Electronic supplementary information

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

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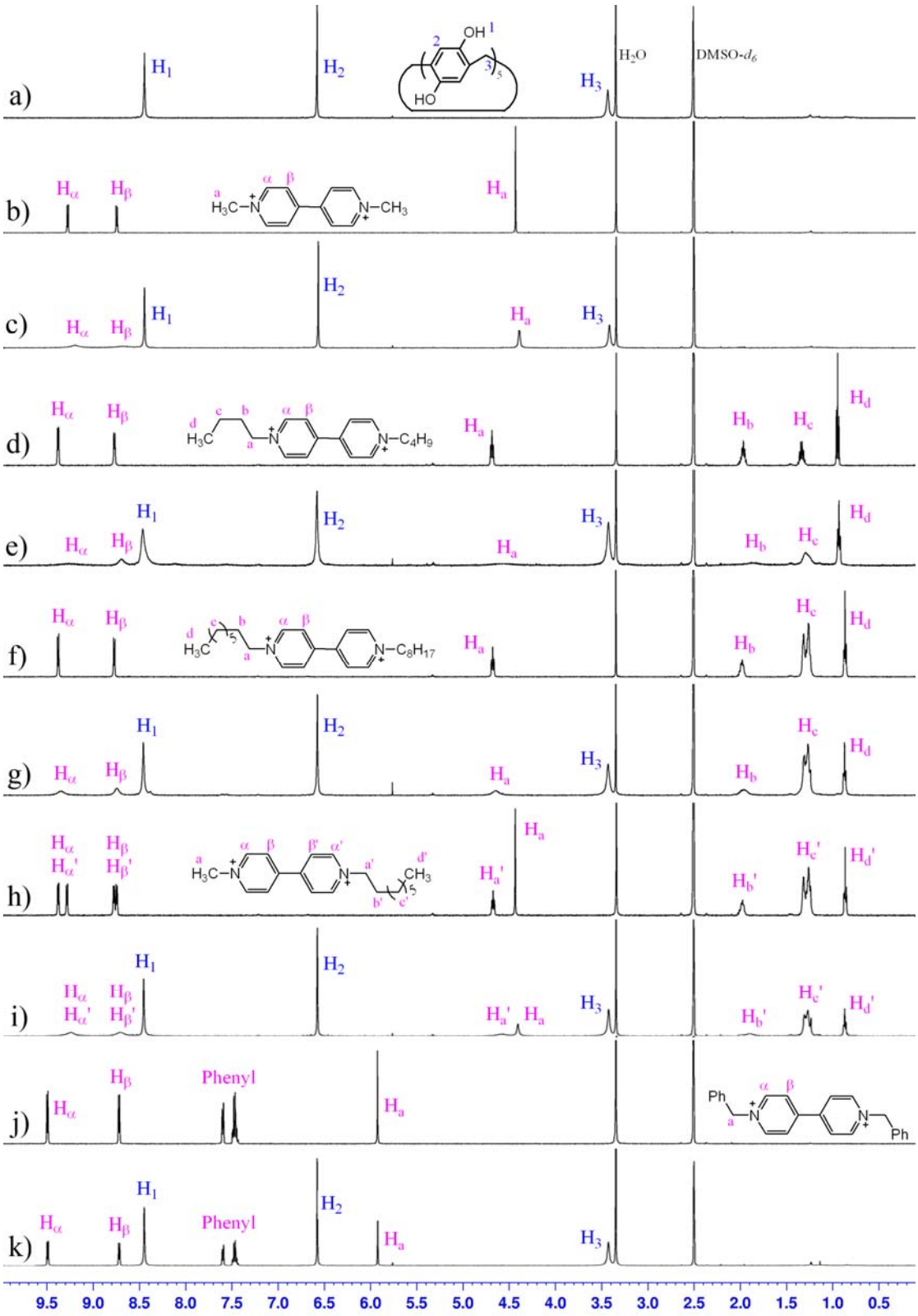

Figure S1. ^{1}H NMR spectra (500 MHz) of (a) **P5A**, (b) **G1**·2PF$_6$, (c) **P5A** + **G1**·2PF$_6$, (d) **G2**·2PF$_6$, (e) **P5A** + **G2**·2PF$_6$, (f) **G3**·2PF$_6$, (g) **P5A** + **G3**·2PF$_6$, (h) **G4**·2PF$_6$, (i) **P5A** + **G4**·2PF$_6$, (j) **G5**·2PF$_6$, (k) **P5A** + **G5**·2PF$_6$ in DMSO-d_6 at about 5 mM.

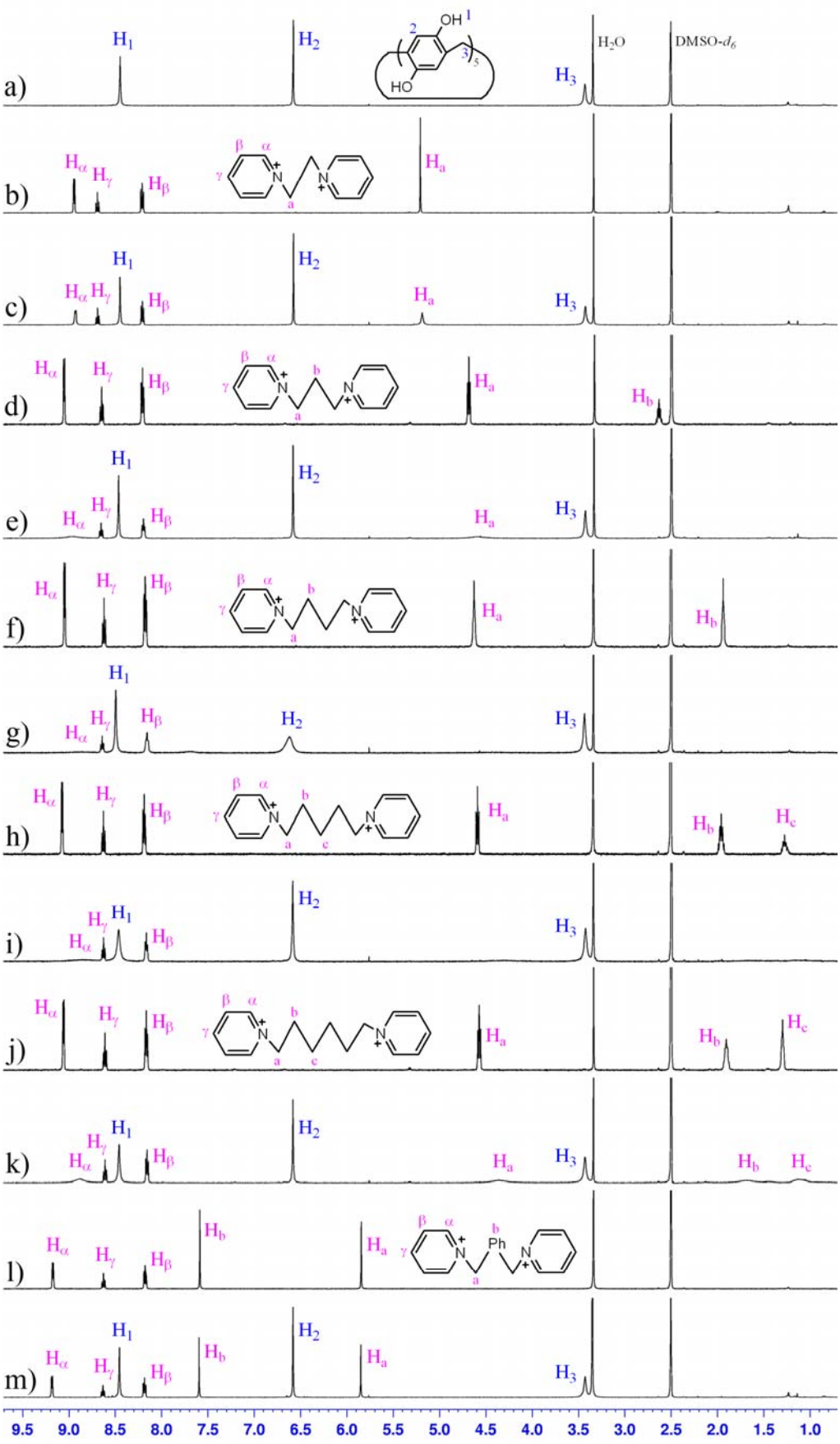

Figure S2. ^{1}H NMR spectra (500 MHz) of (a) **P5A**, (b) **G6**·2PF$_6$, (c) **P5A** + **G6**·2PF$_6$,

(d) **G7**·2PF_6, (e) **P5A** + **G7**·2PF_6, (f) **G8**·2PF_6, (g) **P5A** + **G8**·2PF_6, (h) **G9**·2PF_6, (i) **P5A** + **G9**·2PF_6, (j) **G10**·2PF_6, (k) **P5A** + **G10**·2PF_6, (l) **G11**·2PF_6 and (m) **P5A** + **G11**·2PF_6 in DMSO-d_6 at 4.5~5.0 mM.

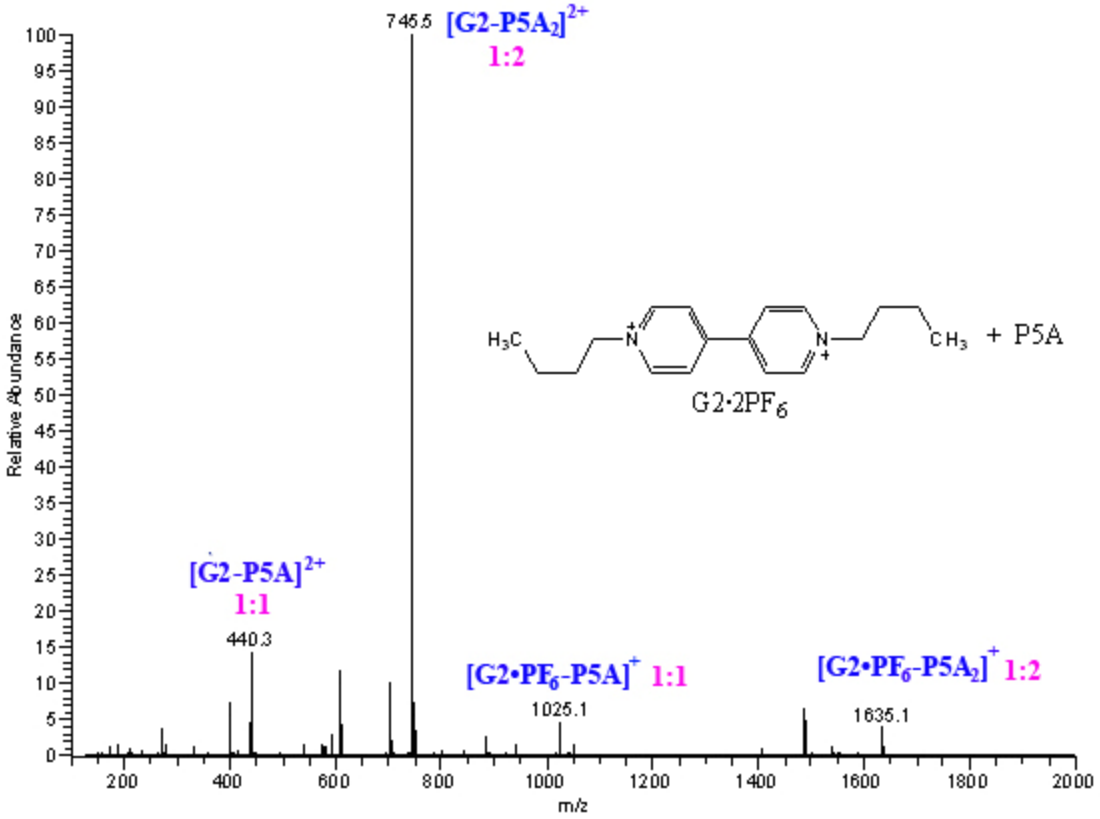

Figure S3. ESI mass spectrum of **G2·2PF$_6$** in the presence of 1.2 eq **P5A** in methanol solution.

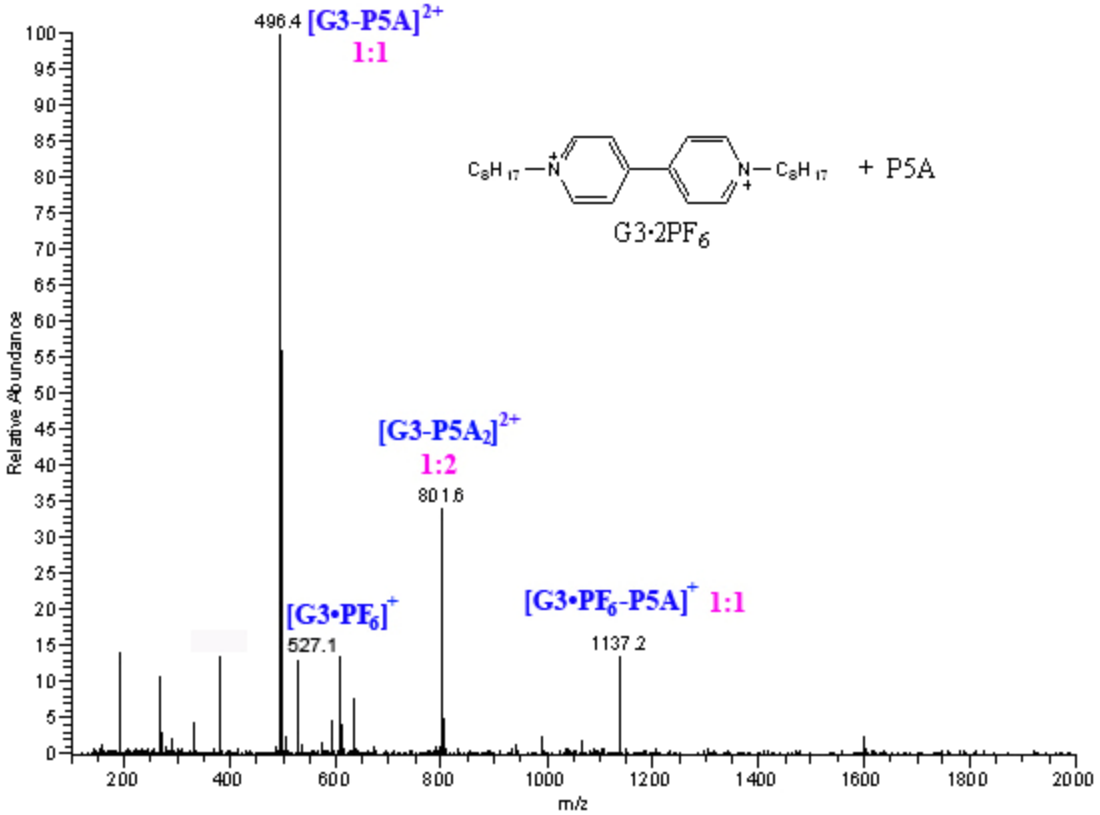

Figure S4. ESI mass spectrum of **G3·2PF$_6$** in the presence of 1.2 eq **P5A** in methanol solution.

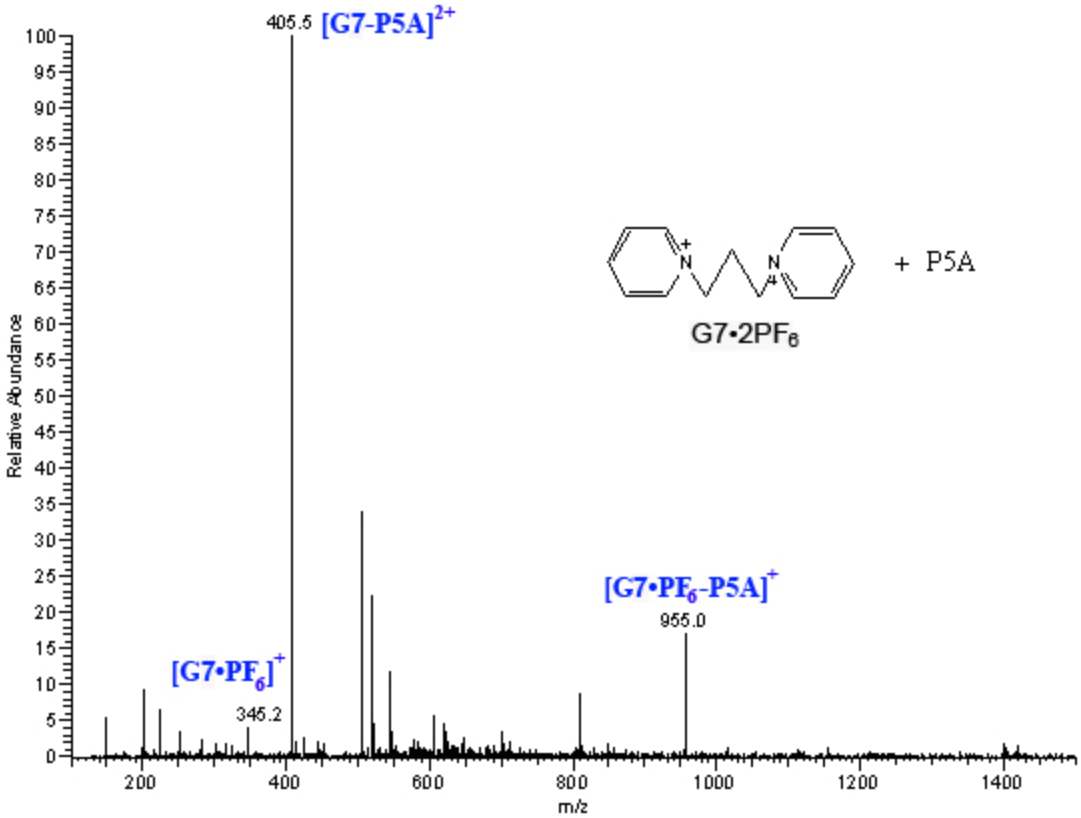

Figure S5. ESI mass spectrum of **G7·2PF$_6$** in the presence of 1.2 eq **P5A** in methanol solution.

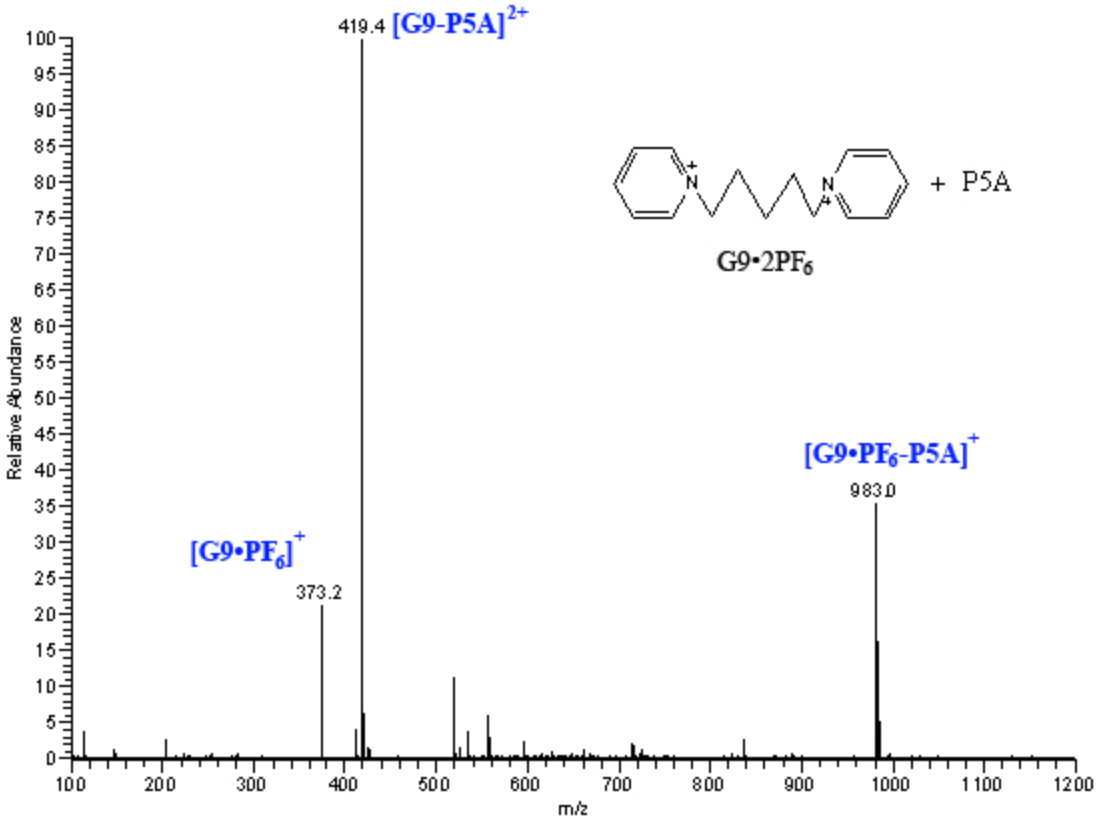

Figure S6. ESI mass spectrum of **G9·2PF$_6$** in the presence of 1.2 eq **P5A** in methanol solution.

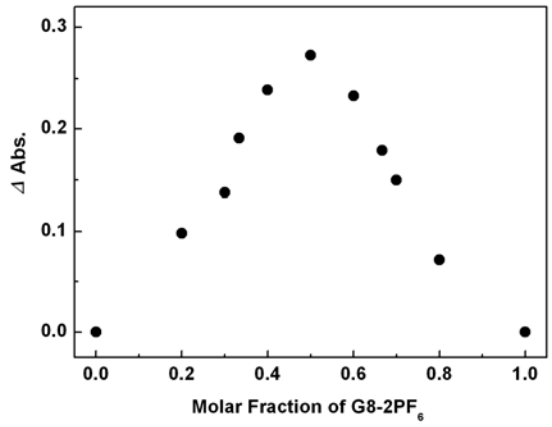

Figure S7. Job plots showing the 1:1 stoichiometry of the complex between **P5A** and **G8**·2PF_6 in DMSO by plotting the absorbance intensity at λ = 370 nm (the host–guest charge transfer band) against the mole fraction of **G8**·2PF_6. ([P5A] + [**G8**·2PF_6] = 4.0 mM)

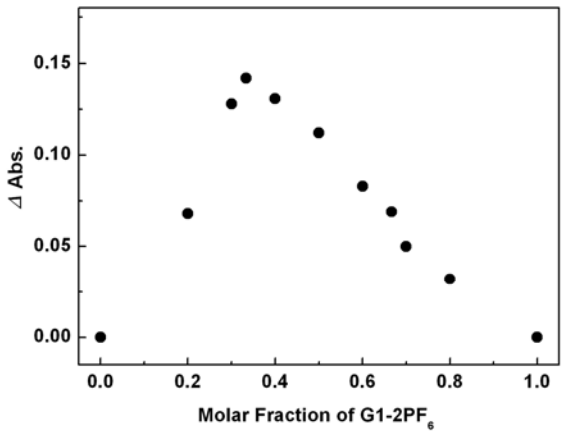

Figure S8. Job plots showing the 2:1 stoichiometry of the complex between **P5A** and **G1**·2PF_6 in DMSO by plotting the absorbance intensity at λ = 448 nm (the host-guest charge transfer band) against the mole fraction of **G1**·2PF_6. ([**P5A**] + [**G1**·2PF_6] = 6.0 mM)

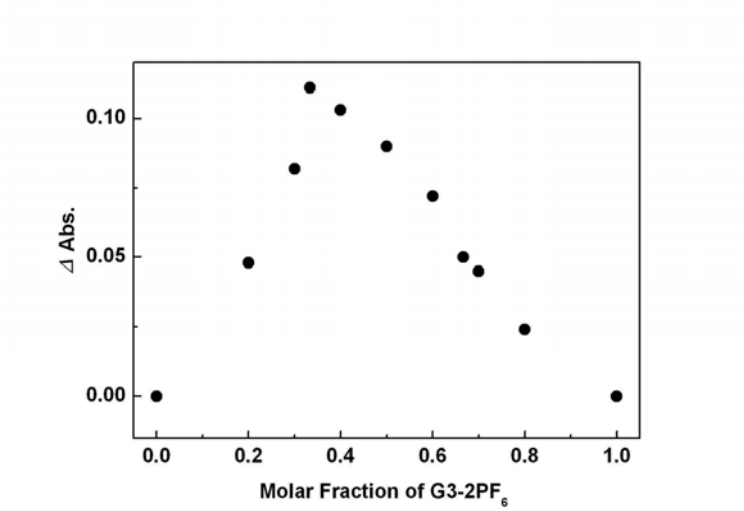

Figure S9. Job plots showing the 2:1 stoichiometry of the complex between **P5A** and **G3**·2PF_6 in DMSO by plotting the absorbance intensity at λ = 445 nm (the host-guest charge transfer band) against the mole fraction of **G3**·2PF_6. ([**P5A**] + [**G3**·2PF_6] = 6.0 mM)

Determination of the association constants.

(1) Method A. For **P5A-G13**·2PF_6 and **P5A-G14**·2PF_6 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 ^{1}H NMR single point method.[S3, S4] (Table 2)

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

(2) Method B. The association constants (K_a) of **G6**~**G12**·2PF_6 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]:

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

After some manipulation, eq 1 yields:

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

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

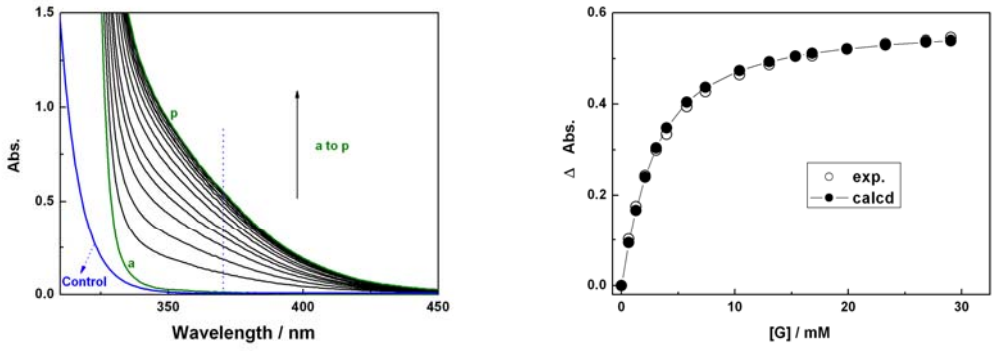

Figure S10. Left: UV-Vis spectra of **P5A** (1.51 mM) in the presence of **G8**·2PF_6 (0, 0.64, 1.26, 2.07, 3.04, 3.98, 5.75, 7.41, 10.4, 13.0, 15.4, 16.8, 19.9, 23.3, 26.9, and 29.0 mM from a to p) in DMSO solution at 298 K. Right: Curve-fitting analyses for

the complexation of **P5A** with **G8**·2PF_6. (λ=370 nm) The "Control" is the UV-vis spectrum of a high concentration of **G8**·2PF_6 (29.0 mM) in the absence of **P5A** host.

The K_a values of bis(pyridinium) derivatives (**G6**~**G12**·2PF_6) by **P5A** are listed in Table 1.

The K_a value for **P5A**/**G13**·2PF_6 system was also determined using UV-vis titration. The K_a value obtained is almost accordant with that from the ^{1}H NMR single point method (Figure S11 & Table S1).

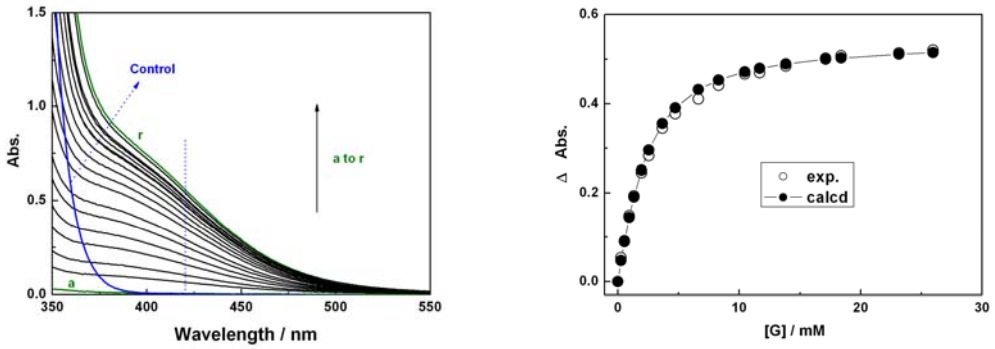

Figure S11. Left: UV-Vis spectra of **P5A** (1.60 mM) in the presence of **G13**·2PF_6 (0, 0.27, 0.54, 0.93, 1.32, 1.94, 2.54, 3.67, 4.72, 6.63, 8.30, 10.5, 11.7, 13.8, 17.1, 18.4, 23.1 and 27.0 mM from a to r) in DMSO solution at 298 K. Right: Curve-fitting analyses for the complexation of **P5A** with **G13**·2PF_6. (λ=420 nm) The "Control" is the UV-vis spectrum of a high concentration of **G13**·2PF_6 (27.0 mM) in the absence of **P5A** host.

TABLE S1. Association constant (K_a/M^{-1}) for complexation of host **P5A** with **G13**·2PF_6 in DMSO (or DMSO-*d6*) at 298 K using different methods.

guest	K_a
G13·2PF_6	$(7.4\pm0.3) \times 10^{2}$ [a]
G13·2PF_6	$(7.6\pm0.4) \times 10^{2}$ [b]

[a] Method A. [b] Method B.

(3) Method C. The association constants (K_a) of **G6**~**G12**·2PF_6 have also been determined using the indirect method based on ^{1}H NMR spectroscopy introduced by Mock in his pioneering work on cucurbituril.[S7] In our implementation of this method, a more tightly binding guest (**G13**·2PF_6) 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:

$$K_{a\ ref} = \frac{[P5A{\cdot}G_{ref}]_c}{[P5A]_{uc}[G_{ref}]_{uc}}$$

$$\therefore\ [P5A]_{uc} = \frac{[P5A{\cdot}G_{ref}]_c}{[G_{ref}]_{uc}K_{a\ ref}}$$

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

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

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

As shown in Table S2, the K_a values for **P5A** with **G6**~**G12**·2PF_6 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**·2PF_6 in DMSO at 298 K using different methods.

	K_a [a]	K_a [b]
G6·2PF_6	– [c]	– [c]
G7·2PF_6	(8.8±0.7) × 10	(8.1±0.8) × 10
G8·2PF_6	(4.5±0.4) × 10^2	(4.1±0.1) × 10^2
G9·2PF_6	(3.7±0.3) × 10^2	(3.5±0.1) × 10^2
G10·2PF_6	(1.2±0.1) × 10^2	(1.1±0.1) × 10^2
G11·2PF_6	– [c]	– [c]
G12·2PF_6	(4.0±0.3) × 10^2	(3.9±0.2) × 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**·2PF_6, the average association constants[S8] with the host (using Method B[S8a&b] or Method C) are very small (K_{av} < 50 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 ^{1}H NMR single point methods. See: (a) Braunschweig, A. B.; Ronconi, C. M.; Han, J.-Y.; Arico, F.; Cantrill, S. J.; Stoddart, J. F.; Khan, S. I.; White, A. J. P.; Williams, D. J. *Eur. J. Org. Chem.* **2006**, 1857–1866. (b) Loeb, S. J.; Wisner, J. A. *Angew. Chem. Int. Ed.* **1998**, *37*, 2838–2840. (c) Loeb, S. J.; Tiburcio, J.; Vella, S. J. *Org. Lett.* **2005**, *7*, 4923–4926. (d) Zhao, J.-M.; Zong, Q.-S.; Han, T.; Xiang, J.-F.; Chen, C.-F. *J. Org. Chem.* **2008**, *73*, 6800–6806. (e) Li, L.; Clarkson, G. J. *Org. Lett.*, **2007**, *9*, 497–500. (f) Castillo, D.; Astudillo, P.; Mares, J.; González, F. J.; Vela, A.; Tiburcio, J. *Org. Biomol. Chem.*, **2007**, *5*, 2252–2256.

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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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