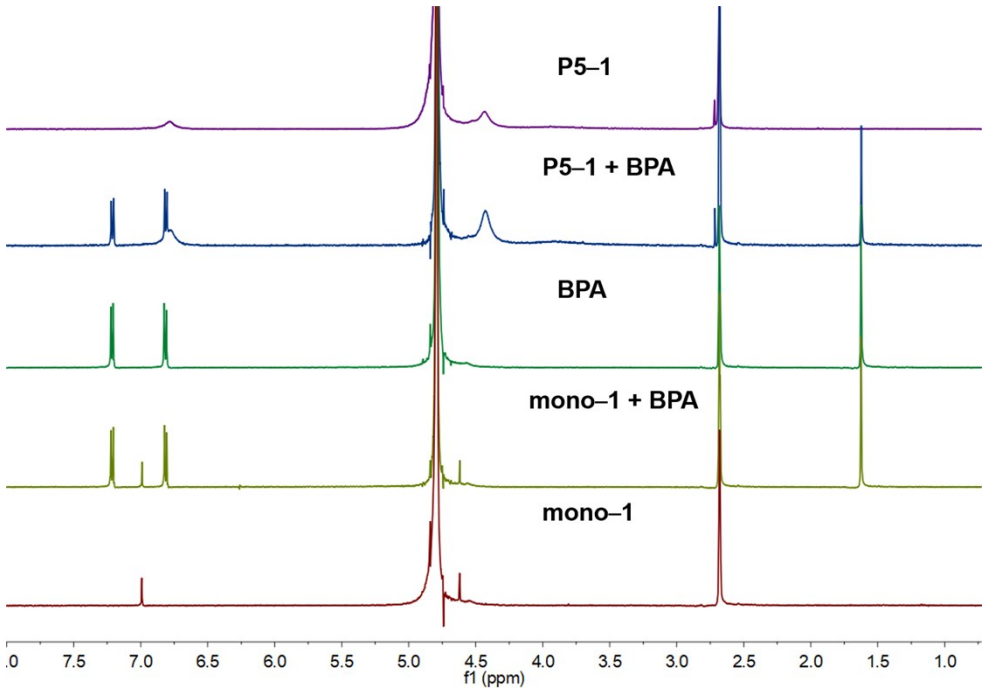


Fig. S20 ^{1}H NMR spectra (600 MHz, D_2O/DMSO-d_6, 10/1, 298 K) of **P5-1**, **P5-1** + BPA, BPA, **mono-1**, and BPA + **mono-1**. The host and guest molar ratio is 1:1 and the concentration is 1.00 mM.

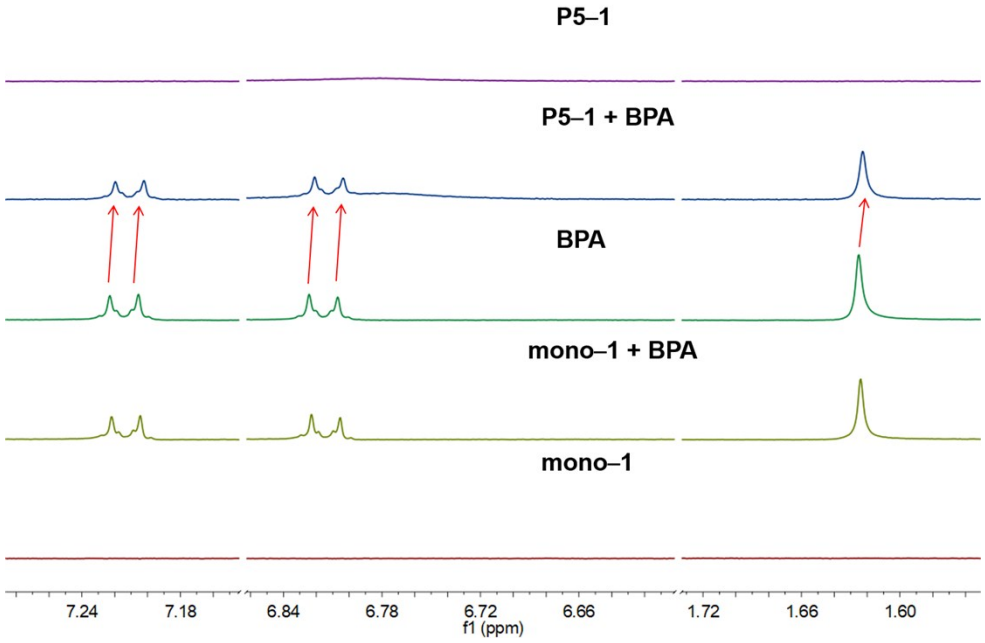


Fig. S21 Partial ^{1}H NMR spectra (600 MHz, D_2O/DMSO-d_6, 10/1, 298 K) of **P5-1**, **P5-1** + BPA, BPA, **mono-1**, and BPA + **mono-1**. The host and guest molar ratio is 1:1 and the concentration is 1.00 mM.

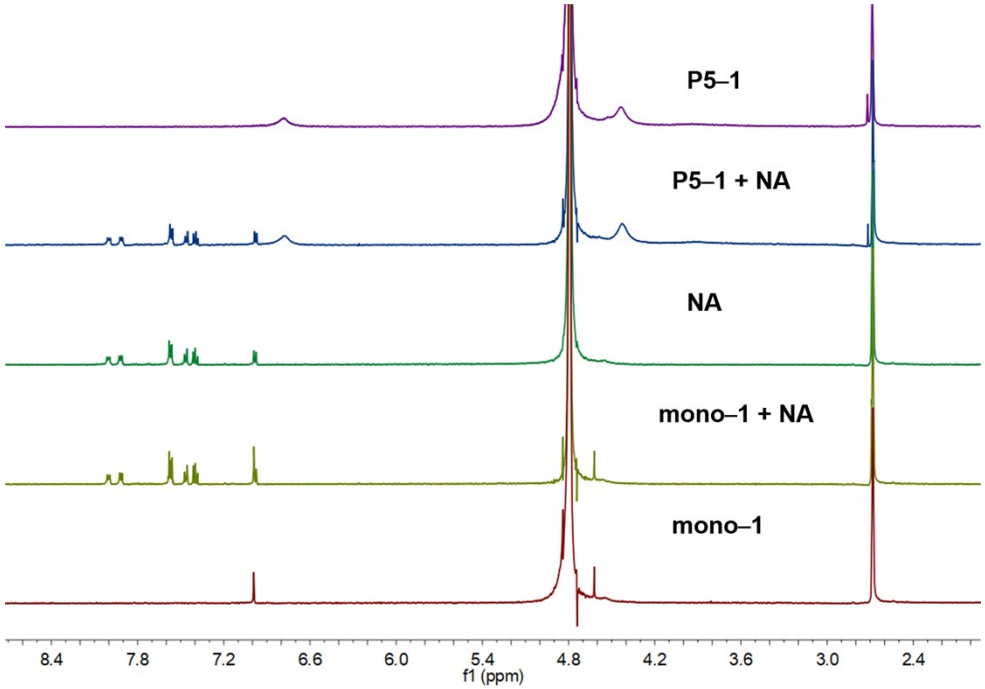


Fig. S22 ^{1}H NMR spectra (600 MHz, D_2O/DMSO-d_6, 10/1, 298 K) of **P5-1**, **P5-1** + NA, NA, **mono-1**, and NA + **mono-1**. The host and guest molar ratio is 1:1 and the concentration is 1.00 mM.

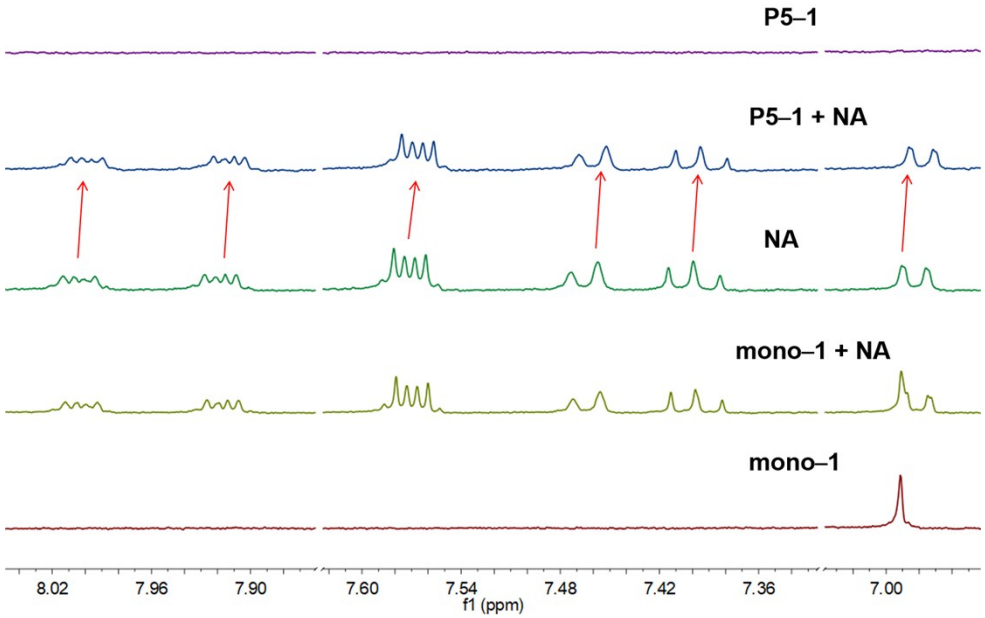


Fig. S23 Partial ^{1}H NMR spectra (600 MHz, D_2O/DMSO-d_6, 10/1, 298 K) of **P5-1**, **P5-1** + NA, NA, **mono-1**, and NA + **mono-1**. The host and guest molar ratio is 1:1 and the concentration is 1.00 mM.

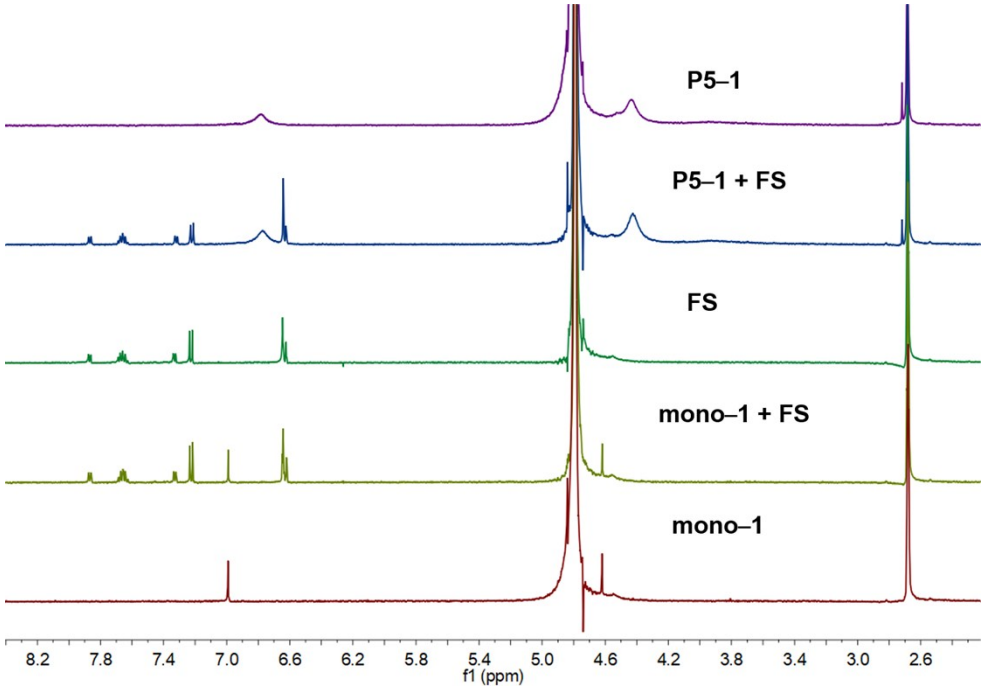


Fig. S24 ^{1}H NMR spectra (600 MHz, D_2O/DMSO-d_6, 10/1, 298 K) of **P5-1**, **P5-1** + FS, FS, **mono-1**, and FS + **mono-1**. The host and guest molar ratio is 1:1 and the concentration is 1.00 mM.

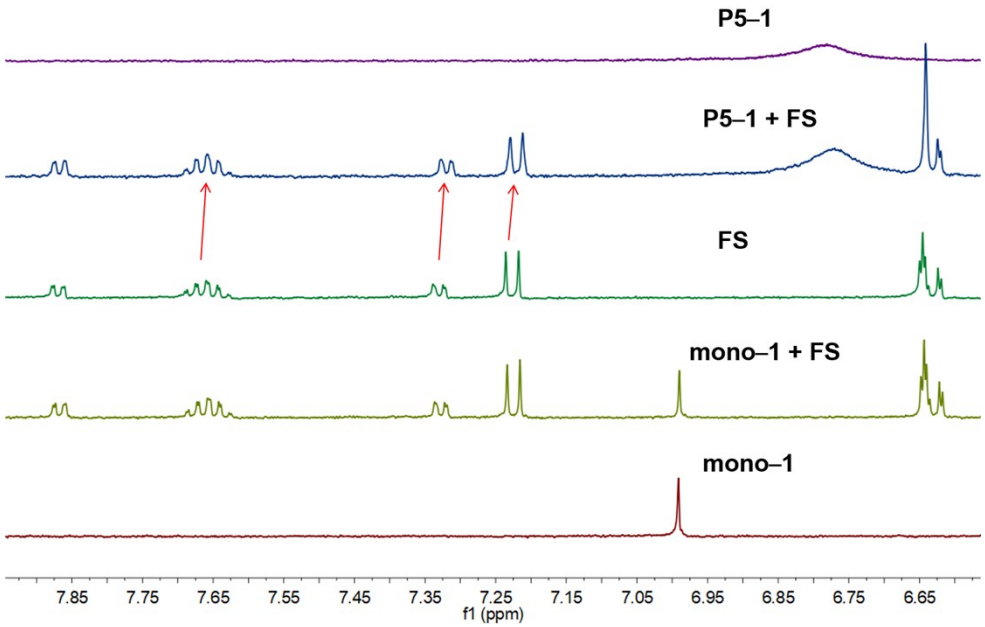


Fig. S25 Partial ^{1}H NMR spectra (600 MHz, D_2O/DMSO-d_6, 10/1, 298 K) of **P5-1**, **P5-1** + FS, FS, **mono-1**, and FS + **mono-1**. The host and guest molar ratio is 1:1 and the concentration is 1.00 mM.

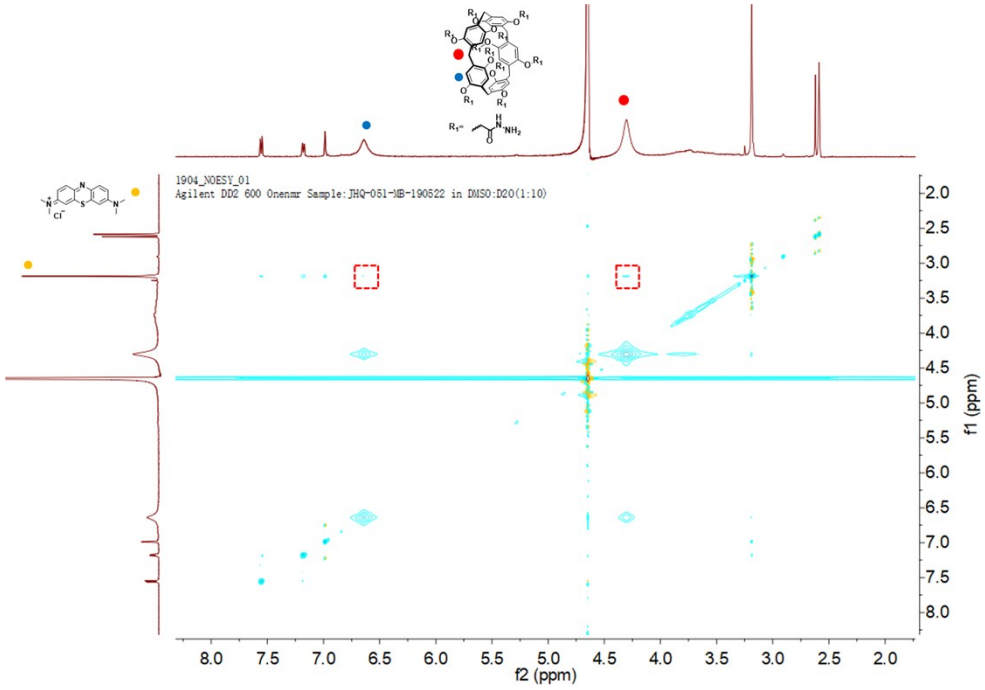


Fig. S26 2D NOESY NMR spectrum (600 MHz, D_2O/DMSO-d_6, 10/1, 298 K) of methylene blue and **P5-1**. The host and guest molar ratio is 1:1 and the concentration is 2.00 mM.

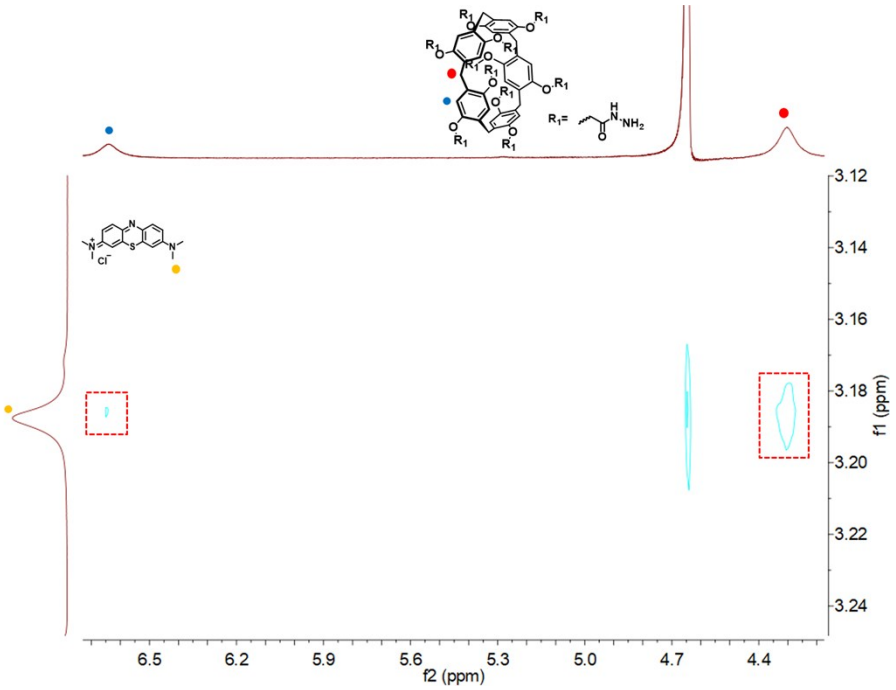


Fig. S27 Partial 2D NOESY NMR spectrum (600 MHz, D_2O/DMSO-d_6, 10/1, 298 K) of methylene blue and **P5-1**. The host and guest molar ratio is 1:1 and the concentration is 2.00 mM.

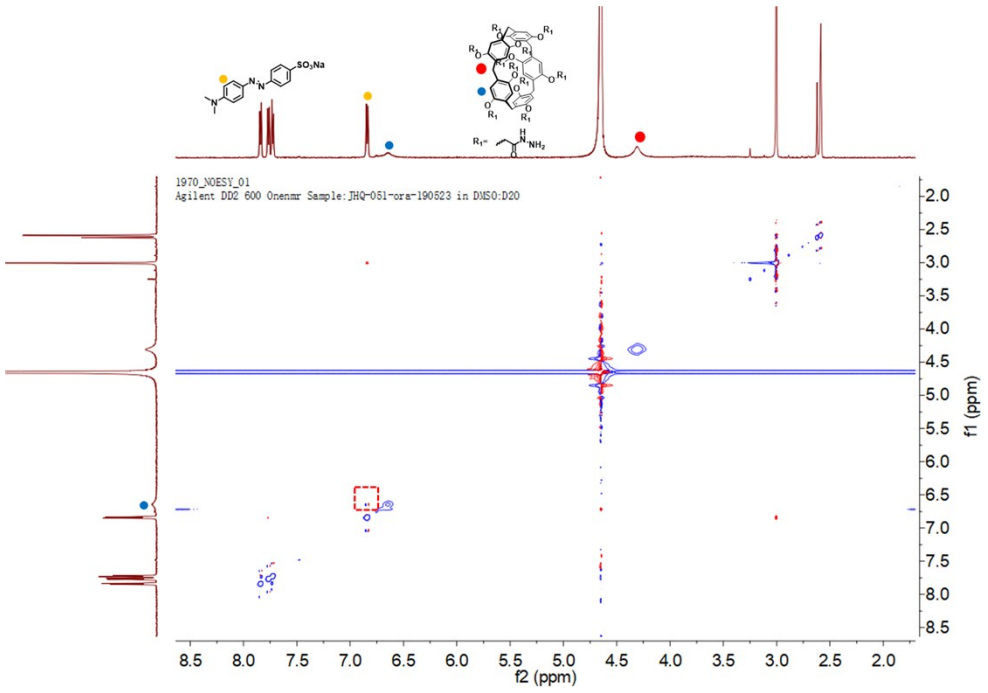


Fig. S28 2D NOESY NMR spectrum (600 MHz, D_2O/DMSO-d_6, 10/1, 298 K) of methyl orange and **P5-1**. The host and guest molar ratio is 1:1 and the concentration is 2.00 mM.

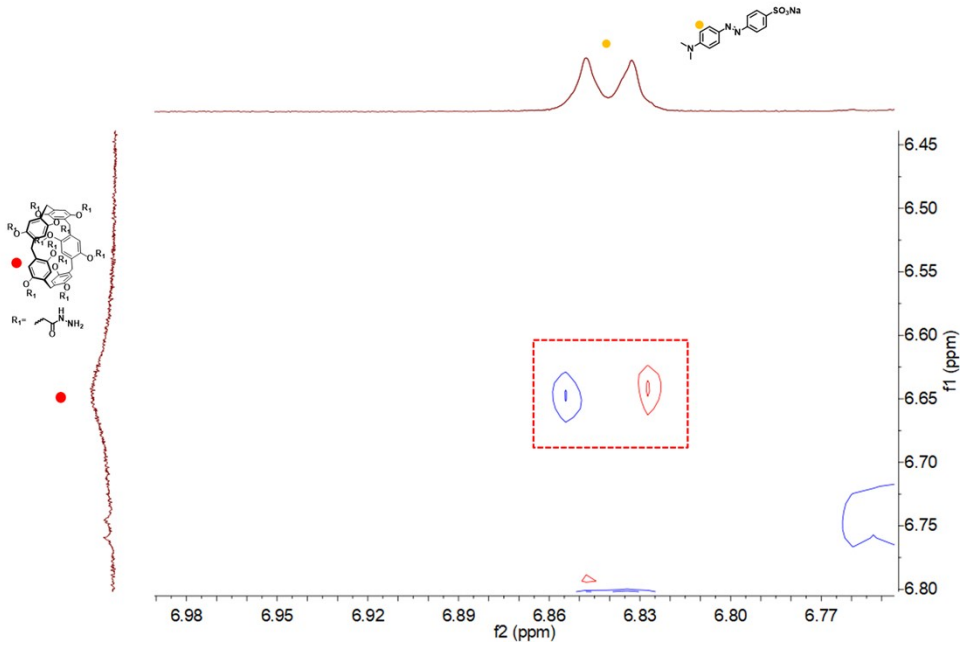


Fig. S29 Partial 2D NOESY NMR spectrum (600 MHz, D_2O/DMSO-d_6, 10/1, 298 K) of methyl orange and **P5-1**. The host and guest molar ratio is 1:1 and the concentration is 2.00 mM.

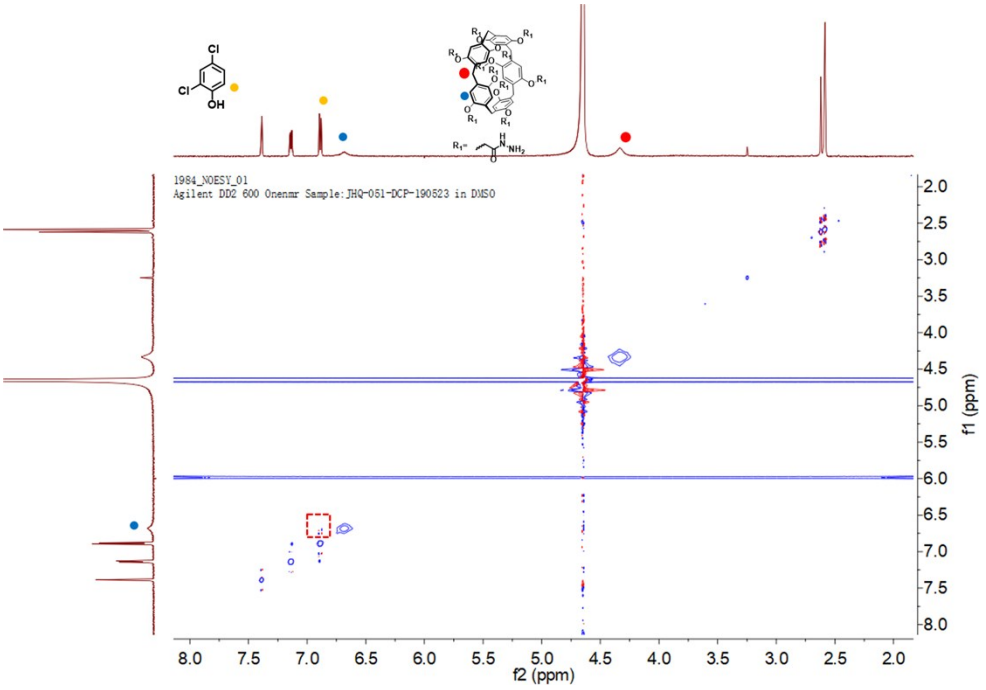


Fig. S30 2D NOESY NMR spectrum (600 MHz, D_2O/DMSO-d_6, 10/1, 298 K) of 2,4-DCP and **P5-1**. The host and guest molar ratio is 1:1 and the concentration is 2.00 mM.

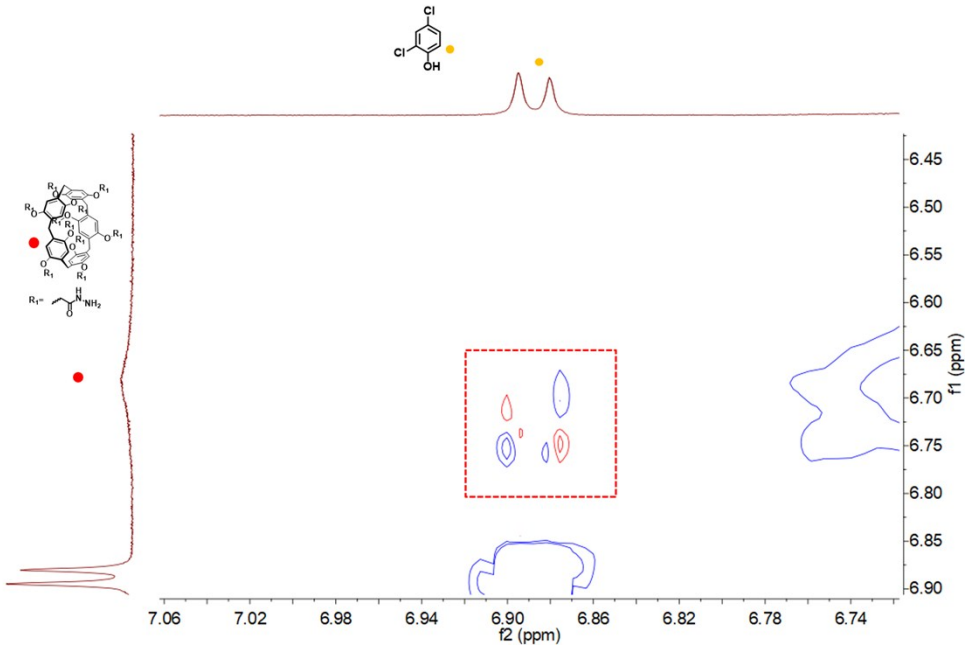


Fig. S31 Partial 2D NOESY NMR spectrum (600 MHz, D_2O/DMSO-d_6, 10/1, 298 K) of 2,4-DCP and **P5-1**. The host and guest molar ratio is 1:1 and the concentration is 2.00 mM.

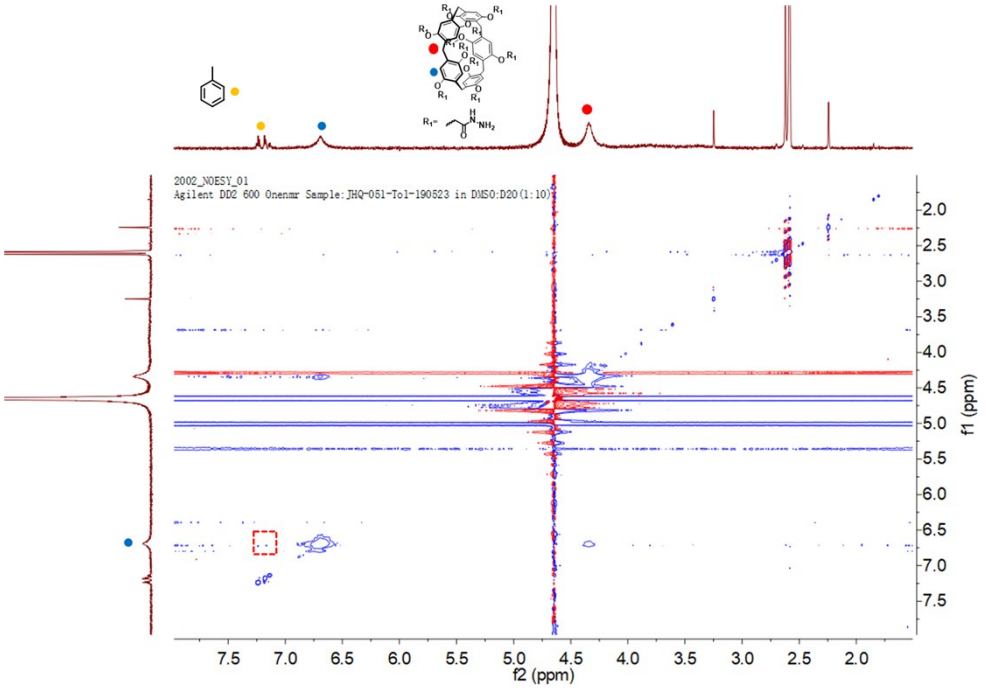


Fig. S32 2D NOESY NMR spectrum (600 MHz, D_2O/DMSO-d_6, 10/1, 298 K) of toluene and **P5-1**. The host and guest molar ratio is 1:1 and the concentration is 2.00 mM.

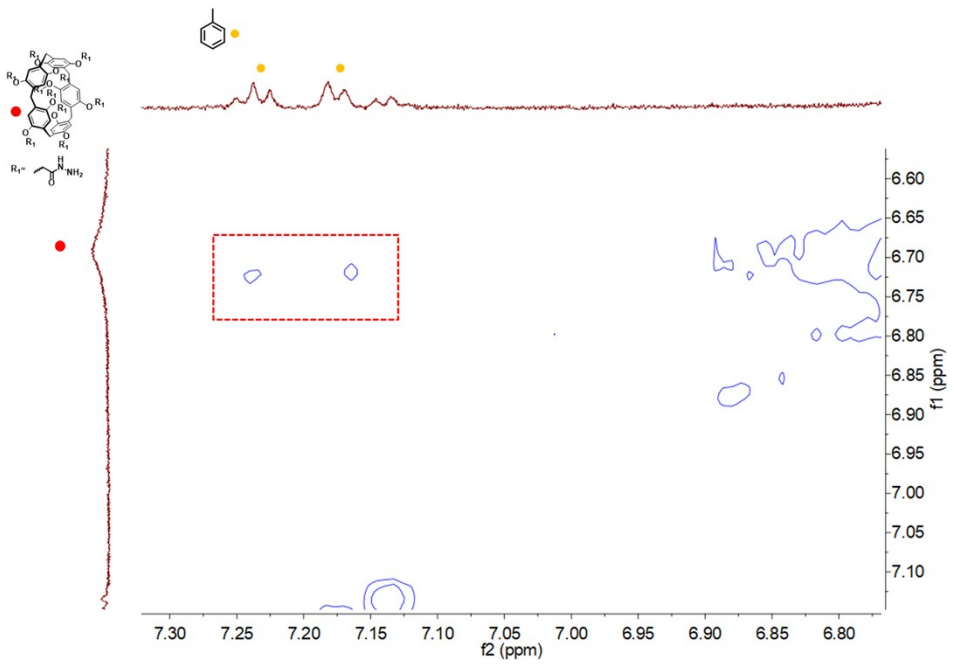


Fig. S33 Partial 2D NOESY NMR spectrum (600 MHz, D_2O/DMSO-d_6, 10/1, 298 K) of toluene and **P5-1**. The host and guest molar ratio is 1:1 and the concentration is 2.00 mM.

13. *References*

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