

Electronic Supplementary Information

Acid/base- and base/acid-switchable complexation between anionic-/cationic-pillar[6]arenes and a viologen dication salt

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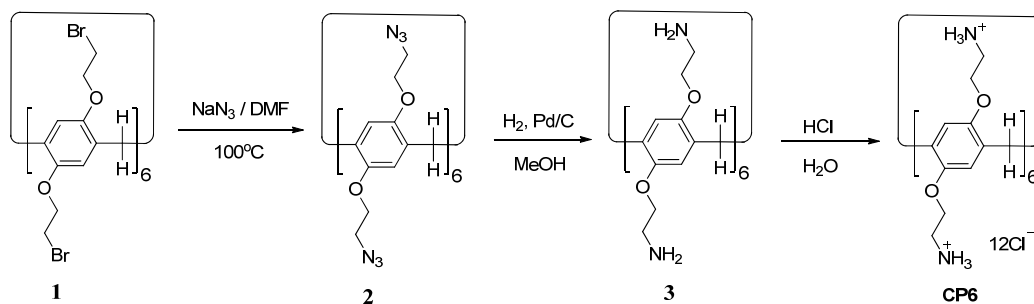
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1. Materials and methods

All reagents were commercially available and used as supplied without further purification. **WP6**^{S1}, **CP6**^{S2} and **G-2TsO**^{S3} were prepared according to the published procedures. NMR spectra were recorded on Bruker Avance III HD 400 spectrometer with use of the deuterated solvent as the lock and the residual solvent as the internal reference. UV-Vis absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Fluorescence spectra were recorded on an Agilent Cary Eclipse fluorescence spectrophotometer.

2. Synthesis of cationic pillar[6]arene (**CP6**)



Scheme S1. Synthetic route of **CP6**.

Synthesis of **CP6**

To the suspension of compound **3** (500 mg, 0.40 mmol) in aqueous solution (20 mL), 12 M aqueous HCl solution was added and stirred 2 h at RT. The resulting solution was evaporated under reduced pressure to give the salt **CP6** as pale-brown solid (675 mg, 100%).

The ^1H NMR spectrum of **CP6** is shown in Figure S1. ^1H NMR (400 MHz, D_2O , 298K) δ (ppm): 6.86 (s, 10H), 4.09 (t, $J = 5.5$ Hz, 20H), 3.96 (s, 10H), 3.25 (t, $J = 5.0$ Hz, 20H). The ^{13}C NMR spectrum of **CP6** is shown in Figure S2. ^{13}C NMR (100 MHz, D_2O , 298K) δ (ppm): 150.02, 129.01, 115.92, 65.38, 38.93, 29.65. LRESIMS is shown in Figure S3: m/z 518.75 [$\text{M} - 5\text{Cl} + 2\text{Na}]^{3+}$ (100%).

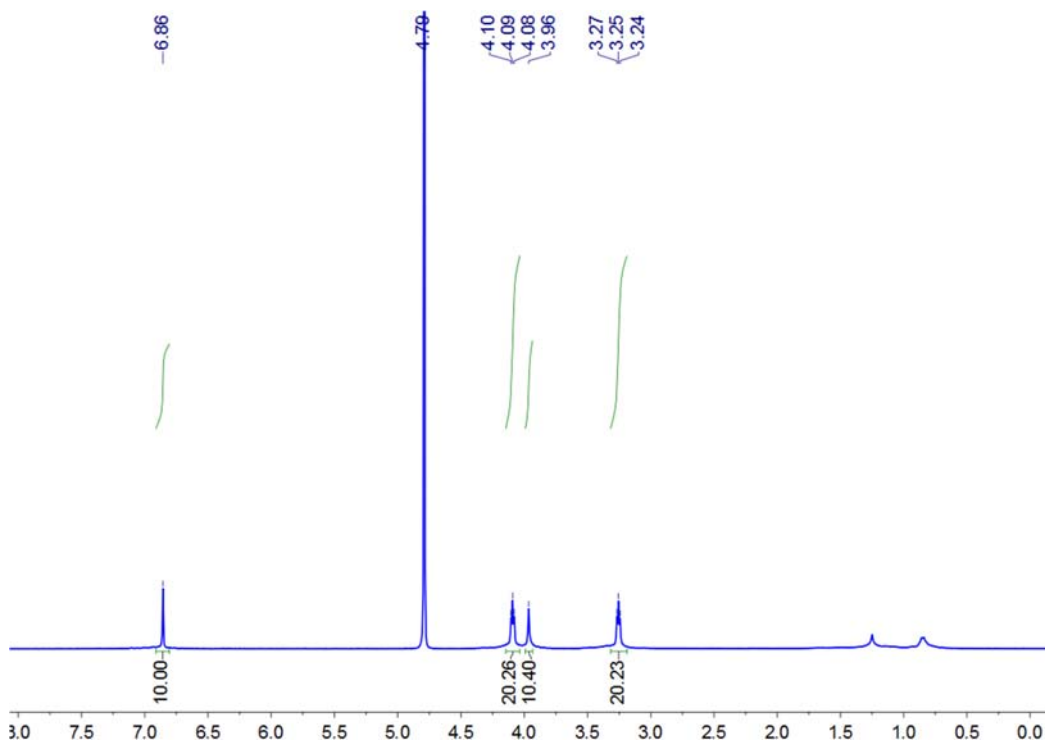


Figure S1. ^1H NMR spectrum (400 MHz, D_2O , 298 K) of CP6.

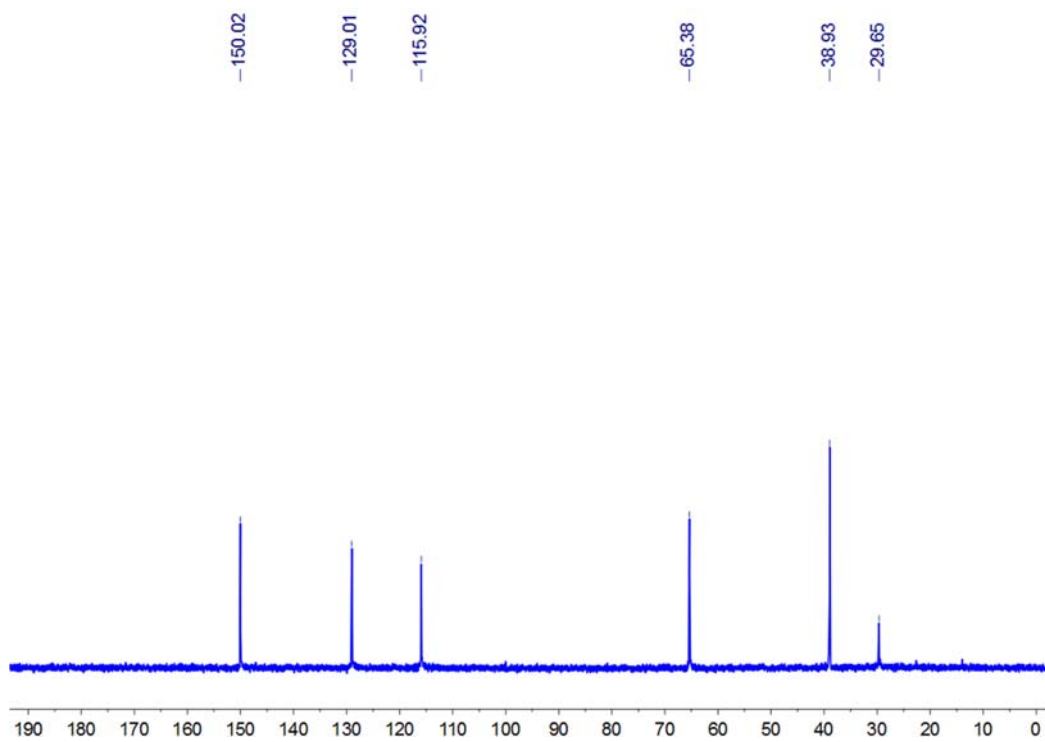


Figure S2. ^{13}C NMR spectrum (100 MHz, D_2O , 298 K) of CP6.

CP6_190306154044 #3-374 RT: 0.01-1.66 AV: 372 NL: 3.18E2
T: ITMS + p ESI Full ms [250.00-2000.00]

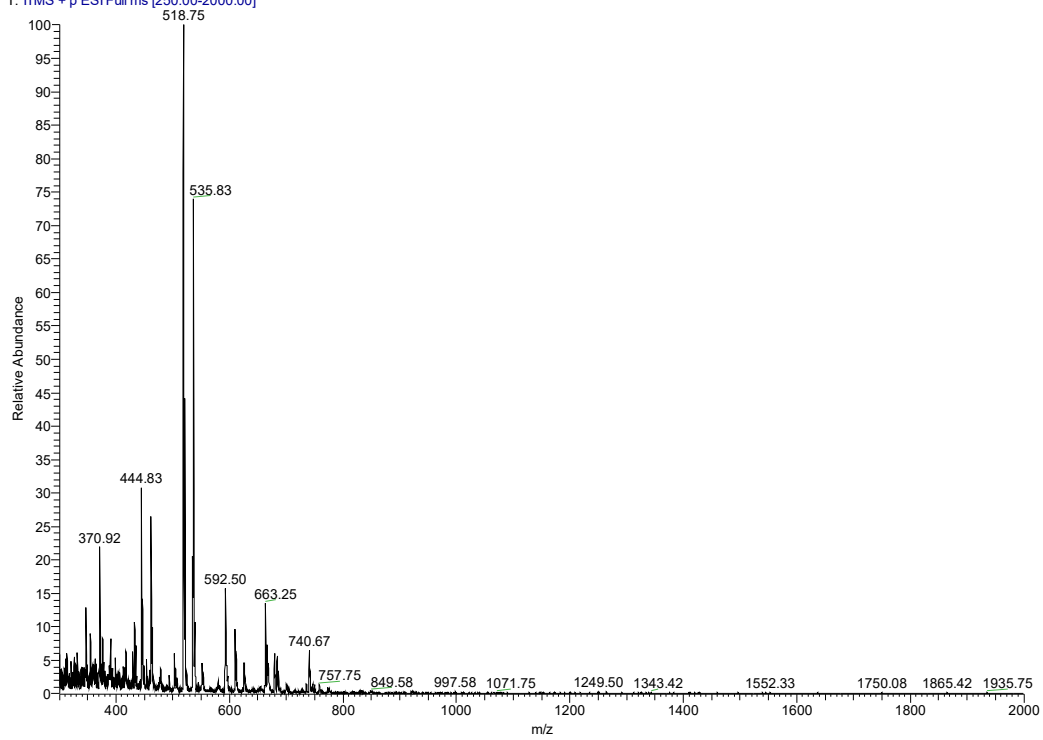


Figure S3. Electrospray ionization mass spectrum of CP6. Assignment of main peaks: m/z 518.75

$[M - 5Cl + 2Na]^{3+}$ (100%).

3. UV-vis spectroscopy investigations of the complexation between **WP6** and **G-2TsO** in H_2O

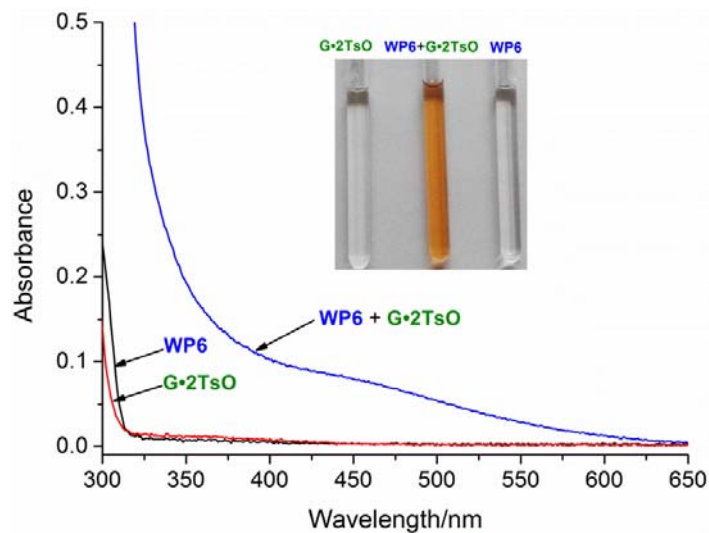


Figure S4. UV-vis spectra of **G-2TsO**, **WP6**, and **G-2TsO** in the presence of 1 equiv of **WP6** (2.50×10^{-4} M) in aqueous solution. The inserted photograph exhibits the color changes of aqueous solutions upon complexation between **WP6** and **G-2TsO**.

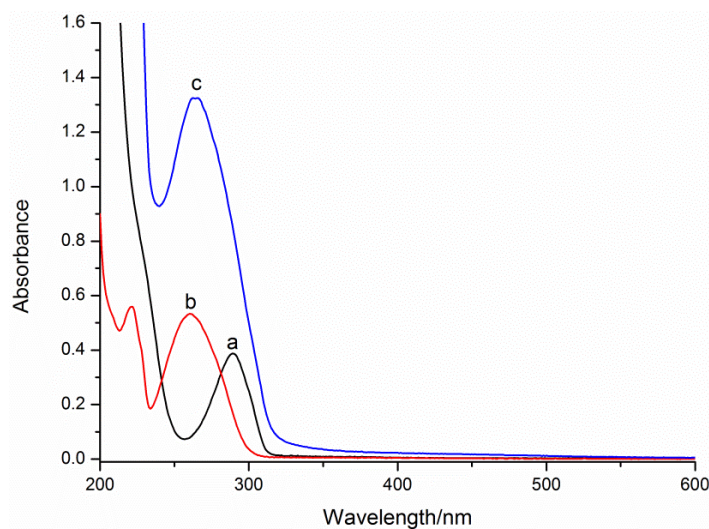


Figure S5. UV-vis spectra of (a) **WP6**, (b) **G-2TsO**, and (c) **G-2TsO** in the presence of 1 equiv of **WP6** (2.50×10^{-5} M) in aqueous solution.

4. 2D NOESY spectra of G^{2+} -WP6 and TsO^- -CP6 complexes

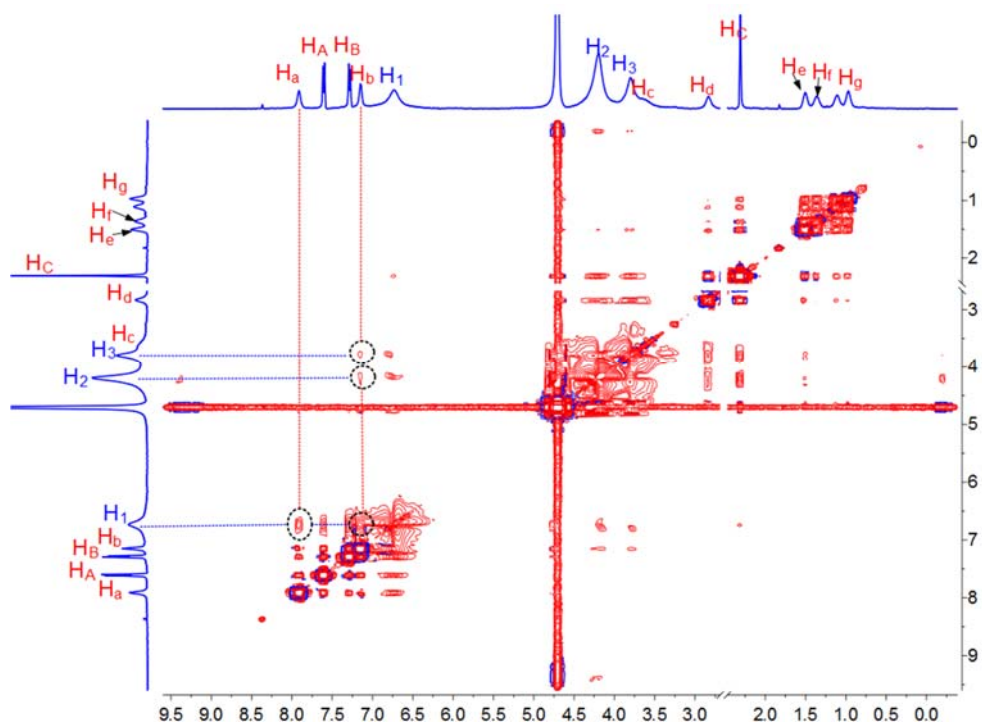


Figure S6. 2D NOESY NMR spectrum of G^{2+} -WP6 (400 MHz, D_2O , 298 K, mixing time = 300 ms), [WP6] = 6.00 mM, [$G \cdot 2TsO$] = 3.00 mM.

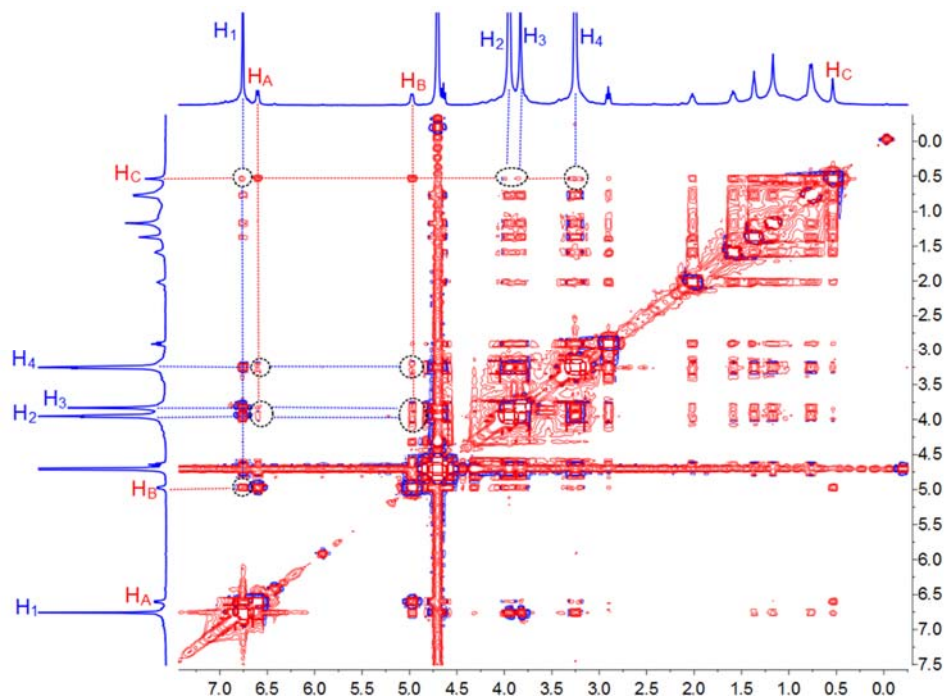


Figure S7. 2D NOESY NMR spectrum of TsO^- -CP6 (400 MHz, D_2O , 298 K, mixing time = 300 ms), [CP6] = 10.67 Mm, [$G \cdot 2TsO$] = 3.00 mM.

5. ^1H NMR spectra of **G-2TsO** upon titration with **CP6**

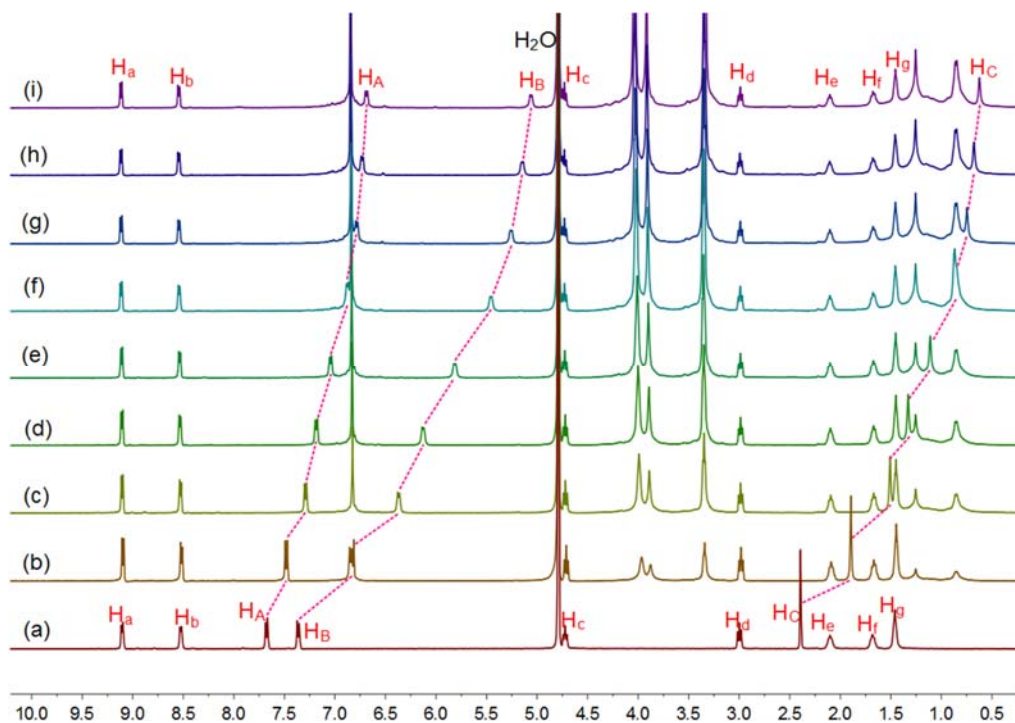


Figure S8. ^1H NMR spectra (D_2O , 293 K, 400 MHz) of **G-2TsO** at a concentration of 3.00 mM with different concentrations (mM) of **CP6**: (a) 0.00, (b) 1.07, (c) 2.73, (d) 3.44, (e) 4.62, (f) 6.28, (g) 8.06, (h) 9.48, (i) 10.67.

6. Determination of the association constants of G^{2+} -WP6 and TsO⁻-CP6 complexes

6.1 Job plot for G^{2+} -WP6 and TsO⁻-CP6 complexes

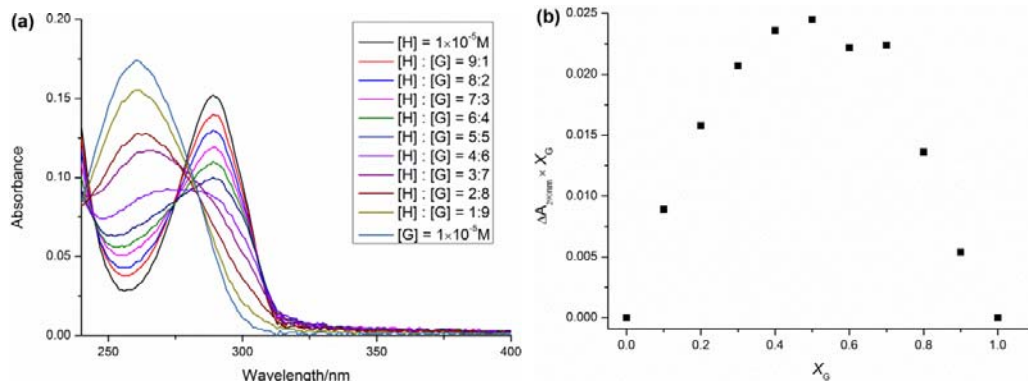


Figure S9. (a) UV-vis absorption of the mixture of WP6 and G-2TsO in water at different molar ratios while $[WP6] + [G-2TsO] = 1.0 \times 10^{-5}$ M. (b) Job plot showing the 1:1 stoichiometry of the complex between WP6 and G-2TsO by plotting the difference in absorption at 290 nm (a characteristic absorption peak of WP6) against the mole fraction of G-2TsO at an invariant total concentration of 0.01 mM in aqueous solution.

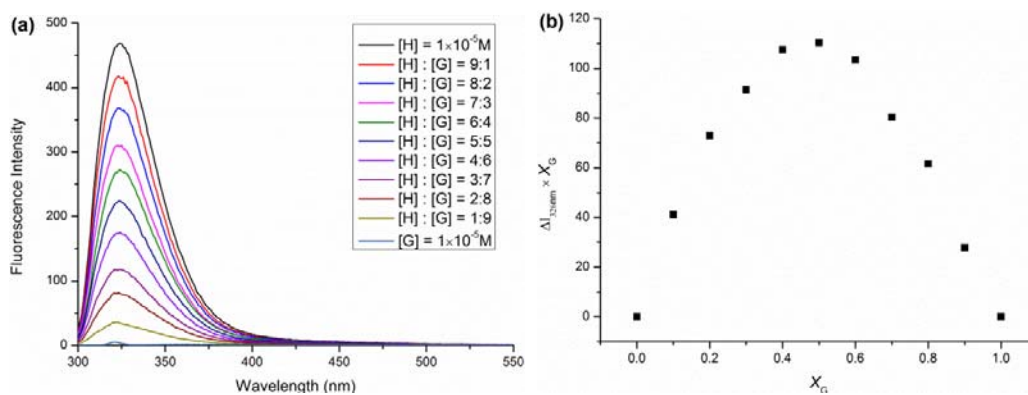


Figure S10. (a) Fluorescence spectra of the mixture of CP6 and G-2TsO in water at different molar ratios while $[CP6] + [G-2TsO] = 1.0 \times 10^{-5}$ M. (b) Job plot showing the 1:1 stoichiometry of the complex between CP6 and G-2TsO by plotting the difference in fluorescent emission intensity at $\lambda_{\text{emission}} = 326$ nm ($\lambda_{\text{excitation}} = 290$ nm) against the mole fraction of G-2TsO at an invariant total concentration of 0.01 mM in aqueous solution.

6.2 Association constants of $G^{2+} \subset WP6$ and $TsO^- \subset CP6$

To determine the association constant for the complexation between **WP6** and G^{2+} and between **CP6** and TsO^- , fluorescence titration experiments were carried out in solutions which had a constant concentration of **WP6** (2.5×10^{-5} M) and **CP6** (7.7×10^{-6} M) and varying concentrations of **G·2TsO**. By a non-linear curve-fitting method, the association constants (K_a) of $G^{2+} \subset WP6$ and $TsO^- \subset CP6$ were estimated.

The non-linear curve-fittings were based on the equation:

$$\Delta F = (\Delta F_{\infty}/[H]_0) (0.5[G]_0 + 0.5([H]_0 + 1/K_a) - (0.5([G]_0^2 + 2[G]_0(1/K_a - [H]_0) + (1/K_a + [H]_0)^2)^{0.5}))$$

(eq. 1)

Where ΔF is the fluorescence intensity changes at 330 nm at $[H]_0$, ΔF_{∞} is the fluorescence intensity changes at 330 nm when **WP6** or **CP6** is completely complexed, $[G]_0$ is the initial concentration of **G·2TsO**, and $[H]_0$ is the fixed initial concentration of **WP6** or **CP6**.^{S4}

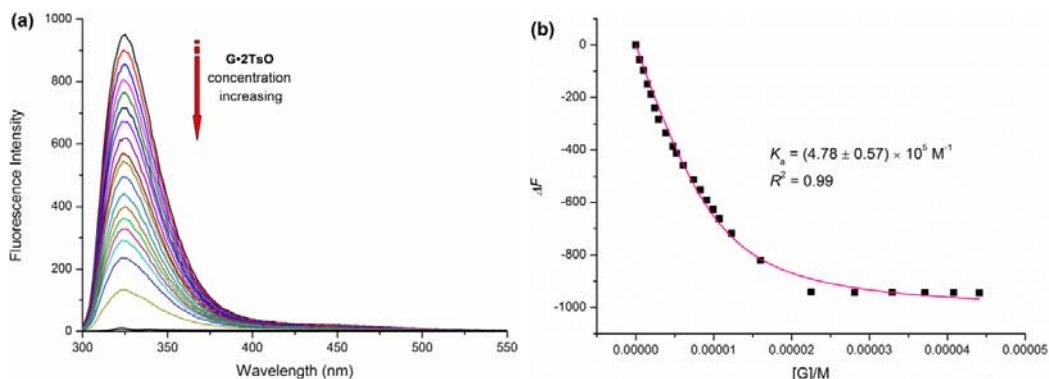


Figure S11. (a) Fluorescence spectra of **WP6** (2.5×10^{-5} M) upon addition of **G·2TsO** ($0-4.41 \times 10^{-5}$ M) in aqueous solution (excited at 290 nm) at room temperature. Upon addition of **G·2TsO**, emission from **WP6** was quenched, indicating the formation of the $G^{2+} \subset WP6$ complex. (b) The fluorescence intensity changes of **WP6** upon addition of **G·2TsO**. The red solid line was obtained from the non-linear curve-fitting using eq. 1.

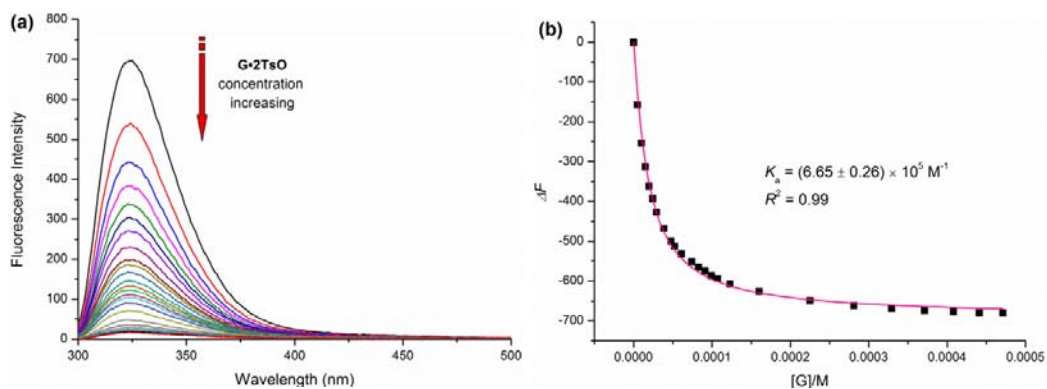


Figure S12. (a) Fluorescence spectra of **CP6** (7.7×10^{-6} M) upon addition of **G·2TsO** (0 – 4.71×10^{-5} M) in aqueous solution (excited at 290 nm) at room temperature. Upon addition of **G·2TsO**, emission from **CP6** was quenched, indicating the formation of the **TsO⁻CP6** complex. (b) The fluorescence intensity changes of **CP6** upon addition of **G·2TsO**. The red solid line was obtained from the non-linear curve-fitting using eq. 1.

7. ¹H NMR spectra of **WP6** and **CP6** mixture

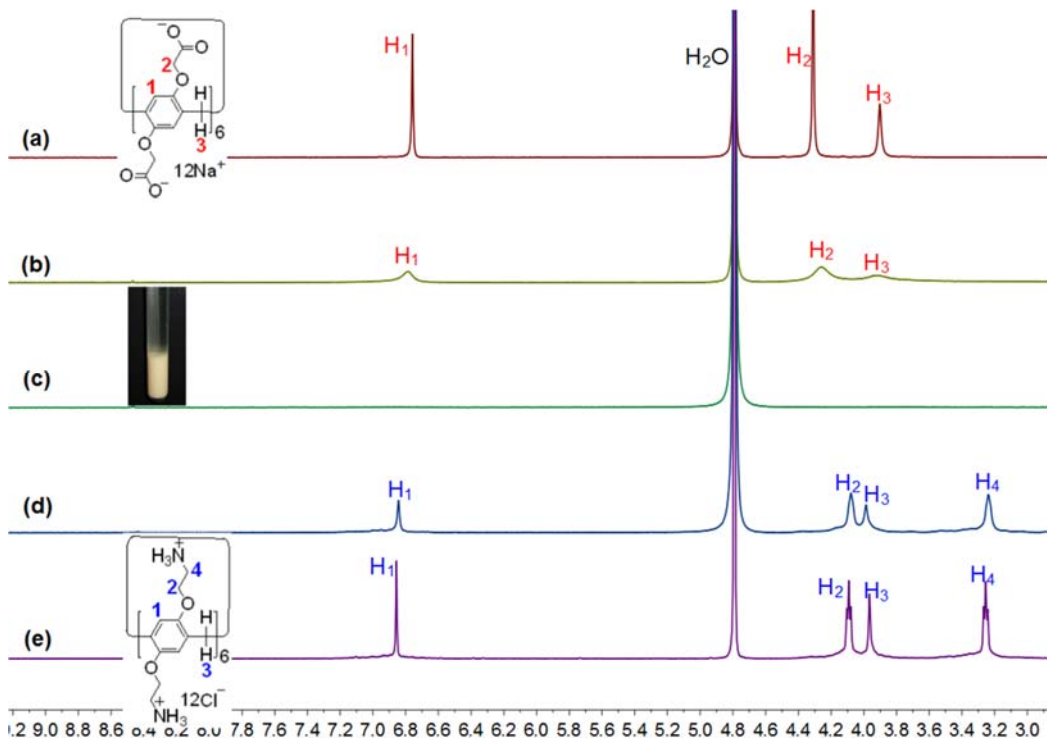


Figure S13. Partial ¹H NMR spectra (400 MHz, D₂O, 298 K): (a) **WP6** (3.00 mM); (b) **WP6** (3.00 mM) + **CP6** (2.00 mM); (c) **WP6** (3.00 mM) + **CP6** (3.00 mM); (d) **WP6** (3.00 mM) + **CP6** (6.00 mM); (e) **CP6** (3.00 mM).

References:

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