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1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Compounds WP5\textsuperscript{S1} and G\textsuperscript{S2} were prepared according to the published procedures. NMR spectra were recorded with a Bruker Avance DMX 500 spectrophotometer or a Bruker Avance DMX 400 spectrophotometer using the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Low-resolution electrospray ionization mass spectra were recorded with a Bruker Esquire 3000 Plus spectrometer. High-resolution mass spectrometry experiments were performed with a Bruker Daltonics Apex III spectrometer. 2D \textsuperscript{1}H-\textsuperscript{1}H NOESY spectrum was collected on a Bruker Advance DMX-500 spectrometer. Mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. UV-vis spectra were taken on a Shimadzu UV-2550 UV-vis spectrophotometer. The fluorescence experiments were conducted on a RF-5301 spectrofluorophotometer (Shimadzu Corporation, Japan). Isothermal titration calorimetric (ITC) measurements were performed on a VP-ITC micro-calorimeter (Microcal, USA). HRMS were obtained on a Bruker 7-Tesla FT-ICRMS equipped with an electrospray source (Billerica, MA, USA). The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus.
2. Proton NMR spectra of G and WP5

Figure S1. $^1$H NMR spectrum (400 Hz, DMSO- $d_6$, 298 K) of G.

Figure S2. $^1$H NMR spectrum (400 Hz, D$_2$O, 298 K) of WP5.
3. NOESY NMR spectrum of WP5 $\rightarrow$ G in D$_2$O

![Partial NOESY NMR spectrum](image)

**Figure S3.** Partial NOESY NMR spectrum (500 MHz, D$_2$O, 298 K) of 10.0 mM WP5 and G.

4. Stoichiometry and association constant determination for WP5 $\rightarrow$ G and WP5 $\rightarrow$ paraquat in H$_2$O

To determine the stoichiometries and association constants of WP5 $\rightarrow$ G and WP5 $\rightarrow$ paraquat, $^1$H NMR titrations were done. By a non-linear curve-fitting method, the association constants between the guests and hosts were calculated. By a mole ratio plot, the stoichiometries were determined.

(a) Stoichiometry and association constant determination for WP5 $\rightarrow$ G in H$_2$O

The non-linear curve-fitting was based on the equation$^{53}$

$$\Delta\delta = (\Delta_c/[[WP5]_0]) (0.5[G]_0 + 0.5([[WP5]_0 + 1/K_a) - (0.5 ([G]_0^2 + (2[G]_0(1/K_a - [WP5]_0)) + (1/K_a + [WP5]_0)^2)^0.5))$$

(Eq. S1)

Where $\Delta\delta$ is the chemical shift change of H$_3$ on WP5 at [G]$_0$, $\Delta_c$ is the chemical shift change of H$_3$ when the host is completely complexed, [WP5]$_0$ is the fixed initial concentration of the host, and [G]$_0$ is the varying concentration of guest G.
Figure S4. $^1$H NMR spectra (400 MHz, D$_2$O, 293 K) of WP5 at a concentration of 1.00 mM with different concentrations of G: (a) 0.00 mM; (b) 0.196 mM; (c) 0.385 mM; (d) 0.566 mM; (e) 0.741 mM; (f) 0.909 mM; (g) 1.07 mM; (h) 1.23 mM; (i) 1.53 mM; (j) 1.94 mM; (k) 2.48 mM; (l) 3.10 mM; (m) 3.94 mM.

Figure S5. The chemical shift changes of H$_3$ on WP5 upon addition of G. The red solid line was obtained from the non-linear curve-fitting using Eq. S1.
Figure S6. Mole ratio plot for the complexation between WP5 and G, indicating a 1 : 1 stoichiometry.

(b) Stoichiometry and association constant determination for WP5 $\rightleftarrows$ paraquat in H$_2$O

$$\Delta \delta = (\Delta_{\infty}/[\text{paraquat}]_0) (0.5[\text{WP5}]_0 + 0.5([\text{paraquat}]_0 + 1/K_a) - (0.5 ([\text{WP5}]_0^2 + (2[\text{WP5}]_0(1/K_a - [\text{paraquat}]_0)) + (1/K_a + [\text{paraquat}]_0)^2)^{0.5})) \quad \text{(Eq. S2)}$$

Where $\Delta \delta$ is the chemical shift change of H$_k$ on paraquat at [WP5]$_0$, $\Delta_{\infty}$ is the chemical shift change of H$_k$ when the guest is completely complexed, [paraquat]$_0$ is the fixed initial concentration of the guest, and [WP5]$_0$ is the varying concentration of host WP5.

Figure S7. $^1$H NMR spectra (400 MHz, D$_2$O, 293 K) of paraquat at a concentration of 1.00 mM with different concentrations of WP5: (a) 0.00 mM; (b) 0.196 mM; (c) 0.385 mM; (d) 0.566 mM; (e) 0.741 mM; (f) 0.909 mM; (g) 1.07 mM; (h) 1.23 mM; (i) 1.53 mM; (j) 1.94 mM; (k) 2.48 mM; (l) 3.10 mM; (m) 3.94 mM.
Figure S8. The chemical shift changes of $H_K$ on paraquat upon addition of WP5. The red solid line was obtained from the non-linear curve-fitting using Eq. S2.

$R^2 = 0.989$

$K_s = (1.32 \pm 0.25) \times 10^5 \text{ M}^{-1}$

Figure S9. Mole ratio plot for the complexation between WP5 and paraquat, indicating a 1 : 1 stoichiometry.
5. UV−vis investigation of WP5→G

**Figure S10.** UV−vis spectra of 10.0 μM G in the presence of 0.200, 0.400, 0.600, 0.800, 1.00, and 1.20 equiv of WP5 in water.

6. Electrospray ionization mass spectrum of G with KCN

**Figure S11.** Electrospray ionization mass spectrum of G with KCN. The peak at m/z 250.1 corresponding to [G + K]^+ was clearly observed.
Figure S12. (Top): The fluorescence intensities at 490 nm and 430 nm for G (3.00 µM) at varied pH values. (Bottom): The fluorescence intensities at 490 nm and 430 nm for G (3.00 µM) in the presence of CN⁻ (20.0 equiv) at varied pH values.
Figure 13. $^1$H NMR spectra (400 MHz, D$_2$O, 298 K): (a) 10.0 mM G; (b) 10.0 mM G and WP5; (c) 10.0 mM WP5.

Figure S14. Partial $^1$H NMR spectra (400 MHz, D$_2$O, 298 K): (a) WP5 (10.0 mM); (b) a solution of G (10.0 mM) and WP5 (10.0 mM), pH = 7.4; (c) a solution of 2.00 mL of aqueous HCl solution (37%), and 0.5 mL of G (10.0 mM) and WP5 (10.0 mM), pH = 6.0; (d) a solution of 1.5 mg of NaOH, 2.00 mL of aqueous HCl solution (37%), and 0.5 mL of G (10.0 mM) and WP5 (10.0 mM), pH = 7.4; (e) G (10.0 mM).
Figure S15. Partial $^1$H NMR spectra (400 MHz, DMSO-$d_6$, 298 K): (a) G (10.0 mM); (b) G (10.0 mM) upon the addition of KCN (1.00 equiv).

Figure S16. Fluorescence intensity ratio ($F_{432}/F_{490}$) of G (3.00 µM) upon addition of 20 equiv. of various anion specie in Tris-HCl buffer (10.0 mM, pH = 6.0). From left to right: (1) no anion (blank); (2) G + CN$^-$; (3) G + F$^-$; (4) G + Cl$^-$; (5) G + Br$^-$(6) G + I$^-$(7) G + NO$_3^-$; (8) G + HSO$_4^-$; (9) G + SCN$^-$; (10) G + AcO$^-$; (11) G + C$_6$H$_5$CO$_2^-$; (12) G + N$_3^-$; (13) G + CH$_3$S$^-$; (14) G + ClO$_4^-$; (15) G + H$_2$PO$_4^-$.
Figure S17. The energy-minimized structures of $\text{WP5} \rightarrow \text{G}$ obtained by PM6 semiempirical molecular orbital methods: (a) $\text{WP5} \rightarrow \text{G}$ (top view), (b) $\text{WP5} \rightarrow \text{G}$ (side view).

References:

