

Dual-pH responsive host–guest complexation between a water-soluble pillar[9]arene and a 2,7-diazapyrenium salt

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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 **WP9**^{S1} and **G1**^{S2} were synthesized according to published literature procedures. NMR spectra were recorded with a Bruker Avance DMX 500 spectrophotometer with the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Low-resolution electrospray ionization mass spectra (LRESI-MS) were obtained on a Bruker Esquire 3000 Plus spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. UV-vis spectroscopy was performed on a Shimadzu UV-2550 instrument at room temperature. The fluorescence experiments were conducted on a RF-5301 spectrofluorophotometer (Shimadzu Corporation, Japan).

2. Partial ^1H NMR spectra of $\text{WP9} \rightleftharpoons \text{G1}$

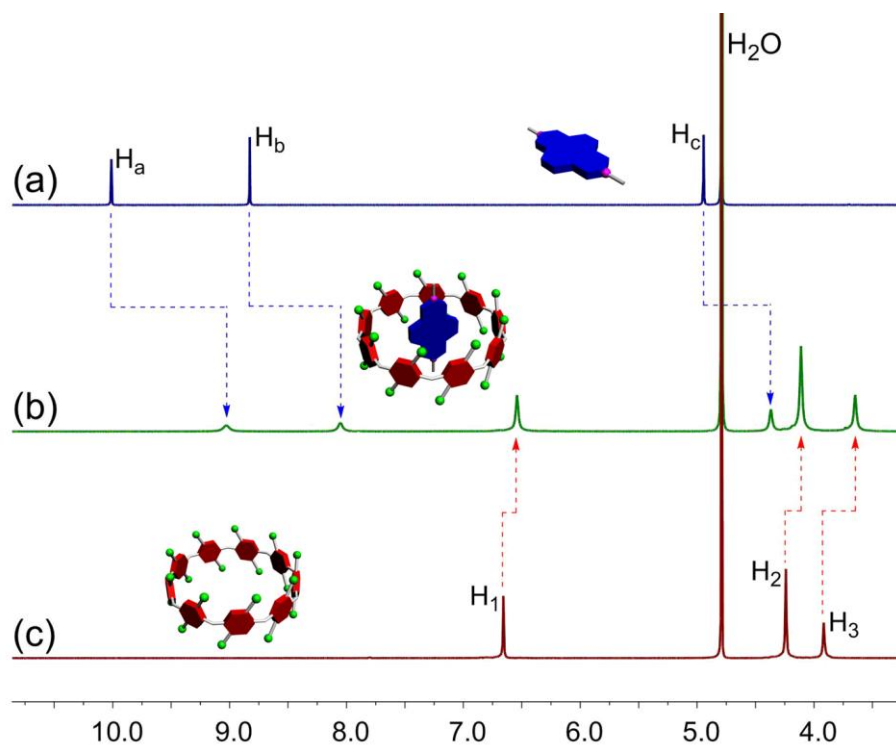


Figure S1. Partial ^1H NMR spectra (500 MHz, D_2O , 293 K): (a) **G1** (2.00 mM); (b) **WP9** (2.00 mM) and **G1** (2.00 mM); (c) **WP9** (2.00 mM).

3. Fluorescence titration experiments of **WP9** and **G1** in H_2O

To determine the stoichiometry and association constant for the complexation between **WP9** and **G1**, fluorescence titration experiments were done with solutions which had a constant concentration of **G1** (1.00×10^{-6} M) and varying concentrations of **WP9**. By a non-linear curve-fitting method, the association constant (K_a) of **WP9** \rightarrow **G1** was determined. By a mole ratio plot, 1:1 stoichiometry was obtained for the complexation between **WP9** and **G1**.

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

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

Where ΔF is the fluorescence intensity changes at 426 nm at $[H]_0$, ΔF_∞ is the fluorescence intensity changes at 426 nm when **WP9** is completely complexed, $[H]_0$ is the initial concentration of **WP9**, and $[G]_0$ is the fixed initial concentration of **G1**.

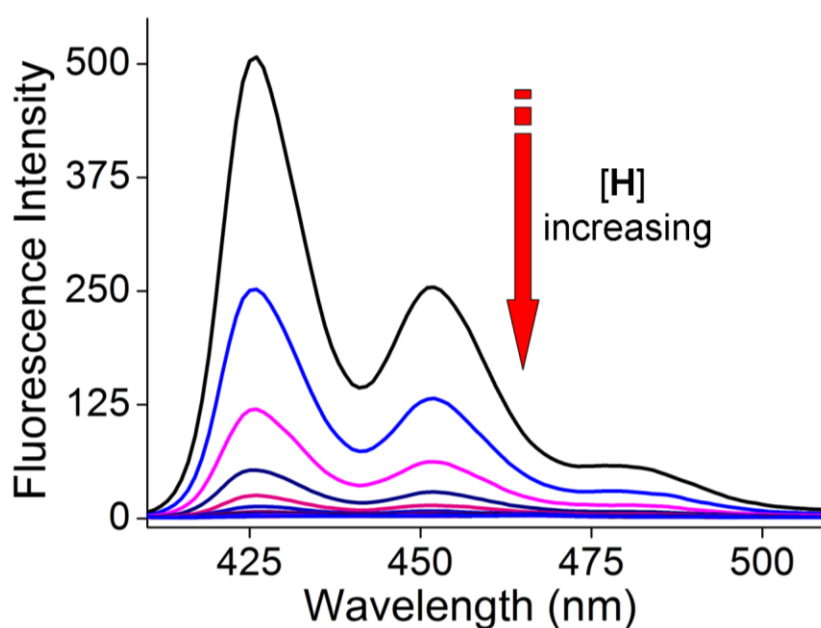


Figure S2. Fluorescence spectra of **G1** at a concentration of 1.00×10^{-6} M in water at room temperature upon addition of **WP9** (from 0 to 2.67×10^{-5} M).

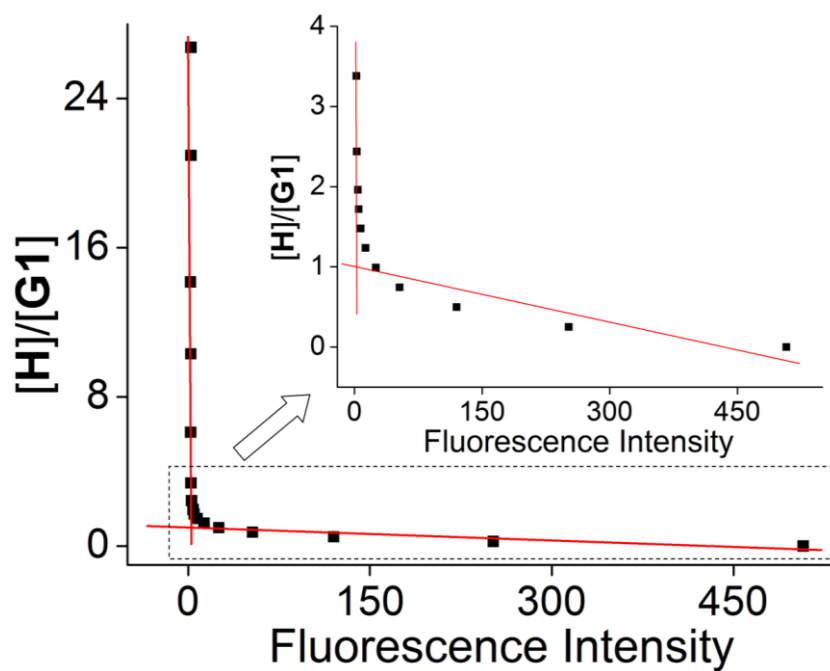


Figure S3. Mole ratio plot for **WP9** and **G1**, showing a 1:1 complexation stoichiometry.

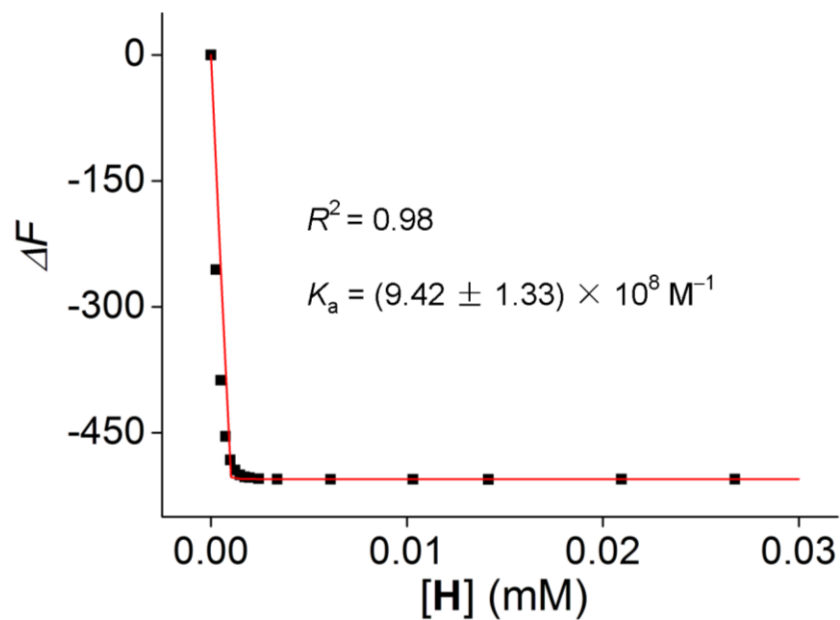


Figure S4. The fluorescence intensity changes of **G1** upon addition of **WP9**. The red solid line was obtained from the non-linear curve-fitting method based on the above equation.

4. UV-vis spectroscopy investigations of the complexation between **WP9** and **G1** in H_2O

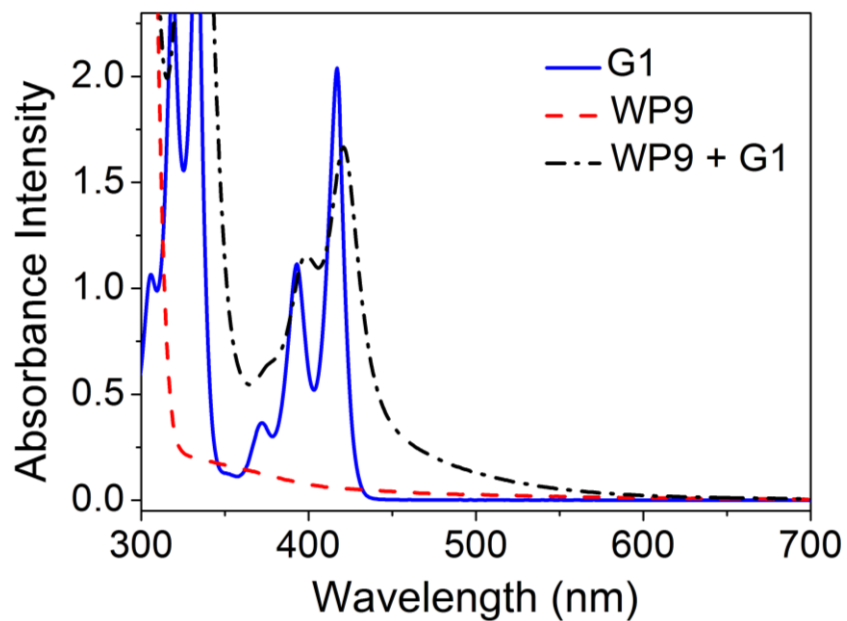


Figure S5. UV-vis spectra of **G1** (1.00×10^{-4} M), **WP9** (1.00×10^{-4} M) and **WP9** (1.00×10^{-4} M) with equimolar **G1** in water at room temperature.

5. Photographs of dual-pH controlled experiments

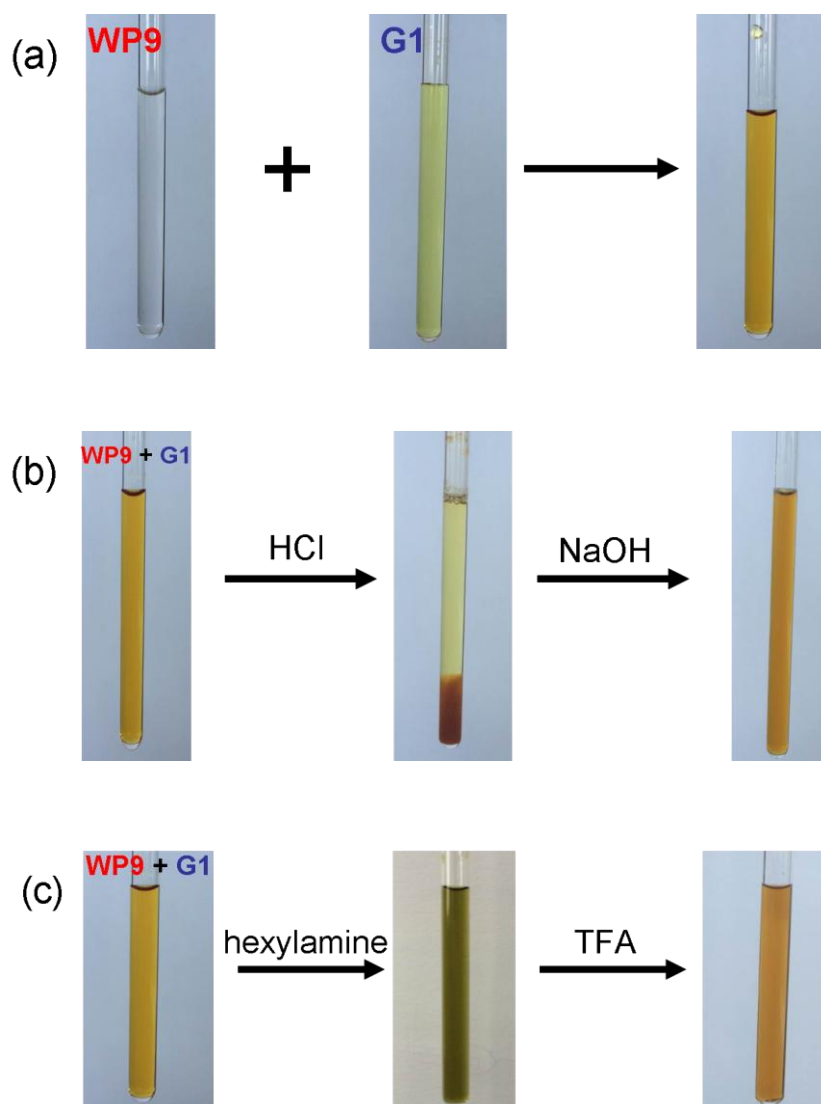


Figure S6. Photographs of aqueous solutions: (a) 2.00 mM **G1**, 2.00 mM **WP9** and their mixture; (b) 2.00 mM solution of **G1** and **WP9** upon sequential addition of HCl (20.0 equiv.) and NaOH (20.0 equiv.); (c) 2.00 mM solution of **G1** and **WP9** upon sequential addition of hexylamine (40.0 equiv.) and TFA (40.0 equiv.).

6. Electrospray ionization mass spectra of **WP9** and **G1** in H_2O

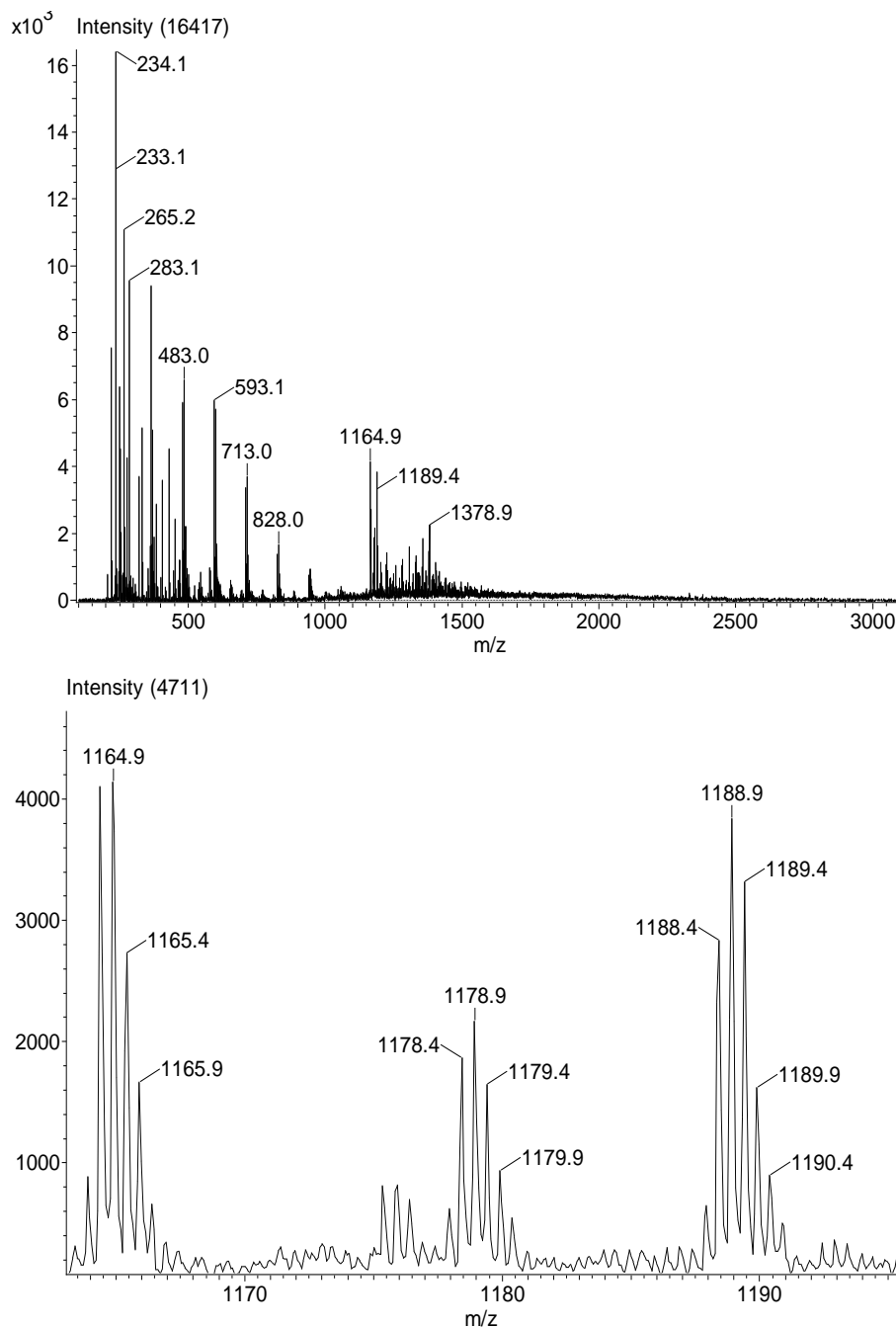


Figure S7. Positive electrospray ionization mass spectrum of **WP9** and **G** in H_2O (upper: full range; bottom: partial range). Mass fragment at m/z 1188.9, corresponding to $[\mathbf{WP9}\supset\mathbf{G1} - 2I - 18NH_3]^{2+}$, indicating the 1:1 complexation stoichiometry between **WP9** and **G1**.

References:

- S1. Z. Li, J. Yang, G. Yu, J. He, Z. Abliz and F. Huang, *Chem. Commun.*, 2014, **50**, 2841–2843.
- S2. M. A. Cejas and F. M. Raymo, *Langmuir*, 2005, **21**, 5795–5802.