Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supramolecular hyperbranched polymer gels based on pillar[5]arene and their applications in removal of micropollutants from water†

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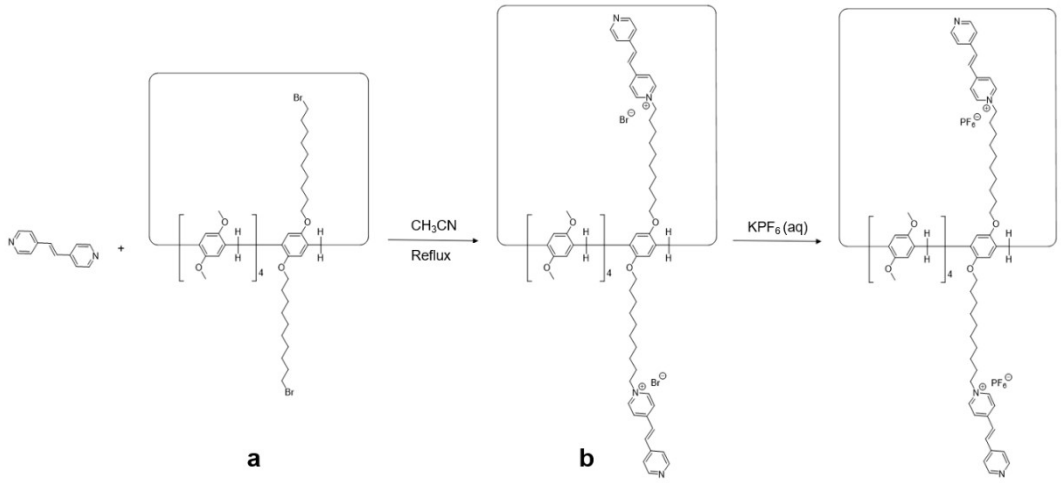
Electronic Supplementary Information (18 pages)

1.Materials and methods.

All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. Compounds **a**[S1], **DMP5**[S2] and **MG** [S3] was prepared according to published procedures. NMR spectra were recorded with a Bruker Avance DMX 600 spectrophotometer. High-resolution mass spectrometry experiments were performed with a Waters UPLC H-Class QDA instrument. Scanning electron microscopy (SEM) investigations were carried out on a JSM-6510 instrument or a ZEISS Gemini 360 instrument. Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) investigations were carried out on a Carl Zeiss Microscopy GmbH 73447 instrument. UV−vis spectra were taken on a SHIMADZU UV−2450 spectrophotometer. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) experiments were performed with a NexION 350 instrument. Rheological testing was taken on a MCR102 Advanced Rheology Expanded Systems. Thermogravimetric analysis (TGA) was taken on a METTLER TG/DSC1/1600.

*2.Synthesis of compound **1**.*



***Scheme S1**. Synthetic route to **1**.*

Compound **a** (1.00 g, 0.86 mmol) and 4,4'-ethene-1,2-diyldipyridine (0.47 g, 2.58 mmol) were added to acetonitrile (50.0 mL). The solution was refluxed 24 h. The solvent was evaporated and the residue was purified by chromatography on silica gel (dichloromethane/methanol, v/v 5:1) to give **b** as a brown solid. Dissolve **b** in a small amount of methanol, add dropwise to 500 mL of saturated aqueous KPF_6 solution, collect the precipitate, filter and dry in vacuo to give **1** as a brown powdery solid. The ^{1}H NMR spectrum of **1** is shown in Fig. S1. ^{1}H NMR (600 MHz, DMSO-*d6*, 298 K) δ (ppm): δ 8.76−8.70 (m, 8H), 8.30 (m, 4H), 8.00 (m, 2H), 7.82−7.79 (m, 2H), 7.68 (s, 4H)，6.79−6.77 (m, 10H), 4.10 (s, 4H)，3.80−3.64 (m, 38H), 1.71−0.80 (m, 34H). The ^{13}C NMR spectrum of **1** is shown in Figure S2. ^{13}C NMR (125 MHz, DMSO-*d6*, 298 K) δ (ppm): 152.37, 150.99, 150.49, 150.38, 149.87, 144.79, 142.62, 138.47, 128.25, 128.08, 125.07, 122.25, 115.11, 113.99, 113.72, 68.70, 60.29, 56.07, 55.92, 55.35, 49.06, 30.68, 29.49, 29.17, 29.02, 28.60, 26.06, 25.97. HRESIMS is shown in Fig. S3: *m/z* 682.38711 $[M - 2PF_6]^{2+}$.

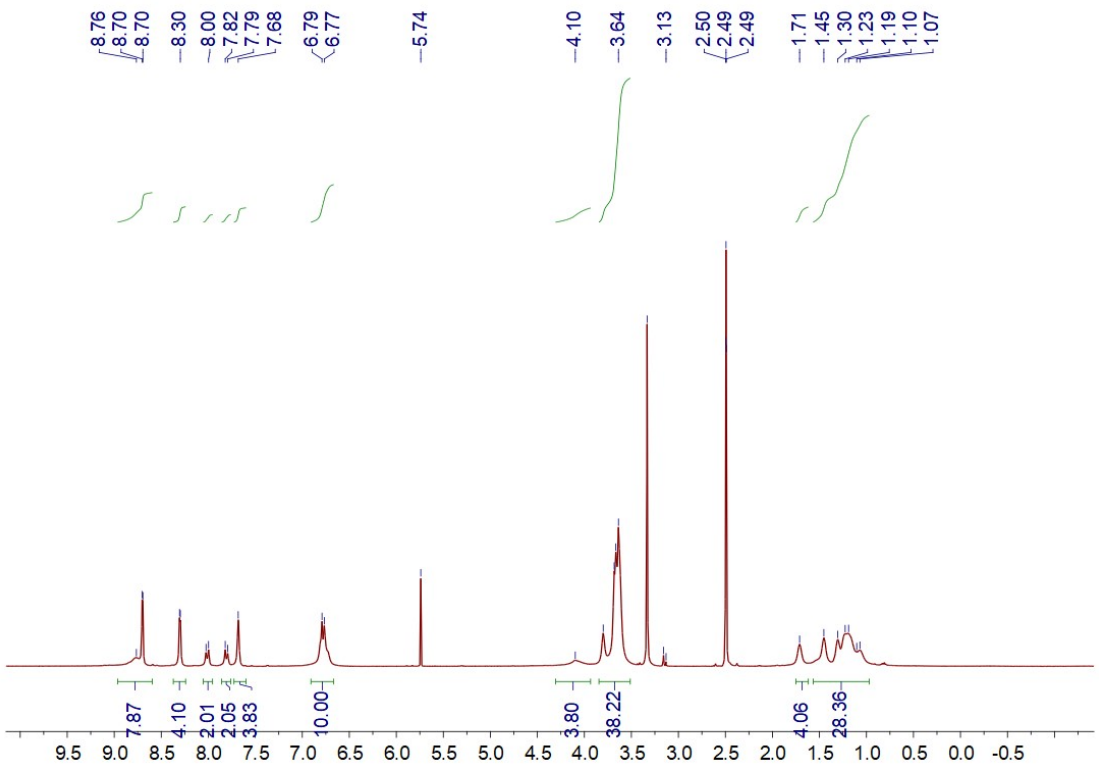


Figure S1. ^{1}H NMR spectrum (600 MHz, DMSO-*d6*, 298 K) of **1**.

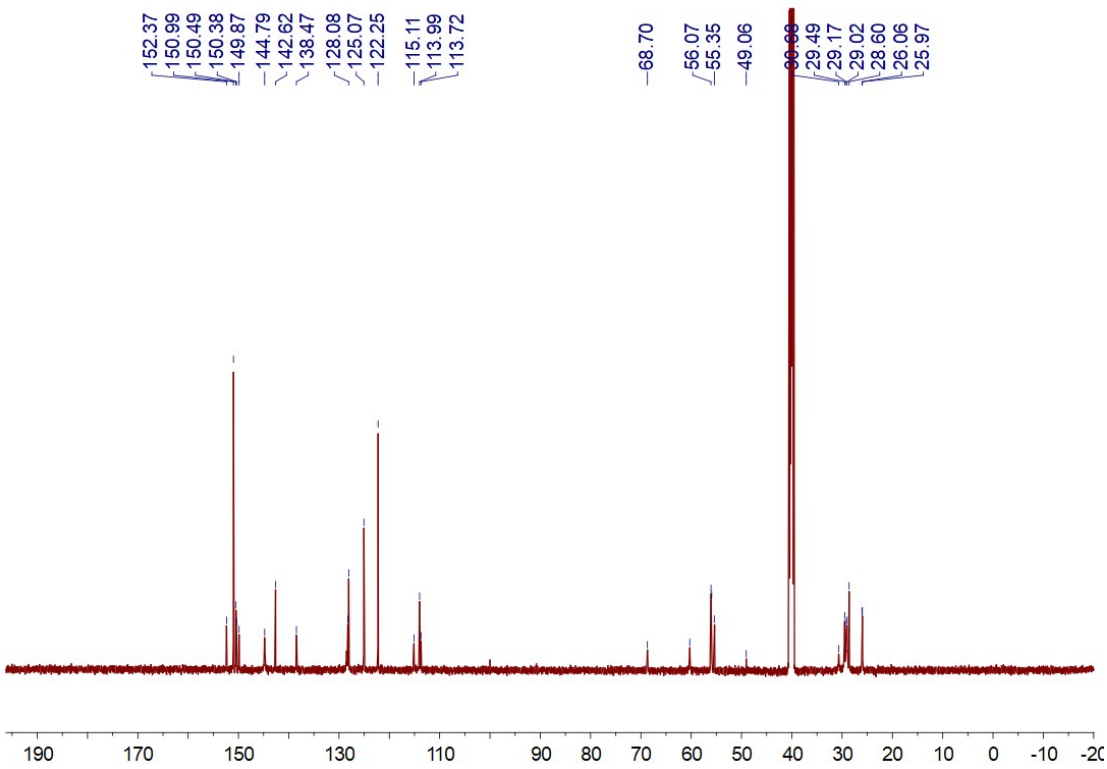


Figure S2. ^{13}C NMR spectrum (125 MHz, DMSO-*d6*, 298 K) of **1**.

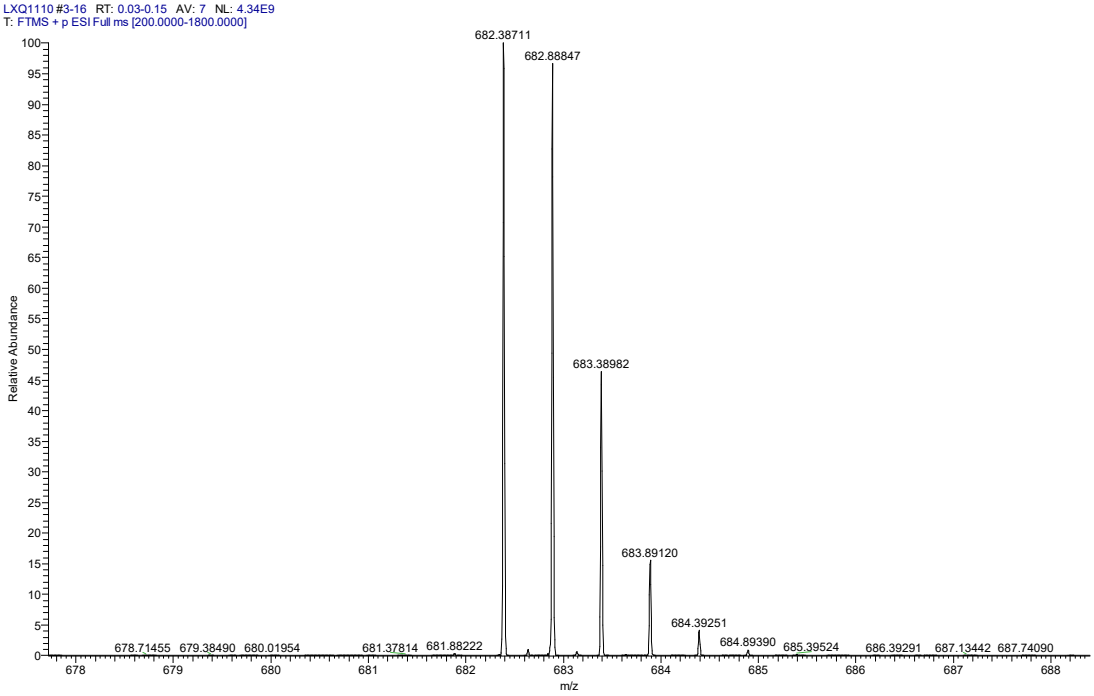


Figure S3. High-resolution mass electrospray ionization mass spectrum of **1**. Main peak: *m/z* 682.38711 $[M - 2PF_6]^{2+}$ (100%).

*3. Study on the complexation between **DMP5** and model guests **MG** and **MG•H**$^+$*

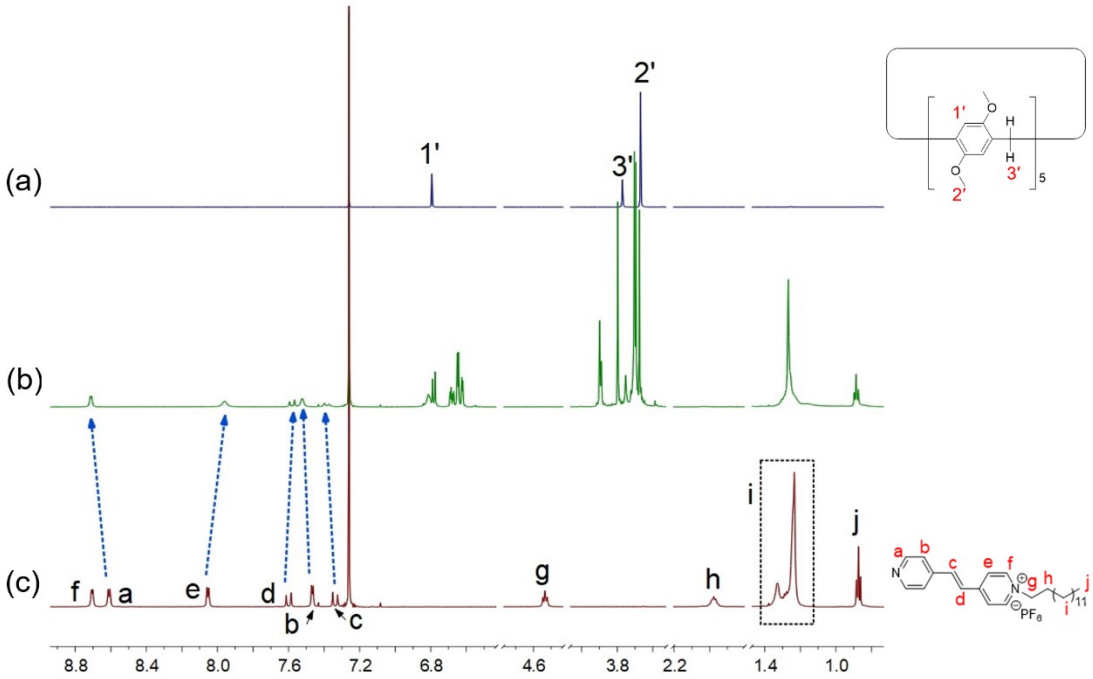


Figure S4. Partial ^{1}H NMR spectra (600 MHz, $CDCl_3$, 298 K) of (a) **DMP5** (5.00 mM), (b) **DMP5** (5.00 mM) and **MG** (5.00 mM), (c) **MG** (5.00 mM).

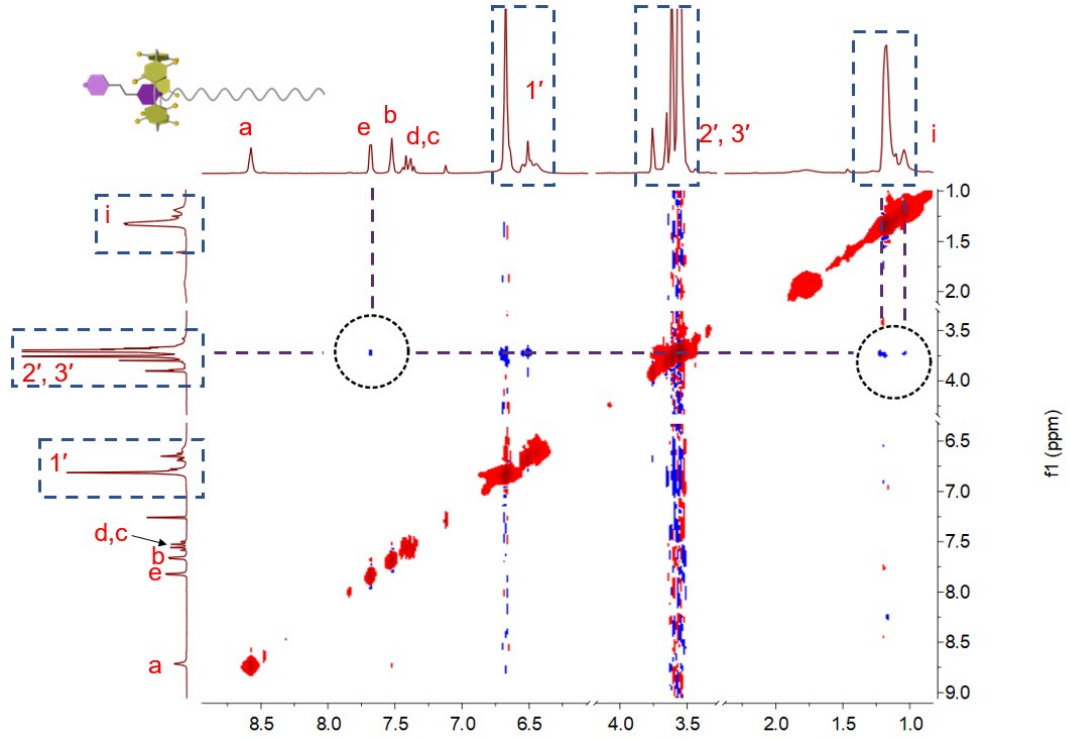


Figure S5. Partial 2D NOESY spectra ($CDCl_3$, 293 K, 600 MHz) of the mixture of **DMP5** (30.0 mM) and **MG** (30.0 mM).

To determine the stoichiometry and association constant between **DMP5** and **MG**

or **MG•H**$^+$, ^{1}H NMR titration was done with solutions which had a constant concentration of **MG** or **MG•H**$^+$ (1.00 mM) and different concentrations of **DMP5**. By a non-linear curve-fitting method, the association constant between the **DMP5** and **MG** or **MG•H**$^+$ was calculated. By a mole ratio plot, a 1:1 stoichiometry was obtained for this system.

The non-linear curve-fitting was based on the equation:

$$\Delta\delta = (\Delta\delta_\infty/[\mathbf{DMP5}]_0)\,(0.5[\mathbf{MG}]_0 + 0.5([\mathbf{DMP5}]_0 + 1/K_a) - (0.5([\mathbf{MG}]_0^2 + (2[\mathbf{MG}]_0(1/K_a - [\mathbf{DMP5}]_0)) + (1/K_a + [\mathbf{DMP5}]_0)^2)\,0.5)) \qquad \text{(Eq. S1)}$$

wherein $\Delta\delta$ is the chemical shift change of H_b on **MG** or the chemical shift change of H_{e*} on **MG•H**$^+$ at $[MG]_0$, $\Delta\delta_\infty$ is the chemical shift change of H_b or H_{e*} when the guest is completely complexed, $[\mathbf{MG}]_0$ is the fixed initial concentration of the guest, and $[\mathbf{DMP5}]_0$ is the varying concentration of **DMP5**.

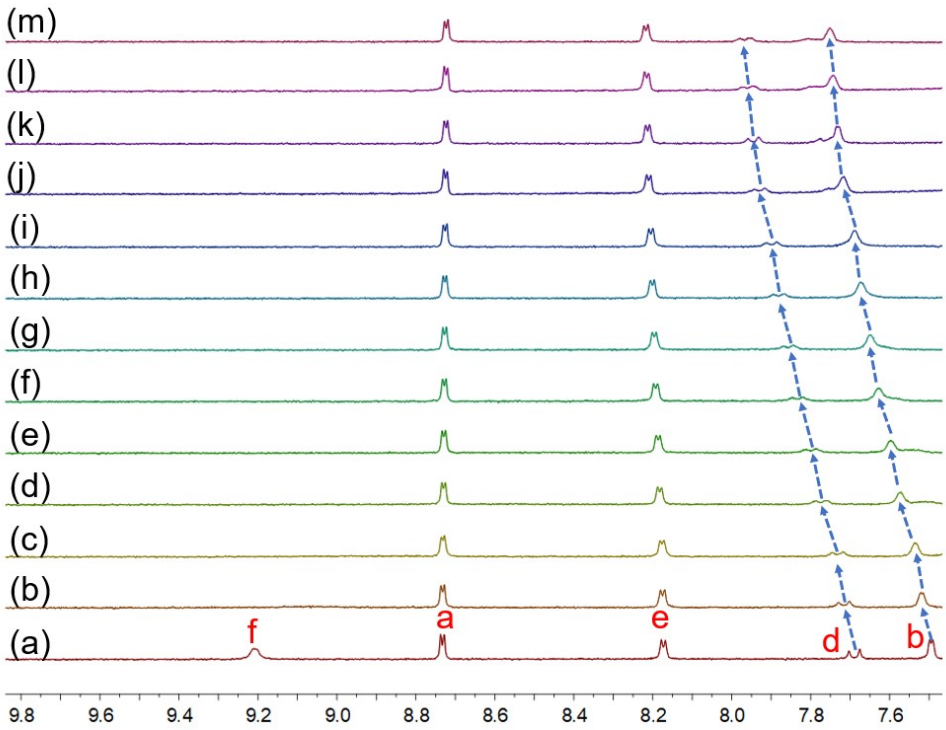


Figure S6. Partial ^{1}H NMR spectra (600 MHz, $CDCl_3$, 298 K) of **MG** at a concentration of 1.00 mM with different concentrations of **DMP5**: (a) 0.00 mM; (b) 0.09 mM; (c) 0.20 mM; (d) 0.38 mM; (e) 0.57 mM; (f) 0.83 mM; (g) 1.07 mM; (h) 1.38 mM; (i) 1.67 mM; (j) 2.31 mM; (k) 2.86 mM; (l) 3.75 mM; (m) 5.00 mM.

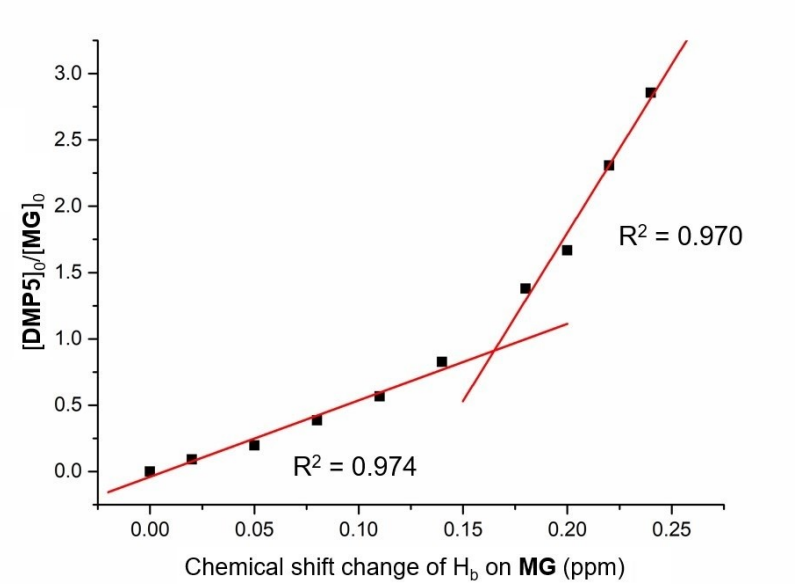


Figure S7. Mole ratio plot for the complexation between **DMP5** and **MG**, indicating a 1:1 stoichiometry.

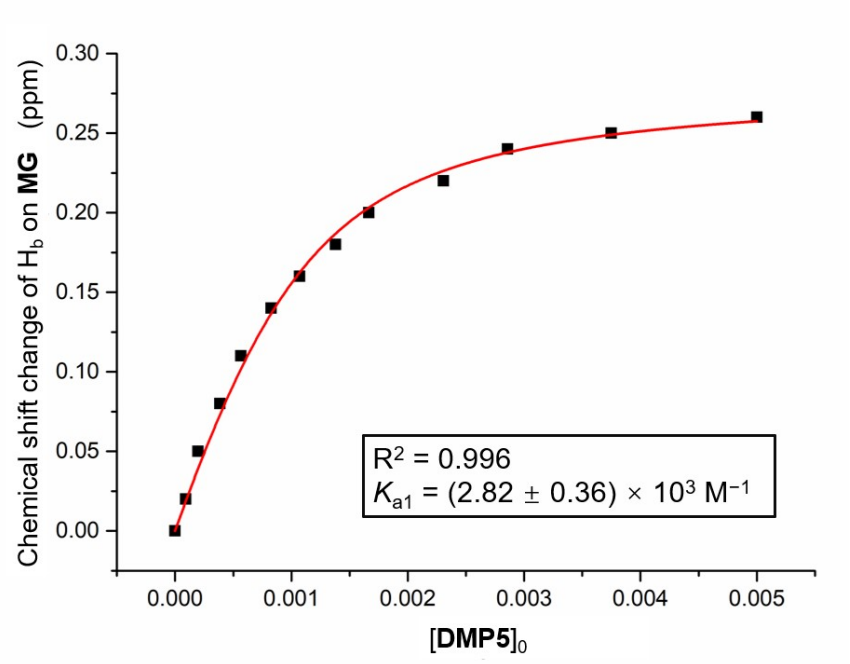


Figure S8. The chemical shift changes of H_b on **MG** upon addition of **DMP5**. The red solid line was obtained from the non-linear curve-fitting using Eq. S1.

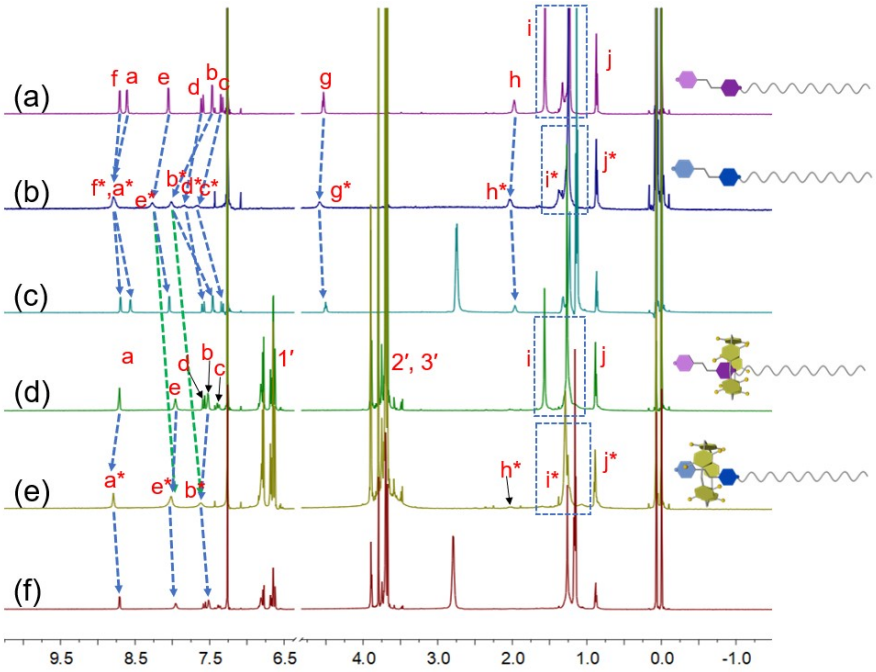


Figure S9. Partial ^{1}H NMR spectra (600 MHz, $CDCl_3$, 298 K) of (a) **MG** (5.00 mM); (b) after addition of TFA of a; (c) after addition of TEA of b; (d) **MG** (5.00 mM) + **DMP5** (5.00 mM); (e) after addition of TFA of d; (f) after addition of TEA of e.

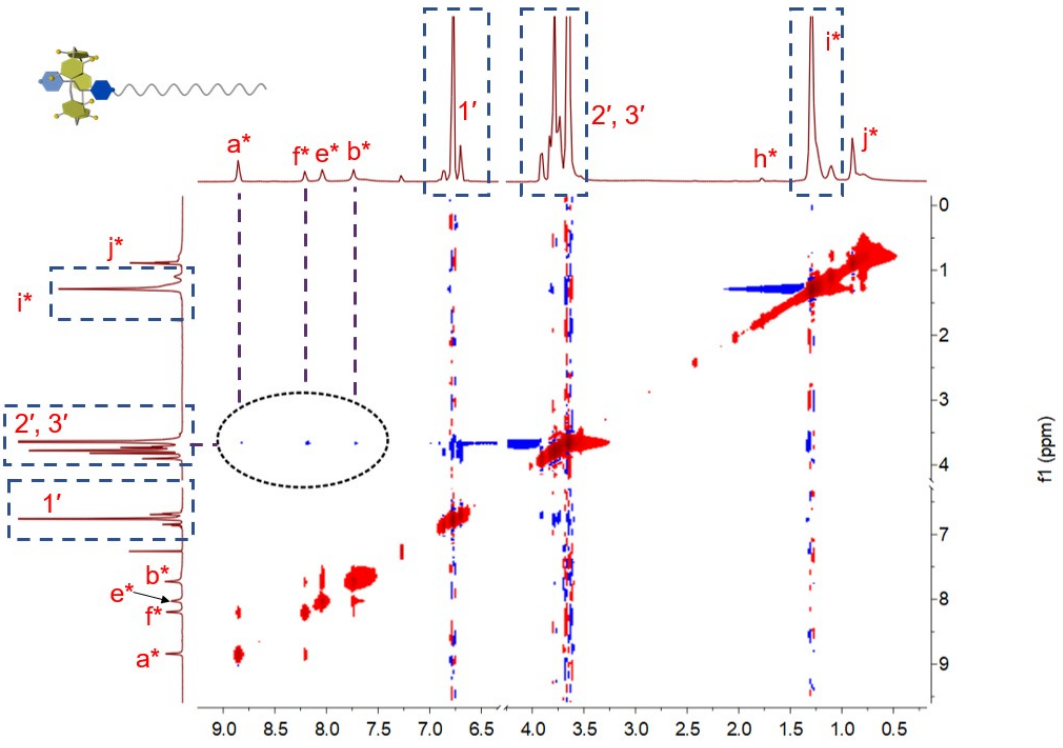


Figure S10. Partial 2D NOESY spectra ($CDCl_3$, 293 K, 600 MHz) of the mixture of **DMP5** (30.0 mM) and **MG•H**$^{+}$ (30.0 mM).

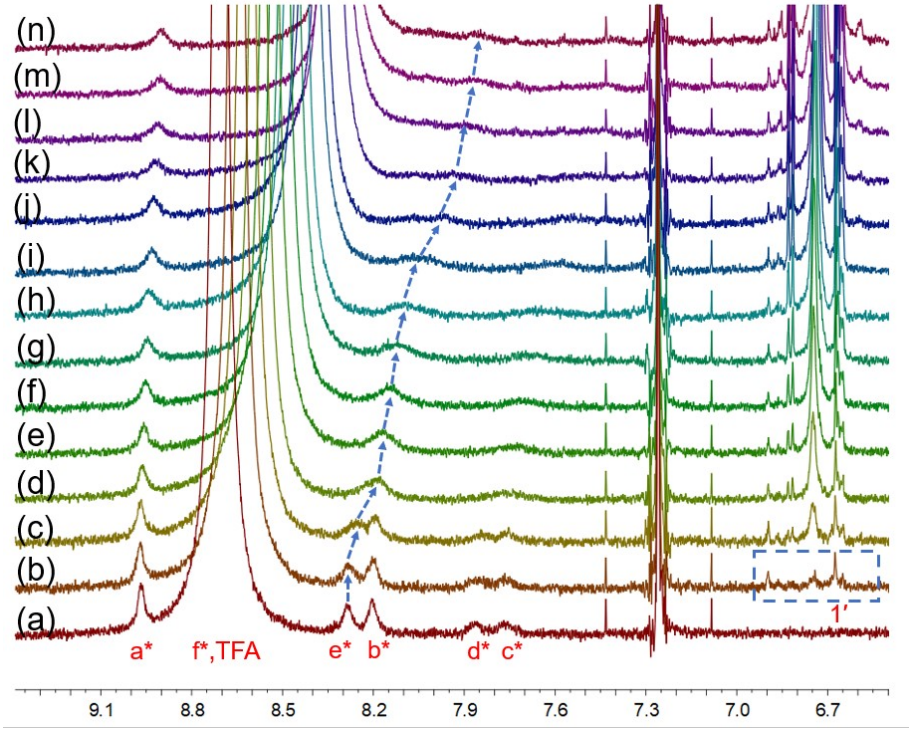


Figure S11. Partial ^{1}H NMR spectra (600 MHz, $CDCl_3$, 298 K) of **MG•H$^+$** at a concentration of 1.00 mM with different concentrations of **DMP5**: (a) 0.00 mM; (b) 0.10 mM; (c) 0.20 mM; (d) 0.38 mM; (e) 0.57 mM; (f) 0.83 mM; (g) 1.07 mM; (h) 1.38 mM; (i) 1.80 mM; (j) 2.42 mM; (k) 3.42 mM; (l) 4.19 mM; (m) 5.28 mM; (n) 6.33 mM.

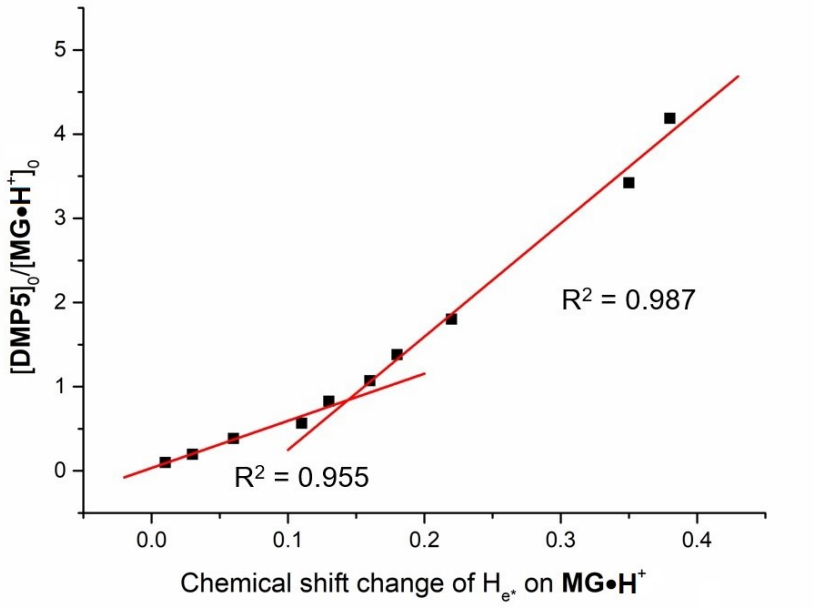


Figure S12. Mole ratio plot for the complexation between **DMP5** and **MG•H$^+$**, indicating a 1:1 stoichiometry.

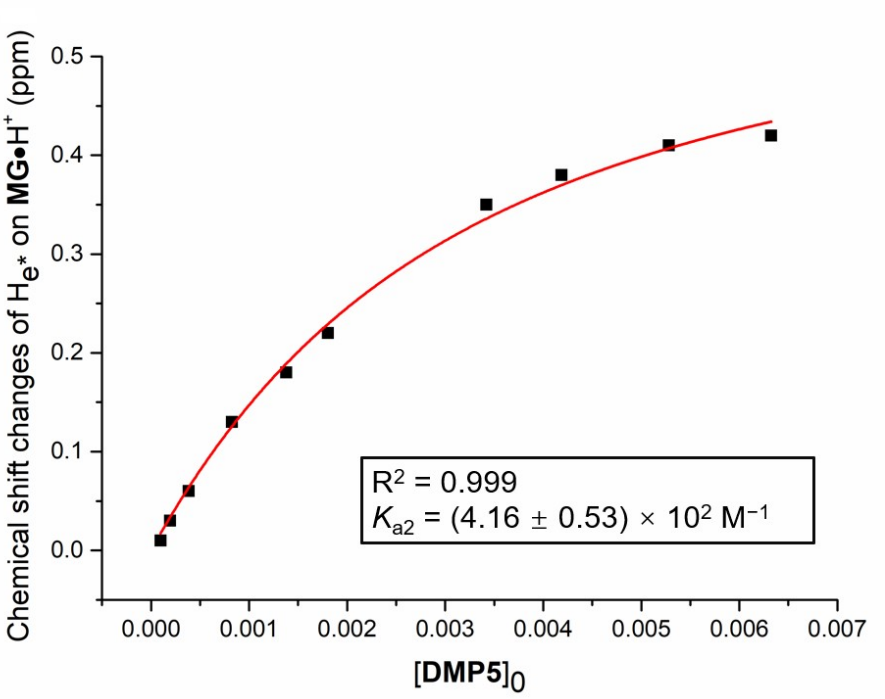


Figure S13. The chemical shift changes of H_{e*} on **MG•H**$^+$ upon addition of **DMP5**. The red solid line was obtained from the non-linear curve-fitting using Eq. S1.

4. Removal of metal ions

Table S1 Residual concentrations of metal ions after adsorbed by **SHPG** for 24 h investigated by ICP experiments.

Metal ions	Residual Concentration μg/L
Ag^{+}	121906.14
Pb^{2+}	100213.28
Cu^{2+}	84501.30
Zn^{2+}	63107.85
Ni^{2+}	54631.44
Pd^{2+}	160.60

*5. SEM images and EDS elemental mapping of **SHPG** after removing Pd^{2+} from water*

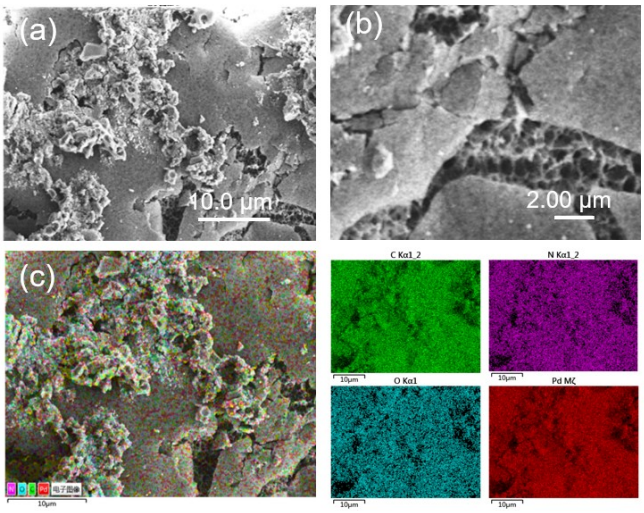


Figure S14. (a) SEM image of **SHPG** after adsorbing Pd^{2+} (b) enlarged image of a; (c) EDS elemental mapping of **SHPG** after removing Pd^{2+} from water.

6. Removal of organic dyes

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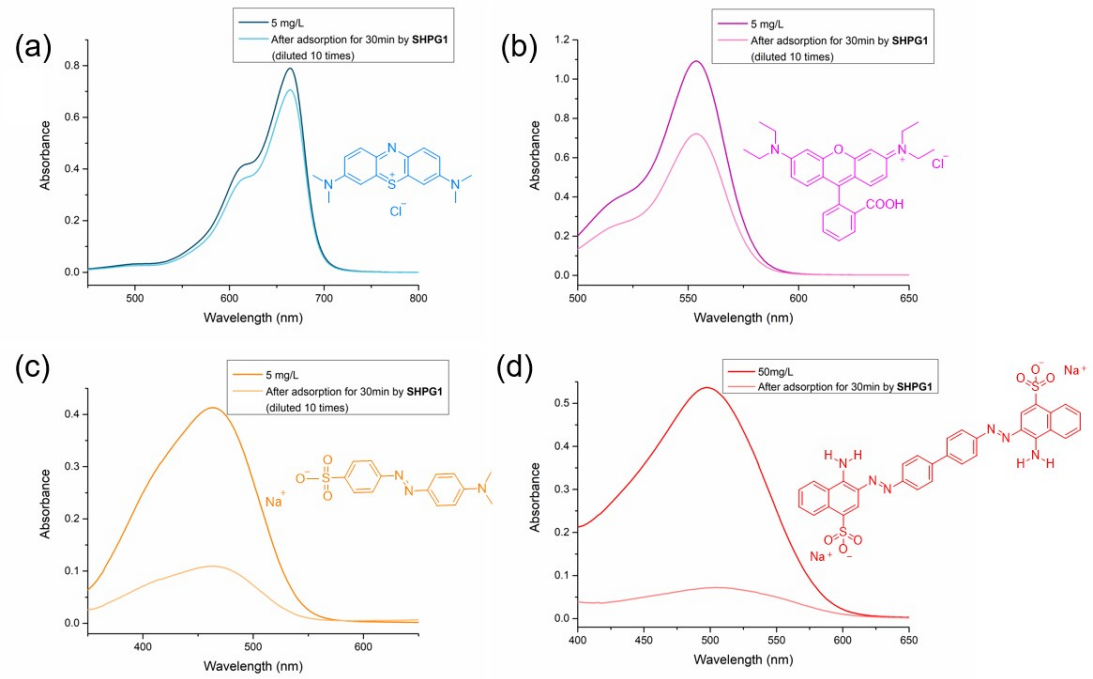

Figure S15. UV−vis spectra of (a) MB, (b) RhB, (c) MO before and after adsorption for 30 min by **SHPG** at 10-fold dilution. UV−vis spectra of (d) CR before and after adsorption for 30 min by **SHPG.**

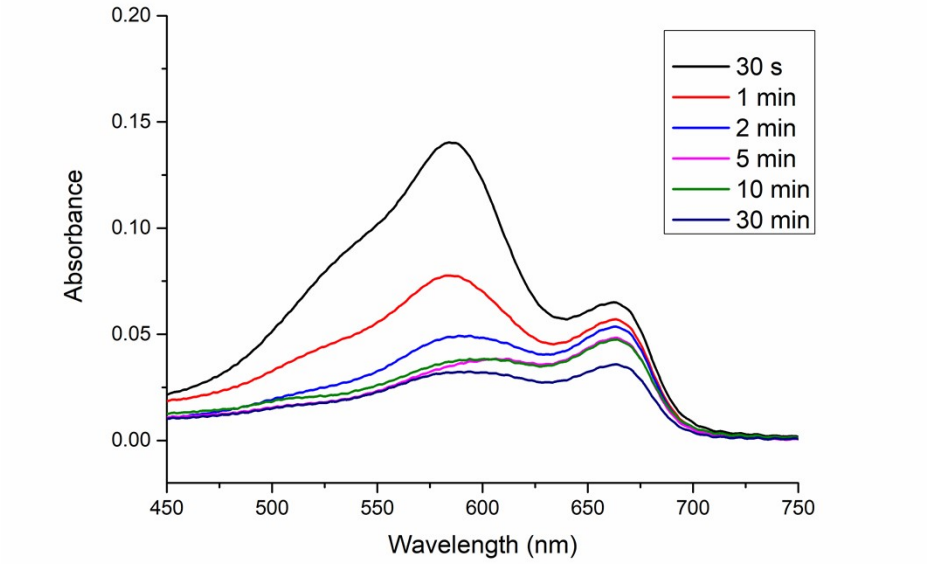

Figure S16. Time-dependent changes in UV−vis spectra of MV by **SHPG**.

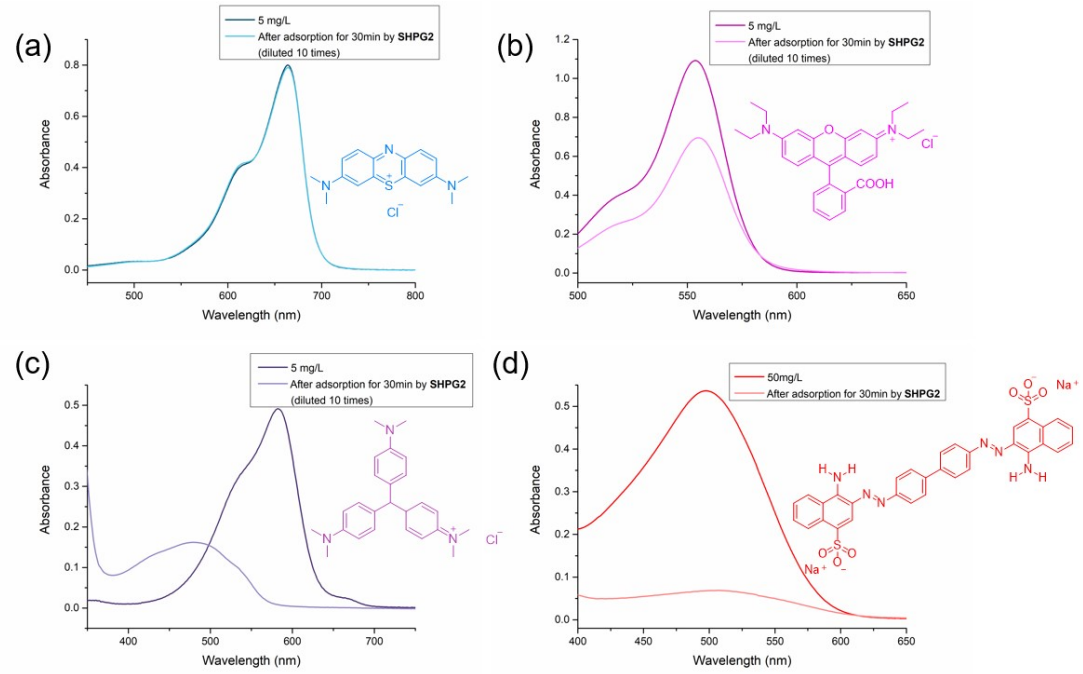

Figure S17. UV−vis spectra of (a) MB, (b) RhB, (c) MV before and after adsorption for 30 min by **SHPG•H**$^+$ at 10-fold dilution. UV−vis spectra of (d) CR before and after adsorption for 30 min by **SHPG•H**$^+$**.**

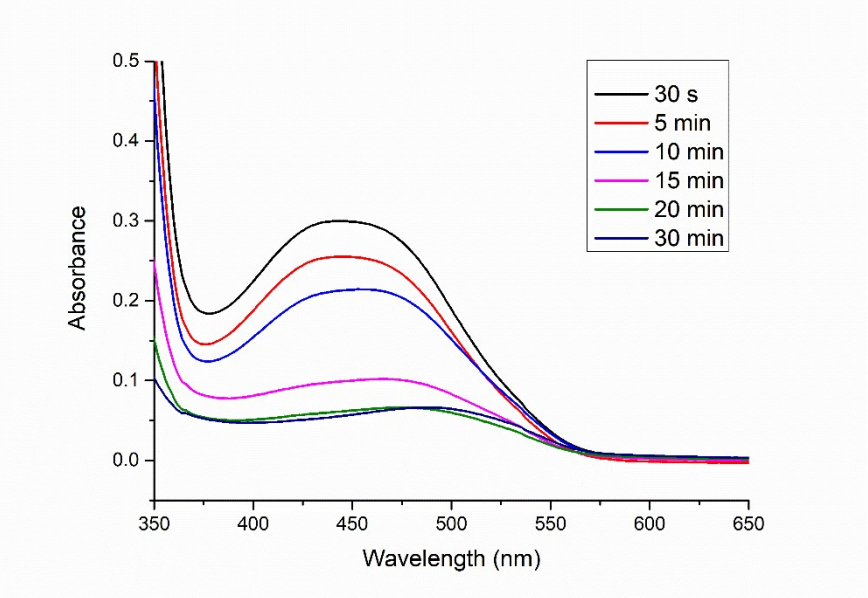

Figure S18. Time-dependent changes in UV−vis spectra of MO by **SHPG•H**$^+$.

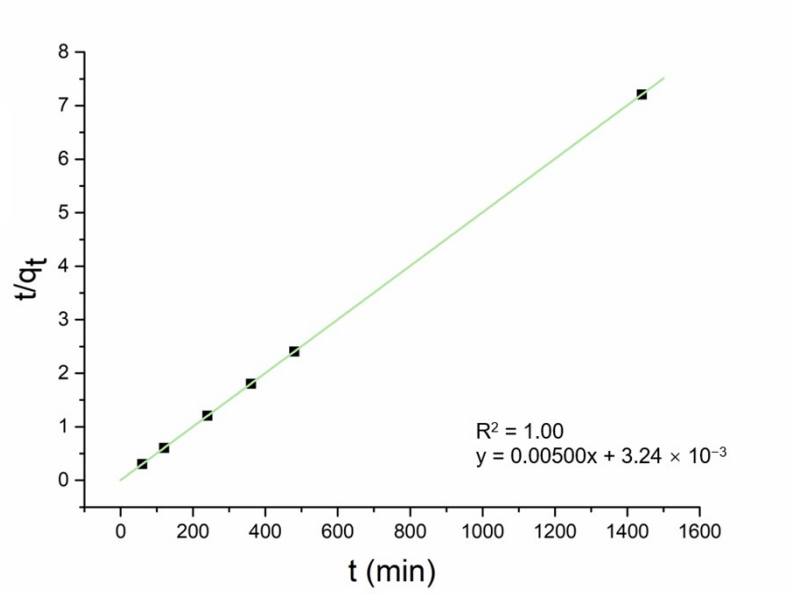

Figure S19. Pseudo-second-order plots for **SHPG** towards Pd^{2+}. Here *t* (min) is the contact time of Pd^{2+} solution with **SHPG** and q_t (mg g^{-1}) is the amount of Pd^{2+} adsorbed per gram of **SHPG**.

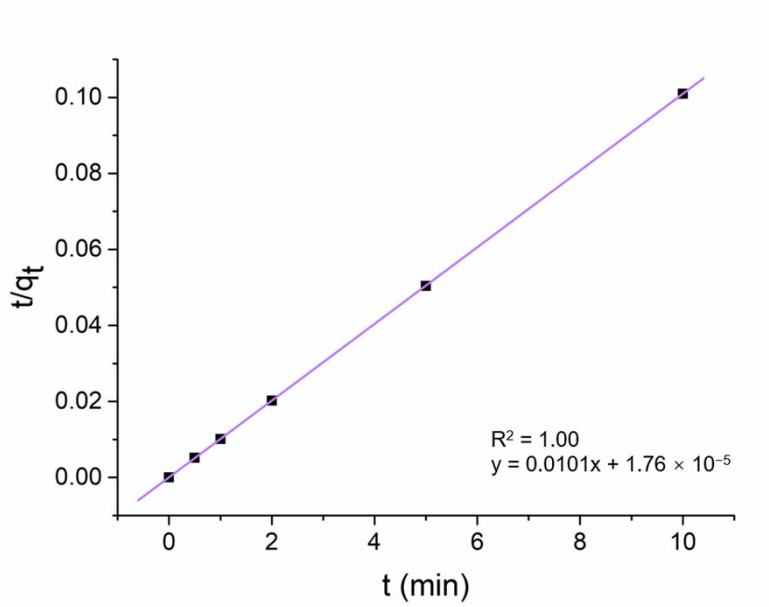

Figure S20. Pseudo-second-order plots for **SHPG** towards MV. Here *t* (min) is the contact time of MV solution with **SHPG** and q_t (mg g^{-1}) is the amount of MV adsorbed per gram of **SHPG**.

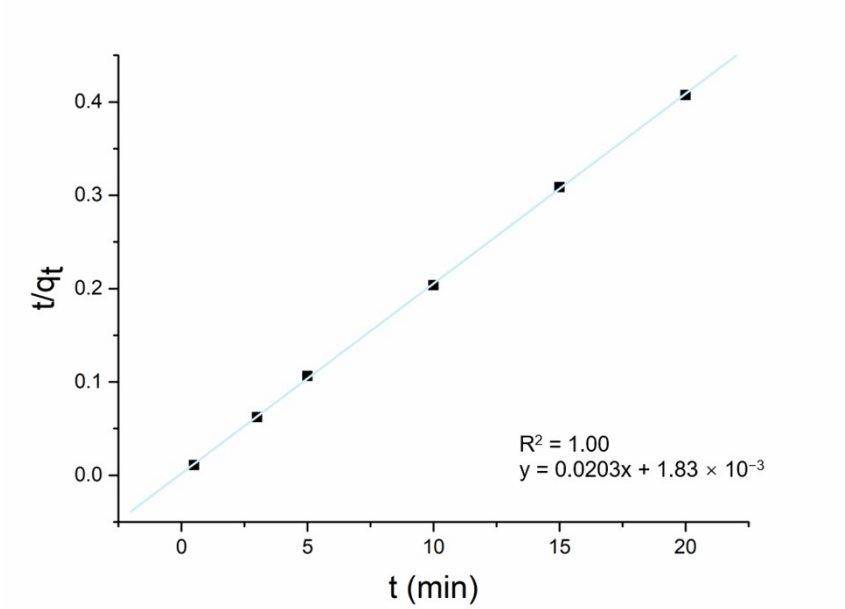

Figure S21. Pseudo-second-order plots for **SHPG•H**$^+$ towards MO. Here t (min) is the contact time of MO solution with **SHPG•H**$^+$ and q_t (mg g^{-1}) is the amount of MO adsorbed per gram of **SHPG•**H$^+$.

7. TG Analysis

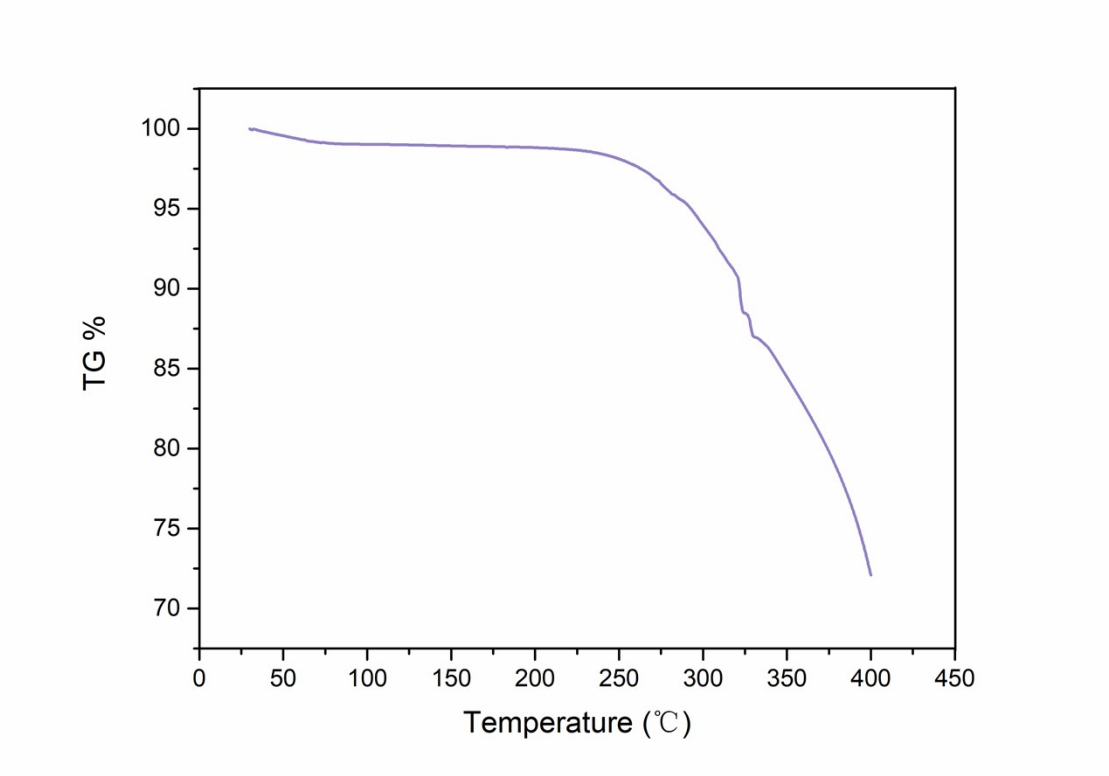

Fig. S22 Thermogravimetric analysis results of **1**.

References

S1. Q. Lin, X. Guan, Y. Zhang, J. Wang, Y. Fan, H. Yao and T. Wei. *ACS Sustainable Chem. Eng.*, 2019, **7**, 14775−14784.

S2. T. Ogoshi, S. Kanai, S. Fujinami, T. Yamagishi and Y. Nakamoto, *J. Am. Chem. Soc.*, 2008, **130**, 5022−5023.

S3. Chekryshkin, Y. S., El'chisheva, N. V., Vnutskikh, Z. A., Shklyaev, Y. V., *Russ. J. Appl. Chem*. 2010, **83**, 1454−1460.