

Electronic supplementary information

Complex Interactions of Pillar[5]arene with Paraquats and Bis(pyridinium) Derivatives

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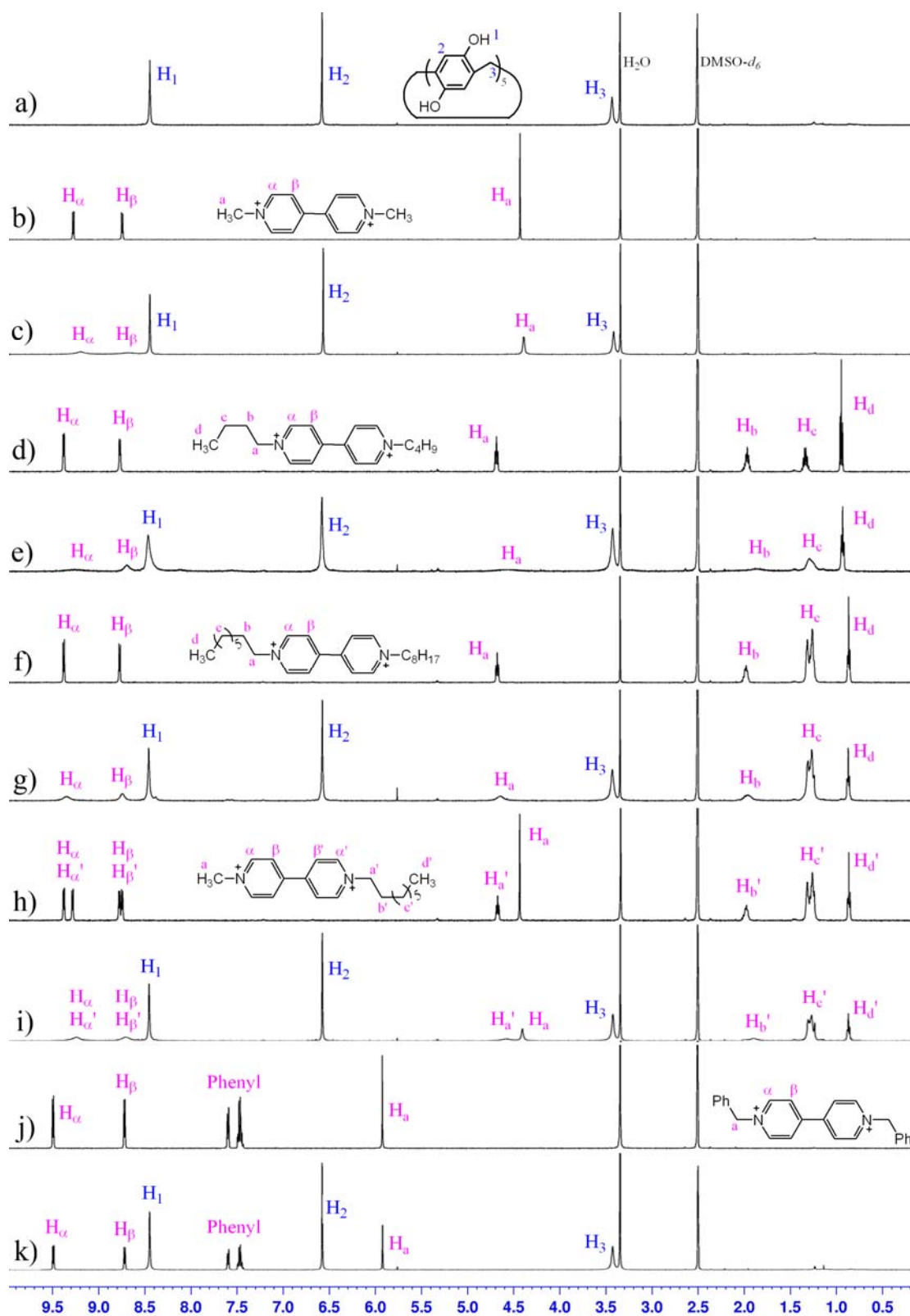


Figure S1. ^1H NMR spectra (500 MHz) of (a) **P5A**, (b) **G1·2PF₆**, (c) **P5A + G1·2PF₆**, (d) **G2·2PF₆**, (e) **P5A + G2·2PF₆**, (f) **G3·2PF₆**, (g) **P5A + G3·2PF₆**, (h) **G4·2PF₆**, (i) **P5A + G4·2PF₆**, (j) **G5·2PF₆**, (k) **P5A + G5·2PF₆** in $\text{DMSO}-d_6$ at about 5 mM.

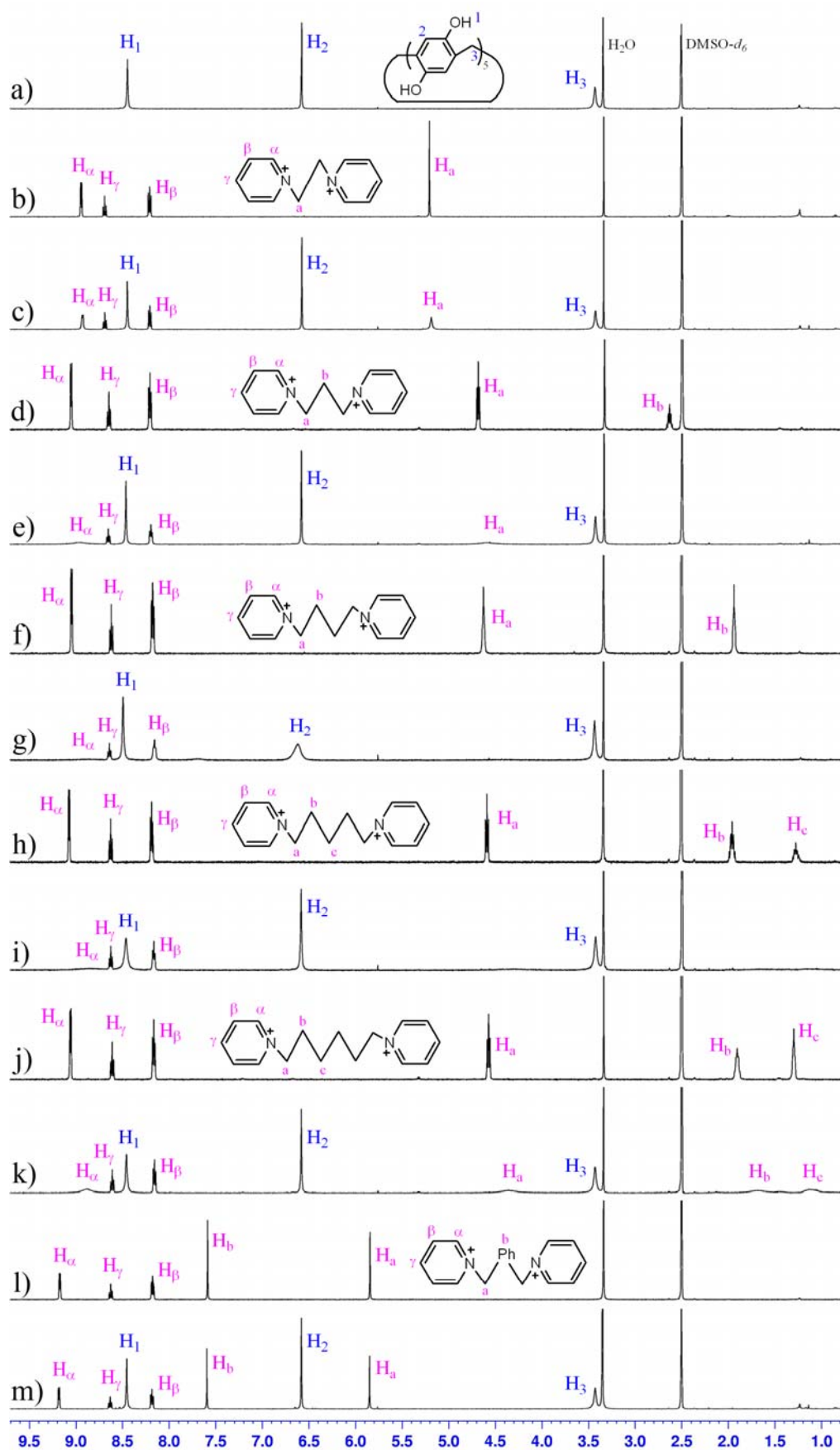


Figure S2. ^1H NMR spectra (500 MHz) of (a) **P5A**, (b) **G6·2PF₆**, (c) **P5A + G6·2PF₆**,

(d) **G7**·2PF₆, (e) **P5A** + **G7**·2PF₆, (f) **G8**·2PF₆, (g) **P5A** + **G8**·2PF₆, (h) **G9**·2PF₆, (i) **P5A** + **G9**·2PF₆, (j) **G10**·2PF₆, (k) **P5A** + **G10**·2PF₆, (l) **G11**·2PF₆ and (m) **P5A** + **G11**·2PF₆ in DMSO-*d*₆ at 4.5~5.0 mM.

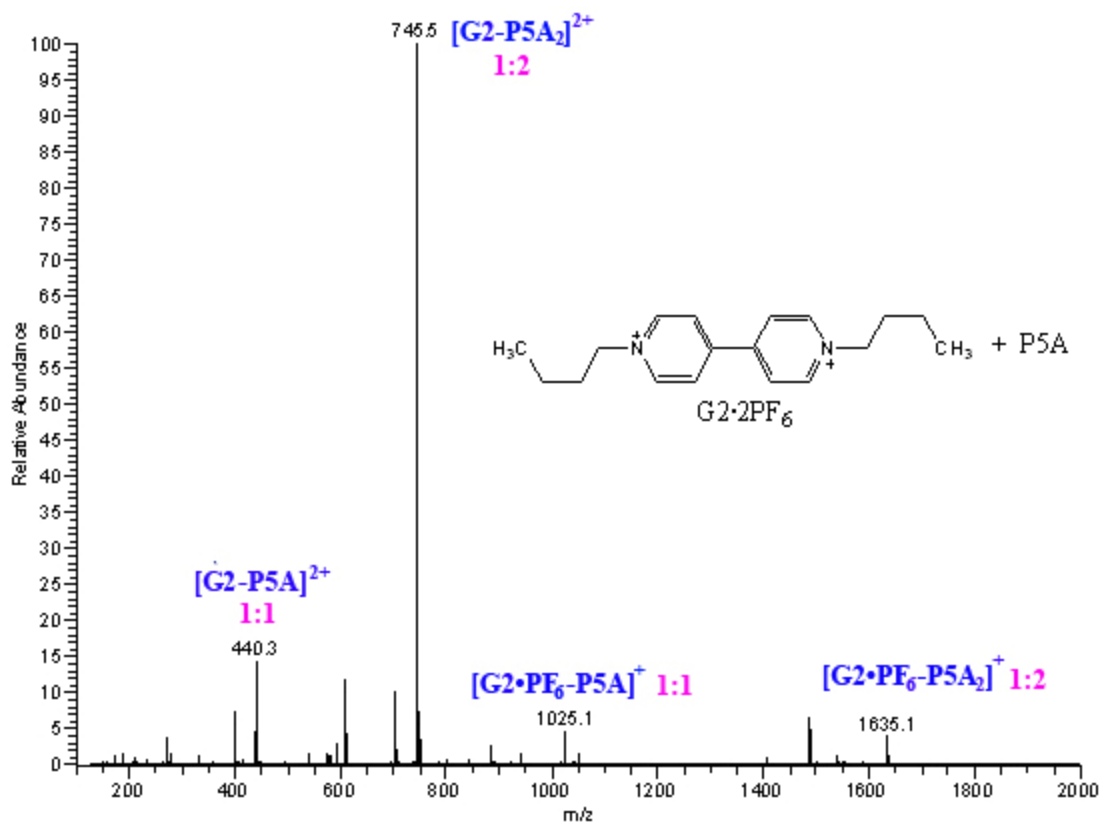


Figure S3. ESI mass spectrum of **G2**·2PF₆ in the presence of 1.2 eq **P5A** in methanol solution.

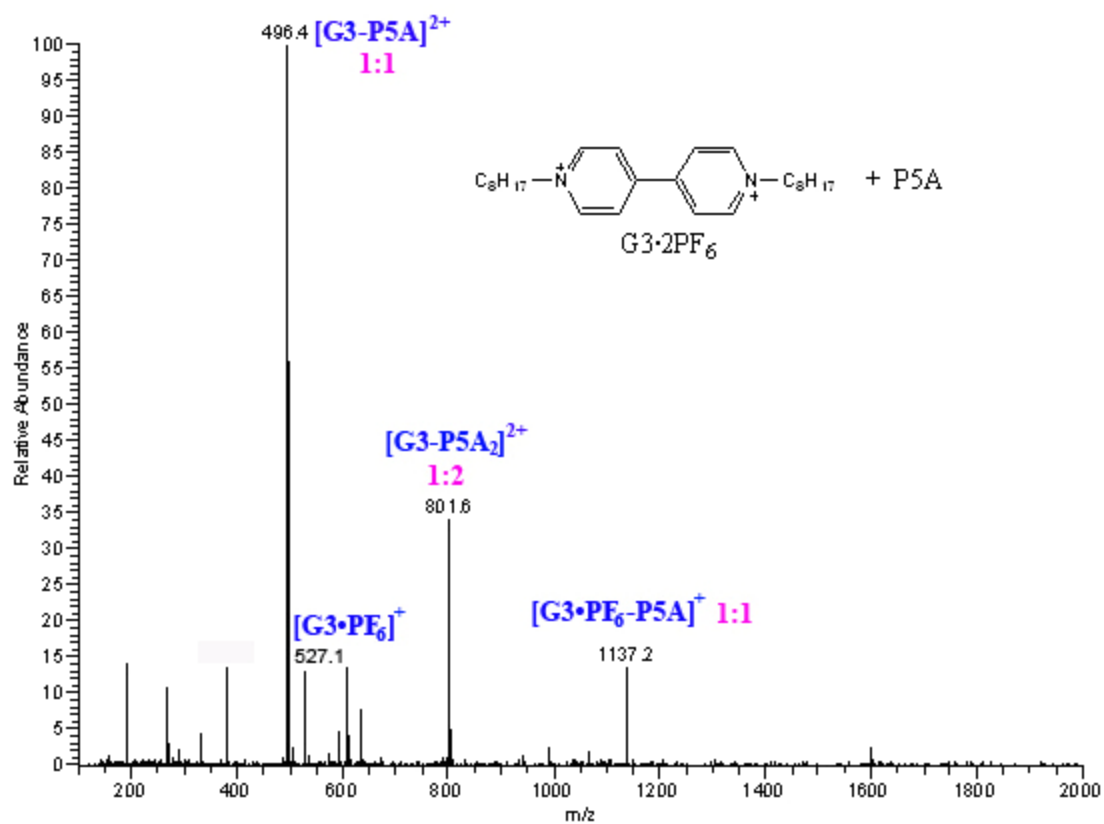


Figure S4. ESI mass spectrum of $\text{G3} \cdot 2\text{PF}_6$ in the presence of 1.2 eq P5A in methanol solution.

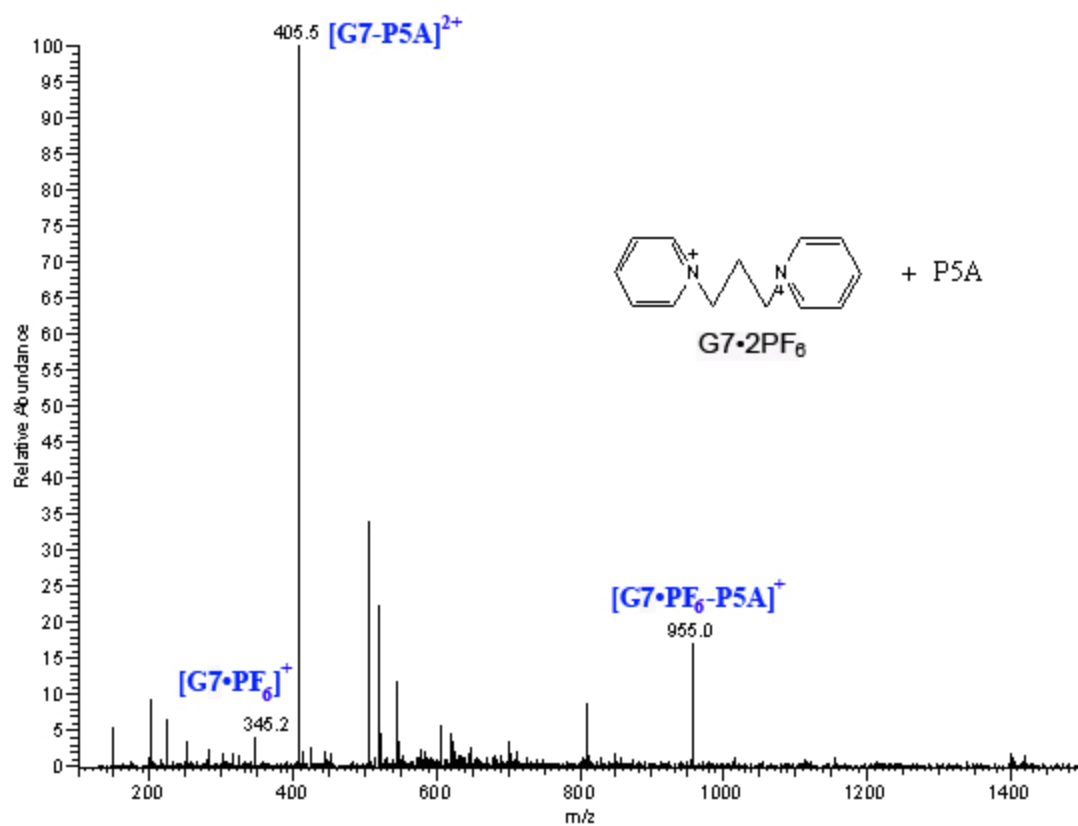


Figure S5. ESI mass spectrum of $G7 \cdot 2PF_6$ in the presence of 1.2 eq **P5A** in methanol solution.

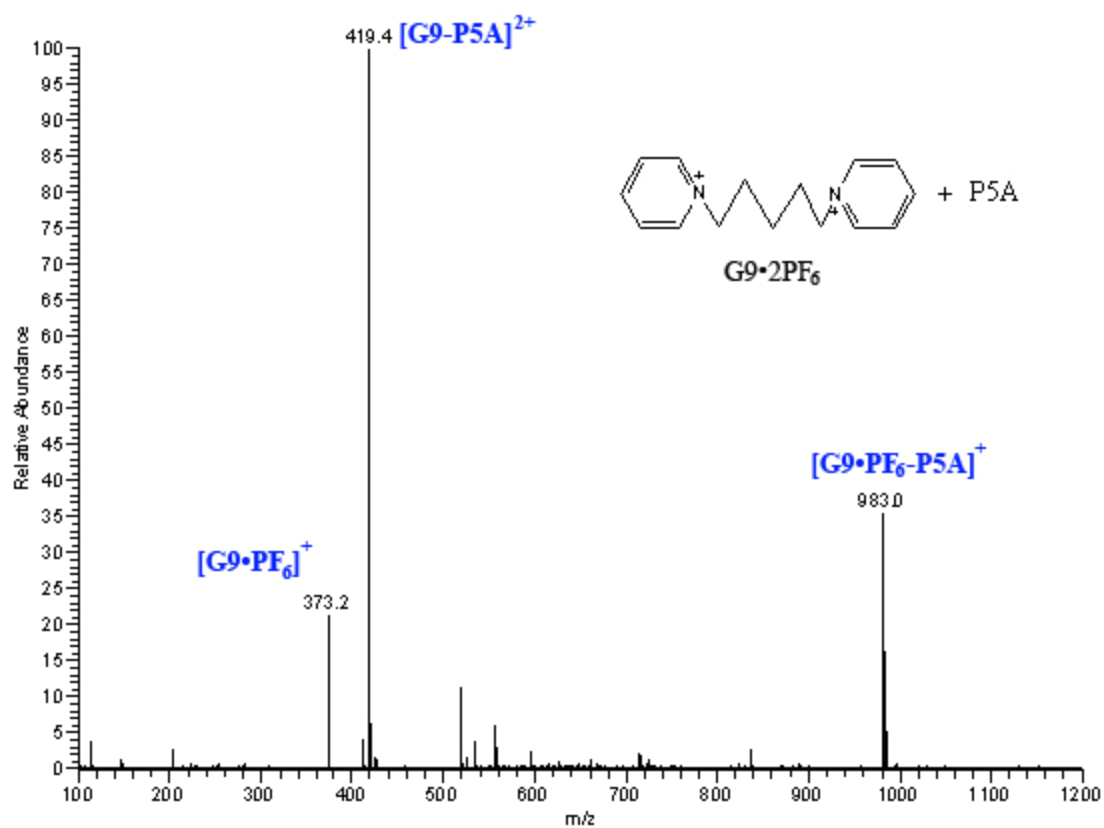


Figure S6. ESI mass spectrum of $G9\cdot 2PF_6$ in the presence of 1.2 eq **P5A** in methanol solution.

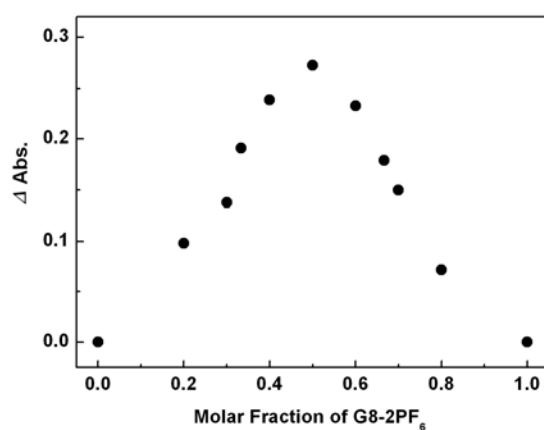


Figure S7. Job plots showing the 1:1 stoichiometry of the complex between **P5A** and **G8·2PF₆** in DMSO by plotting the absorbance intensity at $\lambda = 370$ nm (the host–guest charge transfer band) against the mole fraction of **G8·2PF₆**. ($[\text{P5A}] + [\text{G8·2PF}_6] = 4.0$ mM)

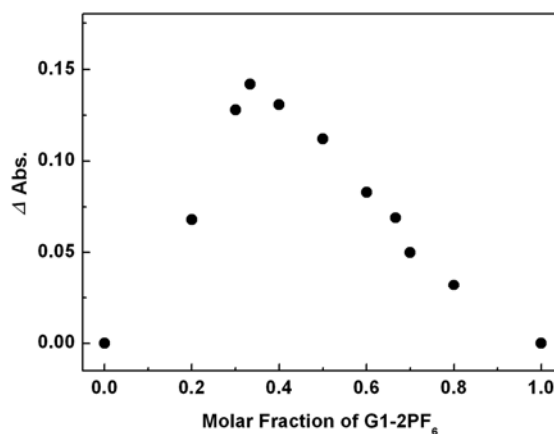


Figure S8. Job plots showing the 2:1 stoichiometry of the complex between **P5A** and **G1·2PF₆** in DMSO by plotting the absorbance intensity at $\lambda = 448$ nm (the host–guest charge transfer band) against the mole fraction of **G1·2PF₆**. ($[\text{P5A}] + [\text{G1·2PF}_6] = 6.0$ mM)

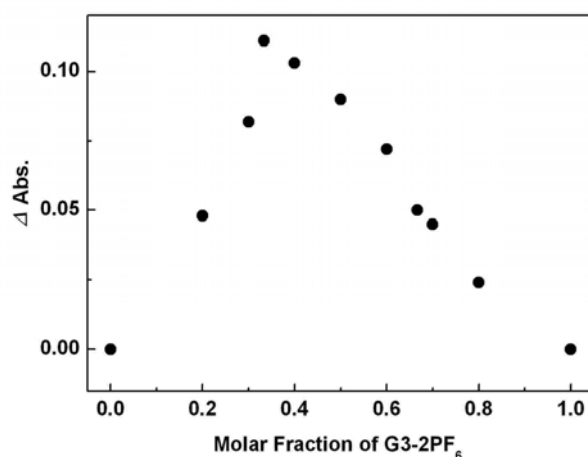


Figure S9. Job plots showing the 2:1 stoichiometry of the complex between **P5A** and **G3·2PF₆** in DMSO by plotting the absorbance intensity at $\lambda = 445$ nm (the host-guest charge transfer band) against the mole fraction of **G3·2PF₆**. ($[\text{P5A}] + [\text{G3·2PF}_6] = 6.0$ mM)

Determination of the association constants.

(1) **Method A.** For **P5A-G13·2PF₆** and **P5A-G14·2PF₆** host-guest complexes, chemical exchange is slow on the NMR time scale and peaks are observed for both complexed and uncomplexed species in the NMR spectra. (Figure 3d) So association constants^{S1, S2} for these complexes could be determined by integration from a 1:1 mixture using the ¹H NMR single point method.^{S3, S4} (Table 2)

$$K_a = \frac{[\text{P5A} \cdot \text{G}]_c}{[\text{P5A}]_{uc}[\text{G}]_{uc}}$$

(2) **Method B.** The association constants (K_a) of **G6~G12·2PF₆** have been determined by probing the charge-transfer bands of the complexes by UV-vis spectroscopy

employing a titration method.^{S5, S6} Progressive addition of a DMSO solution with high guest concentration and low **P5A** concentration to a DMSO solution with the same **P5A** concentration results in an increase of the intensity of the CT band of the complex (Figure S10). Using the nonlinear least squares curve-fitting method, we obtained the association constant for each host-guest combination from the following equation^{S5}:

$$K_a = \frac{[\text{P5A} \cdot \text{G}]}{[\text{P5A}][\text{G}]} = \frac{[\text{P5A} \cdot \text{G}]}{([\text{P5A}]_0 - [\text{P5A} \cdot \text{G}])([\text{G}]_0 - [\text{P5A} \cdot \text{G}])} = \frac{\Delta A / \Delta \varepsilon}{([\text{P5A}]_0 - \Delta A / \Delta \varepsilon)([\text{G}]_0 - \Delta A / \Delta \varepsilon)} \quad (1)$$

After some manipulation, eq 1 yields:

$$\Delta A = \frac{\Delta \varepsilon ([\text{G}]_0 + [\text{P5A}]_0 + \frac{1}{K_a}) \pm \sqrt{\Delta \varepsilon^2 ([\text{G}]_0 + [\text{P5A}]_0 + \frac{1}{K_a})^2 - 4 \Delta \varepsilon^2 [\text{P5A}]_0 [\text{G}]_0}}{2} \quad (2)$$

where $[\text{P5A}]_0$ and $[\text{G}]_0$ denote the initial concentrations of **P5A** host and guests, respectively.

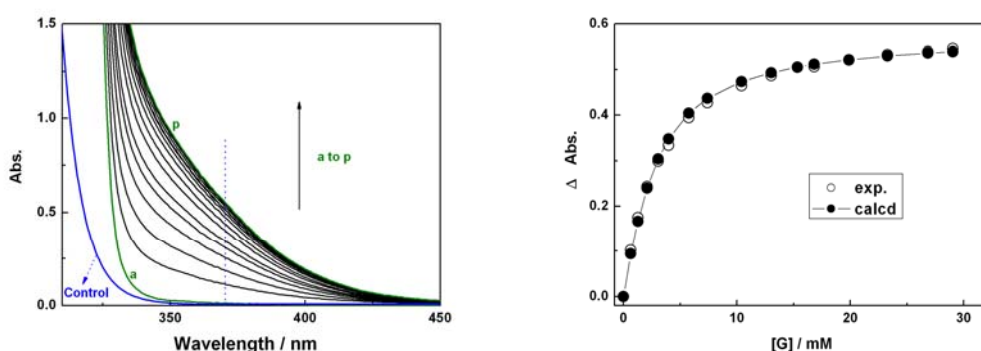


Figure S10. Left: UV-Vis spectra of **P5A** (1.51 mM) in the presence of **G8·2PF₆** (0, 0.64, 1.26, 2.07, 3.04, 3.98, 5.75, 7.41, 10.4, 13.0, 15.4, 16.8, 19.9, 23.3, 26.9, and 29.0 mM from a to p) in DMSO solution at 298 K. Right: Curve-fitting analyses for

the complexation of **P5A** with **G8**·2PF₆. ($\lambda=370$ nm) The “Control” is the UV-vis spectrum of a high concentration of **G8**·2PF₆ (29.0 mM) in the absence of **P5A** host.

The K_a values of bis(pyridinium) derivatives (**G6**~**G12**·2PF₆) by **P5A** are listed in Table 1.

The K_a value for **P5A**/**G13**·2PF₆ system was also determined using UV-vis titration. The K_a value obtained is almost accordant with that from the ¹H NMR single point method (Figure S11 & Table S1).

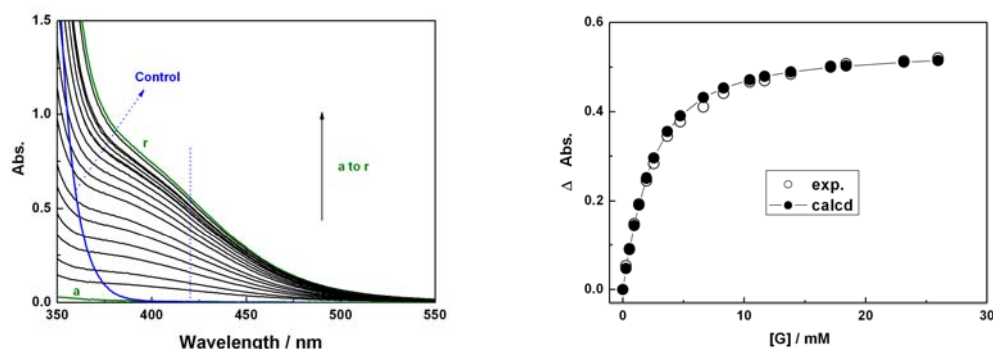


Figure S11. Left: UV-Vis spectra of **P5A** (1.60 mM) in the presence of **G13**·2PF₆ (0, 0.27, 0.54, 0.93, 1.32, 1.94, 2.54, 3.67, 4.72, 6.63, 8.30, 10.5, 11.7, 13.8, 17.1, 18.4, 23.1 and 27.0 mM from a to r) in DMSO solution at 298 K. Right: Curve-fitting analyses for the complexation of **P5A** with **G13**·2PF₆. ($\lambda=420$ nm) The “Control” is the UV-vis spectrum of a high concentration of **G13**·2PF₆ (27.0 mM) in the absence of **P5A** host.

TABLE S1. Association constant (K_a/M^{-1}) for complexation of host **P5A** with **G13·2PF₆** in DMSO (or DMSO-*d*₆) at 298 K using different methods.

guest	K_a
G13·2PF₆	$(7.4 \pm 0.3) \times 10^2$ ^a
G13·2PF₆	$(7.6 \pm 0.4) \times 10^2$ ^b

^a Method A. ^b Method B.

(3) Method C. The association constants (K_a) of **G6~G12·2PF₆** have also been determined using the indirect method based on ¹H NMR spectroscopy introduced by Mock in his pioneering work on cucurbituril.^{S7} In our implementation of this method, a more tightly binding guest (**G13·2PF₆**) that exhibits slow exchange kinetics and an excess of a more weakly binding guest are allowed to compete for a limiting quantity of **P5A**. The integration of the resonances for the free and bound guest then allow for a calculation of the association constant.

In the three component system:

$$K_{a \text{ ref}} = \frac{[\text{P5A} \cdot \text{G}_{\text{ref}}]_{\text{c}}}{[\text{P5A}]_{\text{uc}}[\text{G}_{\text{ref}}]_{\text{uc}}}$$

$$\therefore [\text{P5A}]_{\text{uc}} = \frac{[\text{P5A} \cdot \text{G}_{\text{ref}}]_{\text{c}}}{[\text{G}_{\text{ref}}]_{\text{uc}} K_{a \text{ ref}}}$$

So the unknown K_a could be determined using the following equation:

$$K_a = \frac{[\text{P5A} \cdot \text{G}]_{\text{c}}}{[\text{P5A}]_{\text{uc}}[\text{G}]_{\text{uc}}} = \frac{[\text{P5A}]_0 - [\text{P5A}]_{\text{uc}} - [\text{P5A} \cdot \text{G}_{\text{ref}}]_{\text{c}}}{[\text{P5A}]_{\text{uc}}([\text{G}]_0 - [\text{P5A} \cdot \text{G}]_{\text{c}})}$$

$$= \frac{[\text{P5A}]_0 - [\text{P5A}]_{\text{uc}} - [\text{P5A} \cdot \text{G}_{\text{ref}}]_{\text{c}}}{[\text{P5A}]_{\text{uc}}\{[\text{G}]_0 - ([\text{P5A}]_0 - [\text{P5A}]_{\text{uc}} - [\text{P5A} \cdot \text{G}_{\text{ref}}]_{\text{c}})\}}$$

As shown in Table S2, the K_a values for **P5A** with **G6~G12·2PF₆** systems

determined using this indirect method (Method C) are almost accordant with those from UV-vis titration. (Method B)

TABLE S2. Association constant (K_a/M^{-1}) for complexation of host **P5A** with **G6~G12**·2PF₆ in DMSO at 298 K using different methods.

	K_a^a	K_a^b
G6 ·2PF ₆	— ^c	— ^c
G7 ·2PF ₆	$(8.8 \pm 0.7) \times 10$	$(8.1 \pm 0.8) \times 10$
G8 ·2PF ₆	$(4.5 \pm 0.4) \times 10^2$	$(4.1 \pm 0.1) \times 10^2$
G9 ·2PF ₆	$(3.7 \pm 0.3) \times 10^2$	$(3.5 \pm 0.1) \times 10^2$
G10 ·2PF ₆	$(1.2 \pm 0.1) \times 10^2$	$(1.1 \pm 0.1) \times 10^2$
G11 ·2PF ₆	— ^c	— ^c
G12 ·2PF ₆	$(4.0 \pm 0.3) \times 10^2$	$(3.9 \pm 0.2) \times 10^2$

^a Method B. ^b Method C. ^c The K_a value was too small to be calculated.

(4) For paraquat derivative **G1~G4**·2PF₆, the average association constants^{S8} with the host (using Method B^{S8a&b} or Method C) are very small ($K_{av} < 50 \text{ M}^{-1}$) in DMSO, and can't be calculated accurately.

References.

(S1) K_a reported here should be taken as approximate because it does not take into account the extent of ion pair dissociation on the observed binding interaction

with pillar[5]arene. For a detailed discussion, see ref S2.

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(S4) Association constants determined using the ^1H NMR single point methods. See:

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(S6) Association constants determined using UV-vis titration. See: (a) Zhang, J.; Zhai, C.; Wang, F.; Zhang, C.; Li, S.; Zhang, M.; Li, N.; Huang, F. *Tetrahedron Lett.* **2008**, *49*, 5009–5012. (b) Zhu, K.; Li, S.; Wang, F.; Huang, F. *J. Org. Chem.* **2009**, *74*, 1322–1328. (c) He, C.; Shi, Z.; Zhou, Q.; Li, S.; Li, N.; Huang, F. *J. Org. Chem.* **2008**, *73*, 5872–5880. (d) Zhang, J.; Huang, F.; Li, N.; Wang, H.; Gibson,

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