

Electronic Supplementary Information Accompanying:
**Molecular Recognition. Electrostatic Effects in Supramolecular Self-
assembly**

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Chemical Communications

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General Procedures. All reagents were obtained from commercial suppliers and were used without further purification. All reactions were performed under an atmosphere of argon, unless otherwise specified. Electronic absorption spectra were obtained using a Perkin Elmer Lambda 6 UV/VIS Spectrophotometer. Elemental analyses were

performed by Desert Analytics, Inc., Tucson, Arizona. Conductance measurements were performed at 23 °C in dry acetonitrile on 1×10^{-3} molar samples using an YSI Scientific Model 35 conductance meter. ^1H and ^{13}C NMR spectra were recorded using a Bruker DRX500 Fourier transform spectrometer at 300K, unless otherwise specified. ^{195}Pt NMR spectra were recorded using a Bruker DRX400. Proton and carbon chemical shifts, δ , are reported in ppm, referenced to TMS, and platinum chemical shifts, δ , are reported in ppm, referenced to a saturated solution of $\text{K}_2[\text{PtCl}_6]$ in D_2O . Coupling constants, J , are reported in Hertz. ESI-MS were obtained using an Agilent 1100 MSD LC-MS. GC-MS were obtained using a Varian Saturn 2000. Acetonitrile was dried over CaH_2 , tetrahydrofuran (THF) was dried over potassium/benzophenone ketyl, diethyl ether (Et_2O) was dried over sodium/benzophenone ketyl, methylene chloride (CH_2Cl_2) was dried over CaH_2 , and triethylamine (TEA) was dried over CaH_2 . Thin layer chromatography was carried out using precoated silica gel (Whatman PE SIL G/UV) or precoated aluminum oxide (J. T. Baker, aluminum oxide IB-F). Silica gel 60 Å (Merck, 230 – 400 mesh) and aluminum oxide 58 Å (either activated, basic, Brockman I or activated, neutral, Brockman I) were used for chromatography as indicated. Celite is J.T. Baker Celite 503. $[\text{Pd}_4(4,4'\text{-bipy})_2(\text{L}_r)_2](\text{PF}_6)_8$ (**6**)¹, $[(\text{PdCl})_2\text{L}_r](\text{PF}_6)_2$ (**1**)², $[\text{Pt}(\text{Salap})\text{DMSO}]^3$ and $[\text{Pt}(\text{Salap})\text{NH}_3]$ (**3**)⁴ were prepared as previously described.

$[\text{Pt}(\text{salap})]_2p\text{-xylyenediamine}$ (4). A 50 mL flask was charged with $[\text{Pt}(\text{salap})\text{DMSO}]$ (215 mg, 0.445 mmol) dissolved in warm acetonitrile (10 mL). *p*-xylylenediamine (30 mg, 0.22 mmol) was added to the yellow colored solution. The reaction was stirred at reflux for 4 h, during which time an orange solid began to precipitate. The solution was

cooled and the orange solid was obtained by filtration and was washed with diethyl ether (10 mL) and pentane (10 mL). The solid was crystallized from DMF (5 mL) by vapour diffusion with diethyl ether to yield orange crystals (170 mg, 82 %). ^1H NMR (DMF- d_7 , 343K, 500 MHz): δ 4.27 (t, $J = 6.66$, 4H), 6.05 (t, $J = 6.36$, 4H), 6.63 (m, 2H), 6.74 (m, 2H), 6.98 (dd, $J_1 = 8.26$, $J_2 = 1.22$, 2H), 7.04 (m, 2H), 7.08 (dd, $J_1 = 8.50$, $J_2 = 1.64$, 2H), 7.47 (m, 2H), 7.70 (s, 4H), 7.91 (dd, $J_1 = 8.04$, $J_2 = 1.62$, 2H), 8.15 (dd, $J_1 = 8.32$, $J_2 = 1.20$, 2H), 9.32 (s, 2H). $^3J(^{195}\text{Pt}, \text{H-9.32}) = 84.2$ Hz. ^{13}C NMR (DMF- d_7 , 300K, 125 MHz): δ 49.35, 115.24, 116.31, 116.39, 118.22, 121.92, 123.49, 128.67, 129.45, 132.61, 134.72, 138.86, 140.96, 143.74, 162.34, 169.46. ^{195}Pt NMR (DMF- d_7 , 343K, 86 MHz): δ -1600 ppm. Mass Spectrum (ESI-MS, DMF): $m/z = 948$ (M), 949 (M+1). Anal. Calcd for $\text{C}_{34}\text{H}_{30}\text{N}_4\text{O}_4\text{Pt}_2$: C, 43.04; H, 3.19; N, 5.91. Found: C, 43.11; H, 3.19; N, 5.92.

3-[4-(3-hydroxyprop-1-ynyl)phenyl]prop-2-yn-1-ol

(1,4-(dipropargylalcohol)benzene).⁵ A 50 mL flask was flame dried under a continuous stream of argon and was charged with 1,4-diiodobenzene (2.00 g, 6.06 mmol). The solid was dissolved into dry THF (10 mL) and triethylamine (5 mL) forming a pale yellow solution. CuI (0.230 g, 1.212 mmol) and Pd(PPh₃)₄ (0.699 g, 0.606 mmol) were added as solids in one portion and the flask flushed with argon. The reaction was cooled to -10°C in a MeOH/ice bath and propargyl alcohol (0.424 g, 7.57 mmol) was added. The reaction was stirred at room temperature in the absence of light. During the course of the reaction a white solid precipitated, and the color of the solution changed to brown. After 6 hours, the solvent was removed under reduced pressure and the resulting brown solid was dissolved into diethyl ether (100 mL) and was washed successively with saturated NH_4Cl

solution (2 x 50 mL), H₂O (2 x 50 ml) and saturated NaCl solution (2 x 50 mL). The organic layer was collected and dried over MgSO₄. Filtration, followed by removal of the solvent, yielded the crude product as a orange-brown solid which was chromatographed through 20 g of silica using 100% methylene chloride as the eluant; after the first band was collected the solvent was changed to diethyl ether (100%) and the product was collected as the next band eluted from the column. Removal of the solvent yielded a white solid (1.02g, 91 %). ¹H NMR (CDCl₃, 500 MHz): δ 1.76 (t, J= 5.75, 2H), 4.50 (d, J=5.75, 4H), 7.37 (s, 4H). ¹³C NMR (CDCl₃, 125 MHz): δ 51.62, 85.18, 88.99, 122.64, 131.56. Mass Spectrum (GC-MS, CH₂Cl₂): m/z = 186 (M), 187 (M+1).

2-(3-{4-[3-(1,3-dioxo-1,3-dihydro-2H-isoindol-2-yl)prop-1-ynyl]phenyl}prop-2-ynyl)-1H-isoindole-1,3(2H)-dione (1,4-(dipropargylphthalimido)benzene).^{6,7} A 50 mL flask was flame dried under a continuous stream of argon. The flask was charged with 1,4-dipropargylbenzene (1.00 g, 5.37 mmol), PPh₃ (2.95 g, 11.2 mmol) and phthalimide (1.75 g, 11.8 mmol). 30 ml of dry THF was added to give a pale yellow solution. The reaction was cooled to -10°C in a MeOH/ice bath and diethyl azodicarboxylate (DEAD) (2.33 g, 13.42 mmol) was added. After 2 minutes, a white precipitate began to form. The reaction was slowly warmed to room temperature and was stirred for 3 hours. After this time the reaction was cooled in the refrigerator (30 minutes), then the white solid was isolated by filtration and was washed with cold THF (10 mL), diethyl ether (10 mL) and hexanes (10 mL). (2.08 g, 87 %). ¹H NMR (CDCl₃, 500 MHz): δ 4.66 (s, 4H), 7.31 (s, 4H), 7.74 (m, 4H), 7.88 (m, 4H). ¹³C NMR (CDCl₃, 125 MHz): δ 27.82, 82.49, 84.43, 122.44, 123.56, 131.70, 132.06, 134.17, 167.07. Mass Spectrum (ESI-MS, CH₂Cl₂): m/z

= 444 (M), 445 (M+1). Anal. Calcd for C₂₈H₁₆N₂O₄: C, 75.67; H, 3.63; N, 6.30. Found: C, 75.39; H, 3.57; N, 6.09.

3-[4-(3-aminoprop-1-ynyl)phenyl]prop-2-yn-1-amine (1,4-

(dipropargylamino)benzene).^{7,8} A 100 mL flask was charged with 1,4-(dipropargylphthalimide)benzene (2.00 g, 4.5 mmol) and the solid was slurried in 50 mL of ethanol (95%). N₂H₄·H₂O (0.51 g, 10.3 mmol, 0.50 mL) was added and the reaction was then refluxed for 16 hours. The reaction was cooled to 50°C and concentrated HCl (2.5 mL) was added. The reaction mixture was refluxed for 2 hours. The mixture was allowed to cool (10 minutes), was filtered while still warm and was washed with 3 x 25 mL of ethanol (95%). The filtrate was collected and the volume reduced 5 mL. The white precipitate was isolated by filtration and was washed with cold THF (10 mL), diethyl ether (10 mL) and hexanes (10 mL). (1.04 g, 90%). ¹H NMR (D₂O, 500 MHz): δ 4.08 (s, 4H), 7.53 (s, 4H). ¹³C NMR (D₂O, 125 MHz): δ 29.76, 81.89, 86.01, 121.92, 131.85. The free amine was obtained by dissolving the HCl salt in 1M NaOH and extracting into methylene chloride. The organic layer was dried over Na₂SO₄ and the solvent was removed to yield a white powder. ¹H NMR (CDCl₃, 500 MHz): δ 1.39 (sb, 4H), 3.60 (s, 4H), 7.35 (s, 4H). ¹³C NMR (CDCl₃, 125 MHz): δ 32.17, 82.08, 91.79, 122.84, 131.41. Mass Spectrum (GC-MS, CH₂Cl₂): m/z = 184 (M), 185 (M+1). Anal. Calcd for C₁₂H₁₂N₂: C, 78.23; H, 6.57; N, 15.21. Found: C, 78.11; H, 6.43; N, 14.94.

[Pt(salap)]₂-1,4-(dipropargylamino)benzene (5). A 25 mL flask was charged with [Pt(salap)DMSO] (184 mg, 0.380 mmol) dissolved in warm acetonitrile (5 mL). To this

yellow colored solution was added 1,4-(dipropargylamino)benzene (35 mg, 0.190 mmol). The reaction was refluxed for 3 hours, during which time an orange solid precipitated. The solution was cooled and the orange solid was collected by filtration and was washed with diethyl ether (10 mL) and pentane (10 mL). The solid was recrystallized from DMF (5 mL) by vapour diffusion with CH₂Cl₂ to yield a red-brown powder (140 mg, 74 %).

¹H NMR (DMF-*d*₇, 300K, 500 MHz): δ 4.15 (t, *J* = 6.50, 4H), 6.27 (t, *J* = 6.50, 4H), 6.66 (m, 2H), 6.77 (m, 2H), 7.00 (d, *J* = 7.21, 2H), 7.06 (m, 2H), 7.11 (d, *J* = 8.53, 2H), 7.46 (s, 4H), 7.49 (m, 2H), 7.94 (d, *J* = 8.03, 2H), 8.16 (d, *J* = 8.27, 2H), 9.32 (s, 2H). ³*J*(¹⁹⁵Pt, H-9.32) = 78.8 Hz. ¹³C NMR (DMF-*d*₇, 300K, 125 MHz): δ 36.10, 84.63, 89.84, 115.75, 116.69, 116.84, 118.57, 122.09, 123.78, 123.89, 129.09, 132.63, 133.11, 135.13, 141.27, 144.32, 162.71, 169.70. ¹⁹⁵Pt NMR (DMF-*d*₇, 343K, 86 MHz): δ -1607 ppm. Mass Spectrum (ESI-MS, DMF): *m/z* = 996 (M), 997 (M+1). Anal. Calcd for C₃₄H₃₀N₄O₄Pt₂: C, 45.79; H, 3.03; N, 5.62. Found: C, 45.60; H, 2.88; N, 5.52.

Host-Guest Interaction of [Pt(salap)NH₃] (3) with [(PdCl)₂L_r](PF₆)₂ (1). A series of 3.00 mM solutions of **3** in DMF-*d*₇ containing varying amounts of **1**, ranging from 0.6 mM to 16.6 mM, were prepared. The solutions were permitted to equilibrate for at least an hour before they were examined by ¹H NMR (343K) (Figure 1) and spectrophotometry (Figure 2). The host alone is yellow in color and the guest alone is pale yellow. The host/guest mixtures varied from orange at low concentrations of guest to deep red at high concentrations of guest. The maximum chemical shift change for any proton of the host was 0.89 ppm (H_e). Several other protons of the host had maximum chemical shift changes of approximately 0.2-0.6 ppm. The maximum chemical shift

change observed for the guest was 0.58 ppm (H_b), with several other chemical shifts changing by about 0.2 ppm. The stoichiometry was determined using the “mole ratio” method^{9,10} to be one host molecule per one guest molecule, by plotting the change in chemical shift versus the mole ratio of guest to host for several protons of each (Figure 1). Equilibrium constants were determined using a curve fitting procedure.¹⁰ $K = 2600 \pm 500 \text{ M}^{-1}$. ESI-MS (DMF): $m/z = 820.7 (820.6) [3 \cdot 1]^{2+} (-2PF_6)$

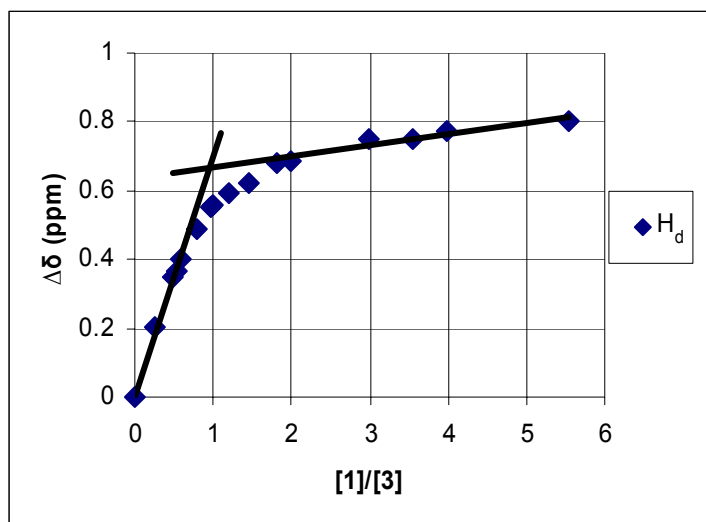


Figure 1. ^1H NMR stoichiometry titration curve for **3** with **1** in $\text{DMF-}d_7$ solution (3.0 mM) at 343K (70°C).

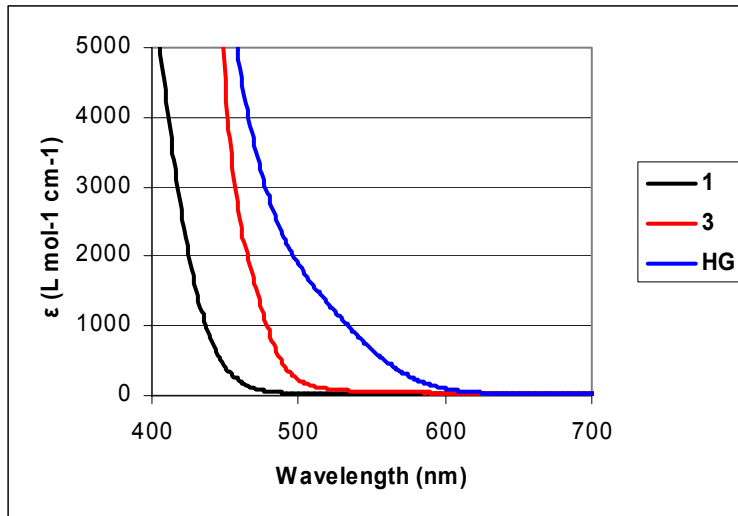


Figure 2. UV spectra for **1** (—), **3** (—) and [**3·1**] host-guest complex (—) in DMF solution (3.0 mM).

Host-Guest Interaction of [Pt(salap)]₂p-xylylenediamine (4) with [(PdCl)₂L_r](PF₆)₂ (1). A series of 1.50 mM solutions of **4** in DMF-*d*₇ containing varying amounts of **1**, ranging from 0.25 mM to 7.7 mM, were prepared. The solutions were permitted to equilibrate for at least an hour before they were examined by ¹H NMR (343K) (Figure 3) and spectrophotometry (Figure 4). The host alone is deep yellow in color and the guest alone is pale yellow. The host/guest mixtures varied from orange at low concentrations of guest to deep red at high concentrations of guest. The maximum chemical shift change for any proton of the host was 0.93 ppm (H_e). Several other protons of the host had maximum changes of approximately 0.25-0.65 ppm. The maximum chemical shift change observed for the guest was 0.54 ppm (H_b), with several other chemical shifts changing by about 0.2 ppm. The stoichiometry was determined using the “mole ratio” method^{9,10} to be one host molecule per one guest molecule, by plotting the change in

chemical shift versus the mole ratio of guest to host for several protons of each (Figure 3). Equilibrium constants were determined using a curve fitting procedure.¹⁰ $K = 1100 \pm 200 \text{ M}^{-1}$. ESI-MS (DMF): $m/z = 1083.1$ (1083.3) $[4 \cdot 1]^{2+}$ (-2PF_6)

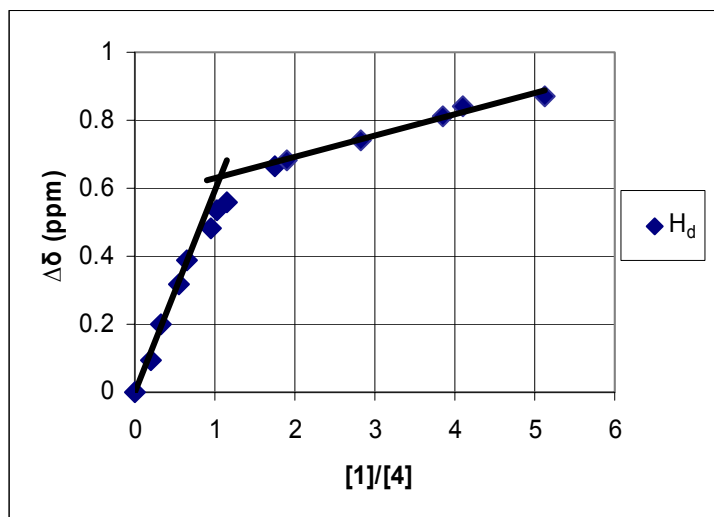


Figure 3. ^1H NMR stoichiometry titration curve for **4** with **1** in $\text{DMF-}d_7$ solution (1.5 mM) at 343K (70°C).

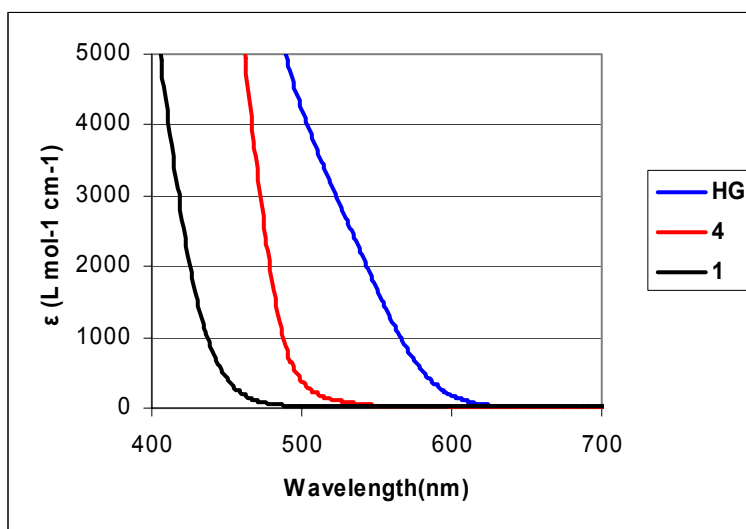


Figure 4. UV spectra for **1** (—), **4** (—) and **[4·1]** host-guest complex (—) in DMF solution (1.5 mM).

Host-Guest Interaction of [Pt(salap)]₂-1,4-propargyldiamine (5) with

[(PdCl)₂L_r](PF₆)₂ (1). A series of 1.50 mM solutions of 5 in DMF-*d*₇ containing varying amounts of 1, ranging from 0.3 mM to 8.6 mM, were prepared. The solutions were permitted to equilibrate for at least an hour before they were examined by ¹H NMR (343K) (Figure 5) and spectrophotometry (Figure 6). The host alone is deep yellow in color and the guest alone is pale yellow. The host/guest mixtures varied from orange at low concentrations of guest to deep red at high concentrations of guest. The maximum chemical shift change for any proton of the host was 0.78 ppm (H_e). Several other protons of the host had maximum changes of approximately 0.2-0.6 ppm. The maximum chemical shift change observed for the guest was 0.42 ppm (H_b), with several other chemical shifts changing by about 0.3 ppm. The stoichiometry was determined using the “mole ratio” method^{9,10} to be one host molecule per two guest molecules, by plotting the change in chemical shift versus the mole ratio of guest to host for several protons of each (Figure 5). Equilibrium constants were determined using a previously described algorithm.¹¹ This procedure yielded values of K₁ = 1000±200 M⁻¹, K₂ = 200±50 M⁻¹.

ESI-MS (DMF): m/z = 1107.3 (1107.3) [5·1]²⁺ (-2PF₆)

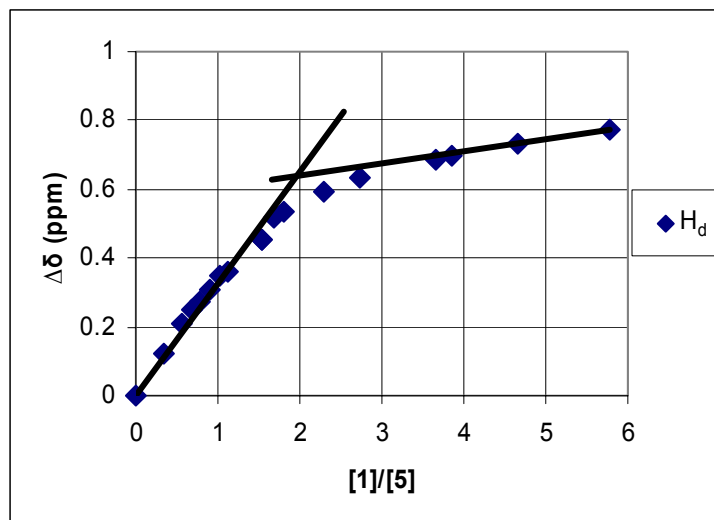


Figure 5. ^1H NMR stoichiometry titration curve for **5** with **1** in $\text{DMF-}d_7$ solution (1.5 mM) at 343K (70°C).

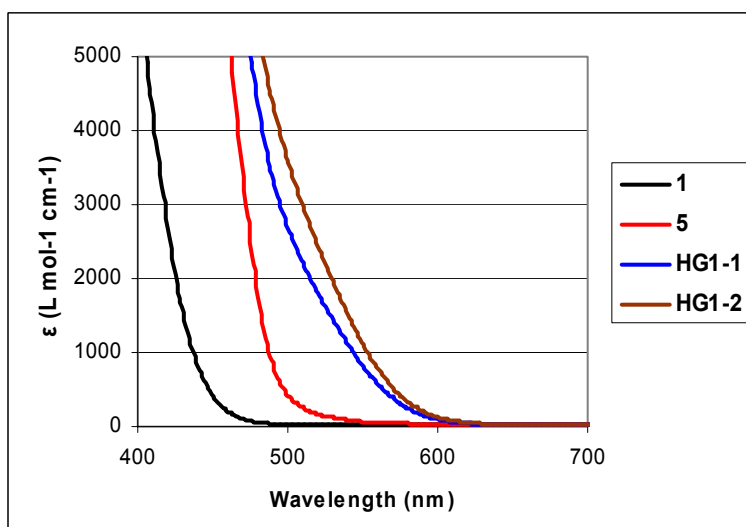


Figure 6. UV spectra for **1** (—), **5** (—) and [**5**·**1**] host-guest complexes, 1:1 stoichiometry (—) and 2:1 stoichiometry (—) in DMF solution (1.5 mM).

Host-Guest Interaction of $[\text{Pd}_4(4,4'\text{-Bipy})_2(\text{L}_r)_2](\text{PF}_6)_8$ (6**) with $[\text{Pt}(\text{salap})]_2p$ -xylylenediamine (**4**).** A series of 3.00 mM solutions of **6** in $\text{DMF-}d_7$ containing varying

amounts of **4**, ranging from 0.54 mM to 14.3 mM, were prepared. The solutions were permitted to equilibrate for at least an hour before they were examined by ^1H NMR (343K) (Figure 7) and spectrophotometry (Figure 8). The host alone is yellow in color and the guest alone is deep yellow. The host/guest mixtures varied from orange at low concentrations of guest to deep red at high concentrations of guest. The maximum chemical shift change for any proton of the host was 0.85 ppm (H_b). Several other protons of the host had maximum changes of approximately 0.24-0.68 ppm. The maximum chemical shift change observed for the guest was 0.46 ppm (H_c), with several other chemical shifts changing by about 0.3 ppm. The stoichiometry was determined using the “mole ratio” method^{9,10} to be one host molecule per one guest molecule, by plotting the change in chemical shift versus the mole ratio of guest to host for several protons of each (Figure 7). Equilibrium constants were determined using a curve fitting procedure.¹⁰ $K = 1500 \pm 200 \text{ M}^{-1}$. ESI-MS (DMF): $m/z = 1426.3$ (**1426.3**) $[\text{6}\cdot\text{4}]^{3+}(-3\text{PF}_2)$, 1033.8 (**1033.6**) $[\text{6}\cdot\text{4}]^{4+}(-4\text{PF}_2)$, 798.2 (**798.3**) $[\text{6}\cdot\text{4}]^{5+}(-5\text{PF}_2)$.

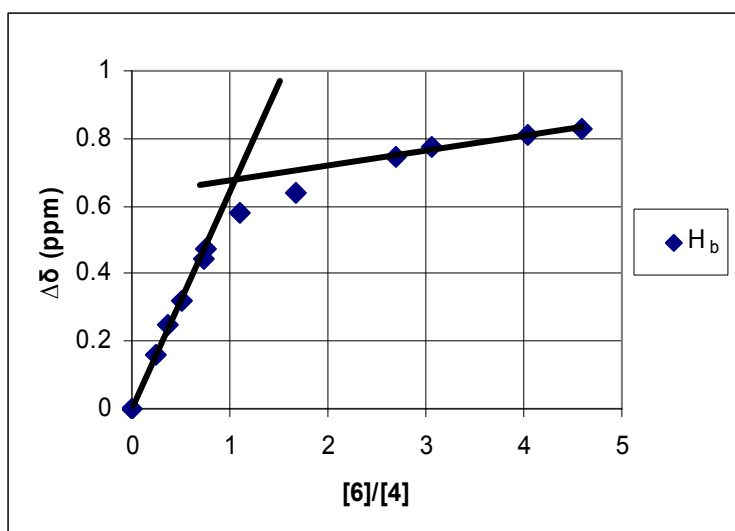


Figure 7. ^1H NMR stoichiometry titration curve for **6** with **4** in $\text{DMF-}d_7$ solution (3.0 mM) at 343K (70°C).

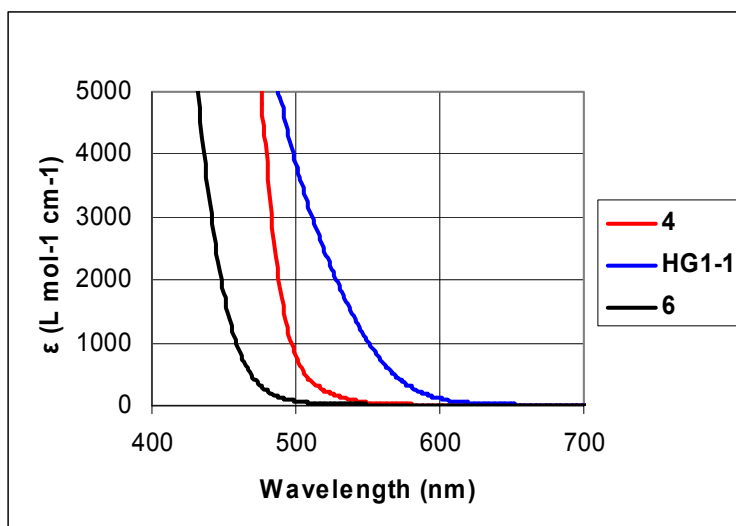


Figure 8. UV spectra for **6** (—), **4** (—) and [**6·4**] host-guest complex (—) in DMF solution
(3.0 mM)

Table 1: Selected Data of Host-Guest complexes.

HOST	GUEST	K (M ⁻¹)	ΔG (kcal/mole)	Stoichiometry (NMR)	ESMS
					Observed (Calculated)
3	1	2600±500	-5.35	1:1	820.7 (820.6) [3·1] ²⁺ (-2PF ₆)
4	1	1100±200	-4.77	1:1	1083.1 (1083.3) [4·1] ²⁺ (-2PF ₆)
5	1	K ₁ 1000±200 K ₂ 200±50	-4.70 -3.61	2:1	1107.3 (1107.3) [5·1] ²⁺ (-2PF ₆)
6	4	1500±200	-4.98	1:1	1426.3 (1426.3) [6·4] ³⁺ (-3PF ₆) 1033.8 (1033.6) [6·4] ⁴⁺ (-4PF ₆) 798.2 (798.3) [6·4] ⁵⁺ (-5PF ₆)

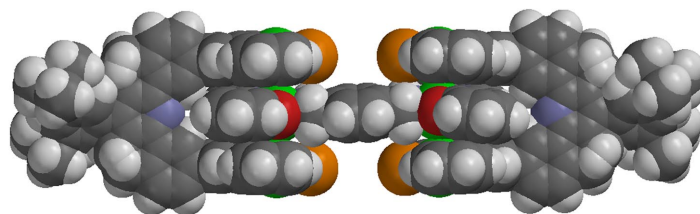


Figure 9. Molecular modelling of the 2:1 complex between **1** and **4**.

(PC Spartan pro, Wavefunction, Irvine, CA)

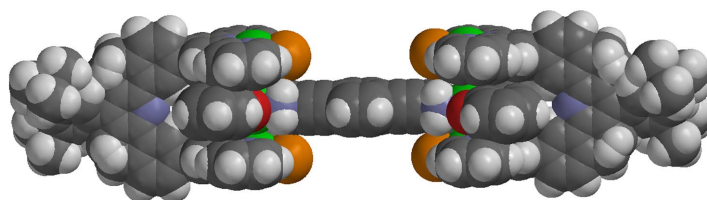


Figure 10. Molecular modelling of the 2:1 complex between **1** and **5**.

(PC Spartan pro, Wavefunction, Irvine, CA)

Electrostatic Repulsion Calculation.¹²

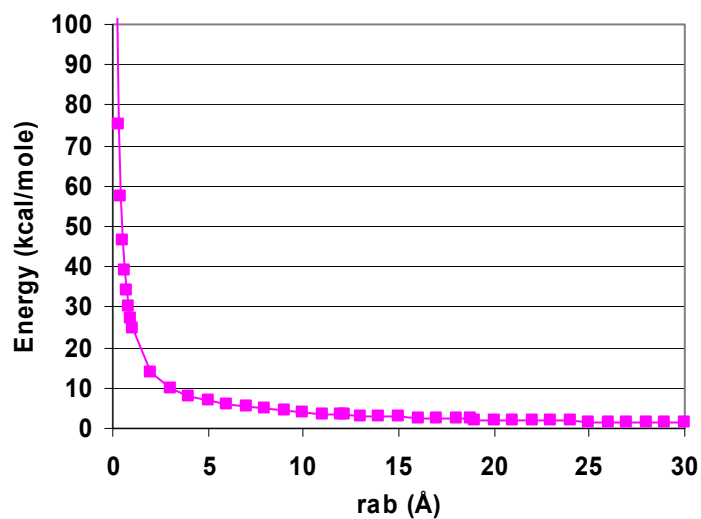
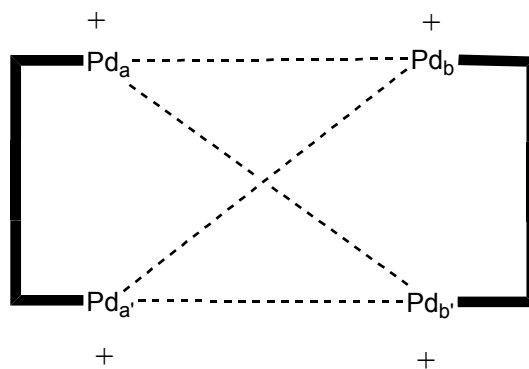


Figure 11. Electrostatic Repulsion Curve - Energy (kcal/mole) vs Distance (Å) (ϵ_{DMF} ,

$_{343\text{K}} = 30.67$)



$$\Delta G = \frac{N_A z^2 e^2}{4\pi\epsilon\epsilon_o} \left(\frac{1}{r_{ab}} + \frac{1}{r_{a'b}} + \frac{1}{r_{ab'}} + \frac{1}{r_{a'b'}} \right)$$

$$e \text{ (Elementary Charge)} = 1.602177 \times 10^{-19} \text{ C.}$$

$$N_a \text{ (Avogadro constant)} = 6.023 \times 10^{23} \text{ mol}^{-1}.$$

$$4\pi\epsilon_o \text{ (Vacuum permittivity)} = 1.11265 \times 10^{-10} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}.$$

$$\epsilon \text{ (Dielectric constant)}_{\text{DMF, 343K}} = 30.67.$$

$$z \text{ (charge)} = z_a = z_{a'} = z_b = z_{b'} = 1+$$

$$r_{aa'} = r_{bb'} = 6.8 \text{ \AA}$$

For the 2:1 complex of **4** with **1**, $r_{ab} = r_{a'b} = 12.2 \text{ \AA}$ and $r_{ab'} = r_{a'b'} = 14.0 \text{ \AA}$

For the 2:1 complex of **5** with **1**, $r_{ab} = r_{a'b} = 18.8 \text{ \AA}$ and $r_{ab'} = r_{a'b'} = 20.0 \text{ \AA}$

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