pH-Responsive assembly and disassembly of a supramolecular cryptand-based pseudorotaxane driven by π-π stacking interaction

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## Electronic Supplementary Information (19 pages)

1. Materials and methods

All reagents were commercially available and used as supplied without further purification. BMP32C10 (**1**), BMP32C10 diol (**5**) was synthesized by published literature procedures.[S1] ^{1}H NMR spectra were collected on a temperature-controlled 400 MHz or 500 MHz spectrometer. ^{13}C NMR spectra were recorded on a Bruker AVANCE DMX-500 spectrometer at 125 MHz. Low-resolution electrospray ionization (LRESI) mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with ESI interface and ion trap analyzer. High-resolution electrospray ionization (HRESI) mass spectra were obtained on a Bruker 7-Tesla FT-ICR mass spectrometer equipped with an electrospray source (Billerica, MA, USA). The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus. The crystals data were collected on an Oxford Diffraction Xcalibur Atlas Gemini ultra.

2. Synthesis of 2 and 3

Scheme S1. Synthesis of **2** and **3**.
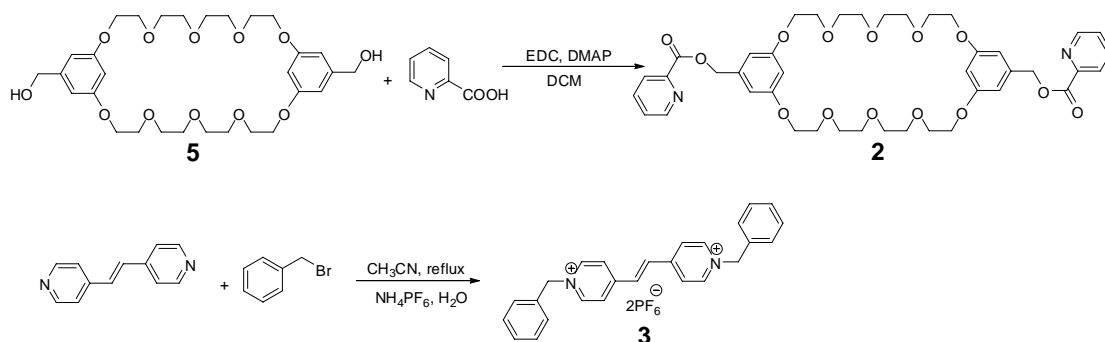
2.1. Synthesis of compound 2
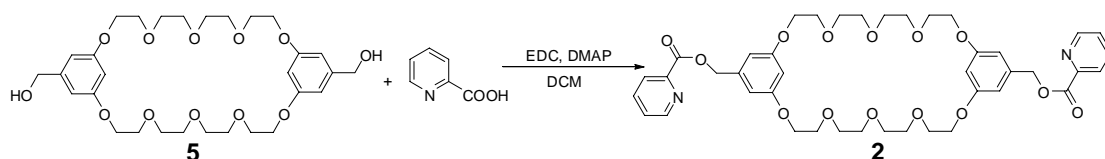
A solution of **5** (597 mg, 1.0 mmol), α-picolinic acid (739 mg, 6.0 mmol) and 4-dimethylaminopyridine (DMAP) (122 mg, 1.0 mmol) in dichloromethane (30 mL) was stirred for 10 minutes at 0 °C. To this solution was added EDC (383 mg, 2.0 mmol). The reaction mixture was stirred for 24 h at room temperature, filtered, and concentrated to give a crude, which was purified by flash column chromatography (methanol/dichloromethane, 100:1 v/v) to afford **2** as a white solid (710 mg, 88%). The ^{1}H NMR spectrum of **2** is shown in Figure S1. ^{1}H NMR (400 MHz, chloroform-d, room temperature) δ (ppm): 8.75 (d, J = 4.0 Hz, 2H), 8.10 (d, J = 8.0 Hz, 2H), 7.79–7.83 (m, 2H), 7.44–7.47 (m, 2H), 6.60 (d, J = 1.6 Hz, 4H), 6.43 (s, 2H), 5.33 (s, 4H), 4.03–4.06 (m, 8H), 3.79–3.81 (m, 8H), 3.59–3.73 (m, 16H). mp 79.6–81.3 °C. The ^{13}C NMR spectrum of **2** is shown in Figure S2. ^{13}C NMR (125 MHz, chloroform-d, room temperature) δ (ppm): 67.54, 67.78, 69.81, 71.03, 71.06, 101.54, 107.37, 125.54, 127.19, 137.23, 137.92, 148.10, 150.12, 160.26, and 165.11. LRESIMS is shown in Figure S3: m/z 807.3 [M + H]$^+$ (100%), 829.3 [M + Na]$^+$ (100%), 845.2 [M + K]$^+$ (100%). HRESIMS: m/z calcd for [M]$^+$ $C_{42}H_{50}N_2O_{14}$, 806.3262; found 806.3246, error −2.0 ppm.
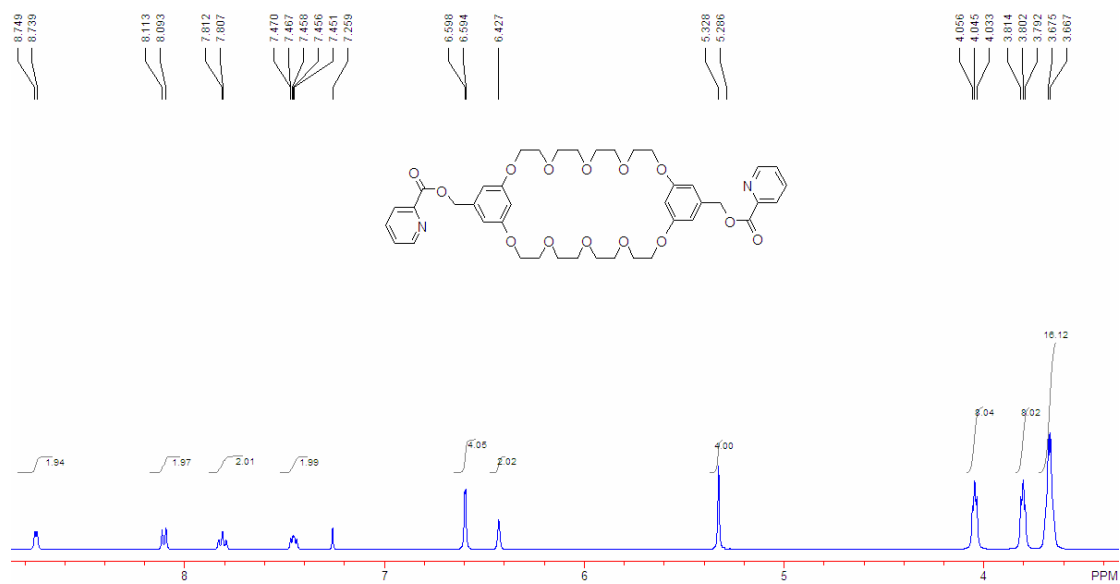
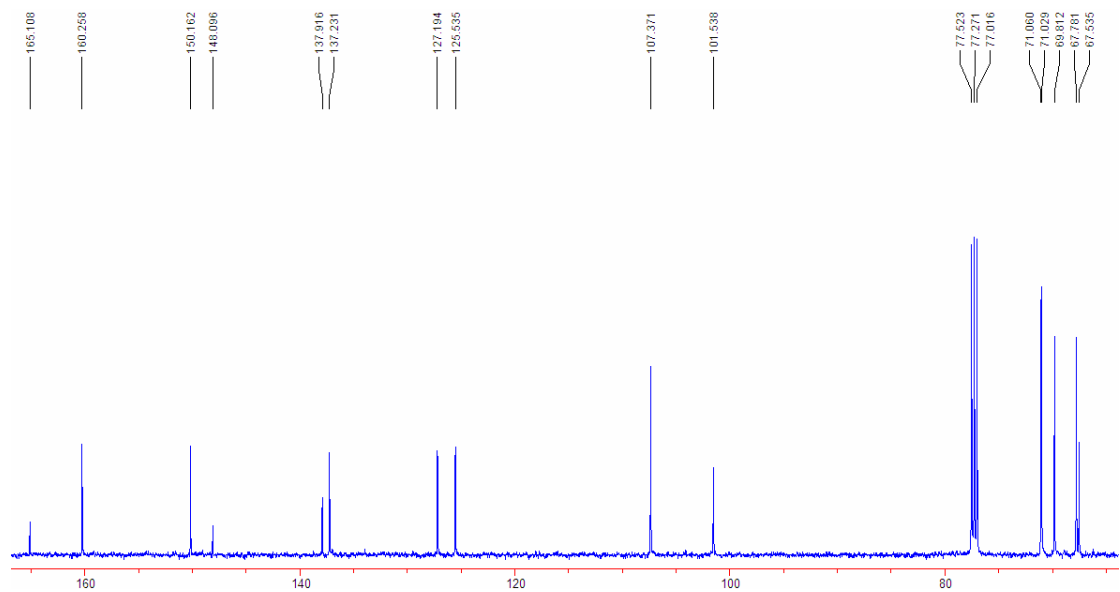**Figure S1.** ^{1}H NMR spectrum (400 MHz, chloroform-*d*, room temperature) of **2**.

Figure S2. ^{13}C NMR spectrum (125 MHz, chloroform-*d*, room temperature) of **2**.

Display Report

Analysis Info

Analysis Name	11041228.d		Acquisition Date	04/12/11 10:16:52
Method	Copy of E3Kp Default.ms		Operator	Administrator
Sample Name	YXZ-229		Instrument	esquire3000plus
Comment				

Acquisition Parameter

|						
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Capillary Exit	203.5 Volt	Skim 1	40.0 Volt	Trap Drive	55.5
Accumulation Time	685 µs	Averages	5 Spectra	Auto MS/MS	off
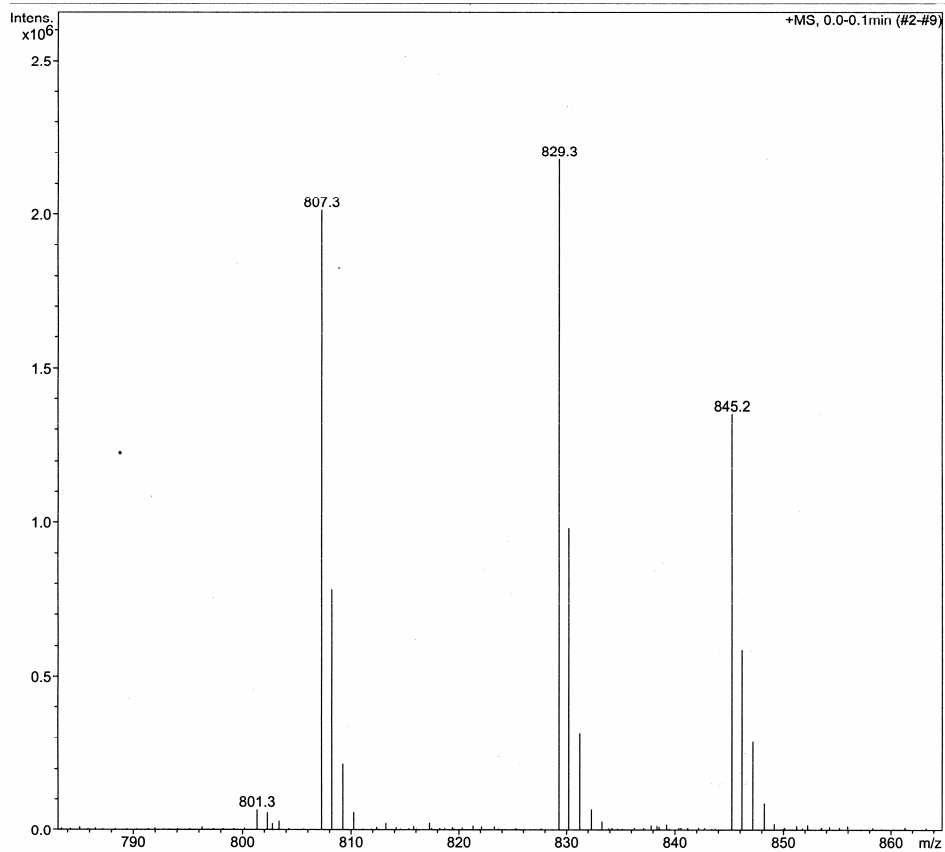
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Figure S3. Electrospray ionization mass spectrum of **2**.

2.2. Synthesis of compound 3
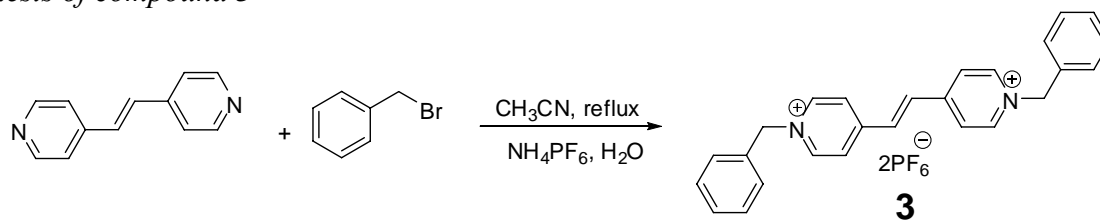
A mixture of benzyl bromide (1.03 g, 6.0 mmol) and 1,2-bis(4-pyridyl)ethylene (182 mg, 1.0 mmol) was dissolved in CH_3CN (10 mL) and was stirred under N_2 for 24 h at reflux. Till cooled, the precipitate was filtered off. This solid was dissolved in hot water (100 mL) and saturated aqueous NH_4PF_6 was added. The precipitate was collected and washed with H_2O to yield **3** as a white solid (654 mg, 98%). mp 265.9–267.5 °C. The ^{1}H NMR spectrum of **3** is shown in Figure S4. ^{1}H NMR (400 MHz, acetone-d_6, room temperature) δ (ppm): 9.26 (d, J = 6.4 Hz, 4H), 8.50 (d, J = 6.8 Hz, 4H), 8.23 (s, 2H), 7.58–7.67 (m, 4H), 7.46–7.52 (m, 6H), 6.05 (s, 4H). The ^{13}C NMR spectrum of **3** is shown in Figure S5. ^{13}C NMR (125 MHz, acetonitrile-d_3, room temperature) δ (ppm): 65.11, 127.13, 130.20, 130.54, 130.94, 133.84, 135.03, 145.76, and 152.50. LRESIMS is shown in Figure S6: m/z 363.1 $[M - 2PF_6]^{2+}$ (100%), 509.0 $[M - PF_6]^+$ (100%). HRESIMS: m/z calcd for $[M - 2PF_6]^{2+}$ $C_{26}H_{24}N_2^{2+}$, 364.1939; found 364.1927, error −3.3 ppm.
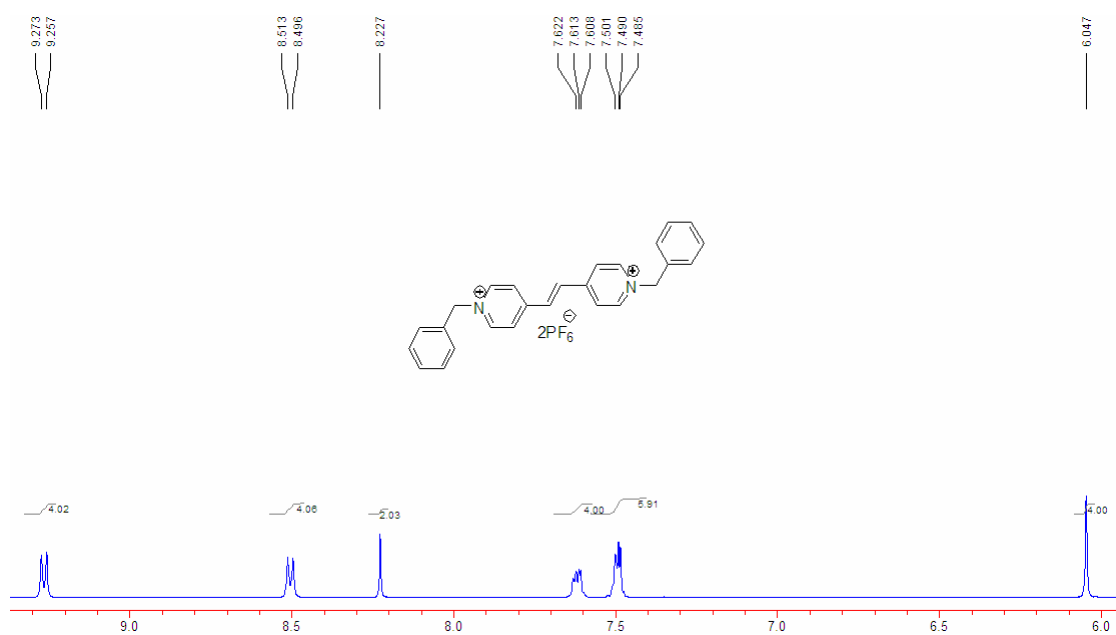
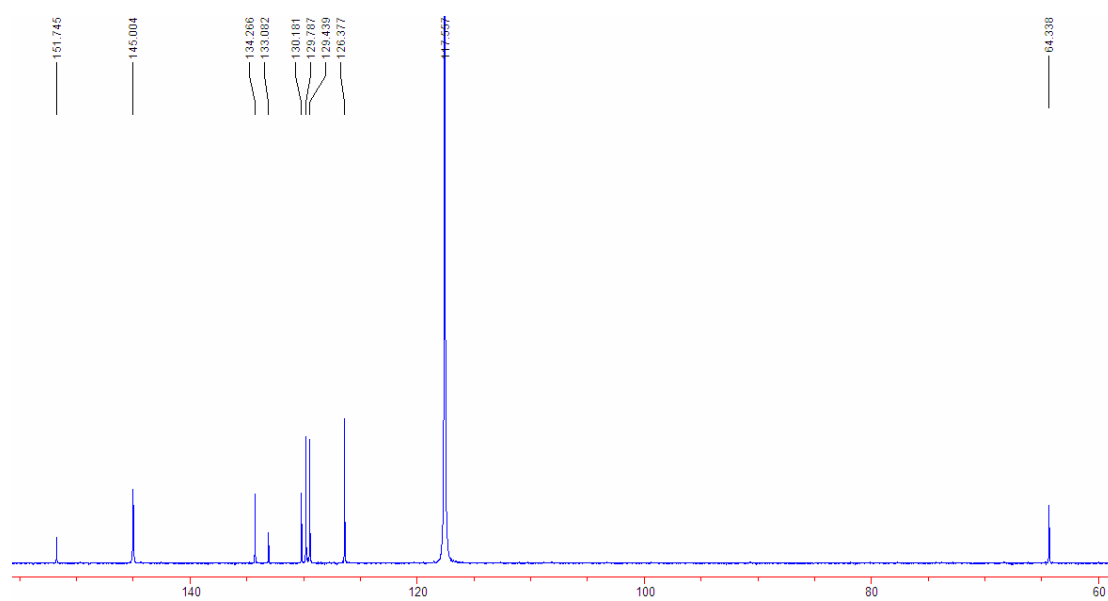***Figure S4.*** ^{1}H NMR spectrum (400 MHz, acetone-d_6, room temperature) of **3**.

Figure S5. ^{13}C NMR spectrum (125 MHz, acetonitrile-d_3, room temperature) of **3**.

Display Report

Analysis Info

Analysis Name	11041928.d	Acquisition Date	04/19/11 20:10:39
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Sample Name	YXZ-2516	Instrument	esquire3000plus
Comment			

Acquisition Parameter

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Mass Range Mode	Std/Normal	Scan Begin	103 m/z	Scan End	1000 m/z		
Capillary Exit	226.0 Volt	Skim 1	40.0 Volt	Trap Drive	62.2		
Accumulation Time	465 µs	Averages	5 Spectra	Auto MS/MS	off		

+MS, 0.0-0.1min (#2-#10)
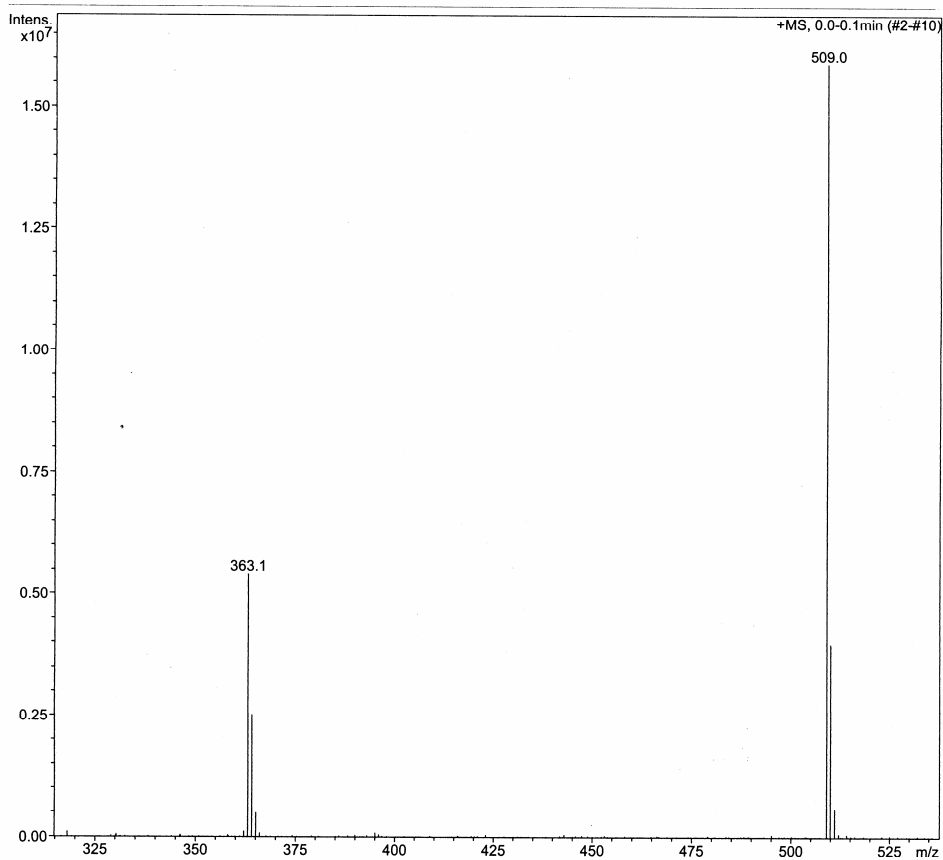
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Figure S6. Electrospray ionization mass spectrum of **3**.

*3. Job plots of **1**⊃**3**, **2**⊃**3**, and **2**⊃**4** based on UV-Vis data in acetone*

(a)

(b)

(c)
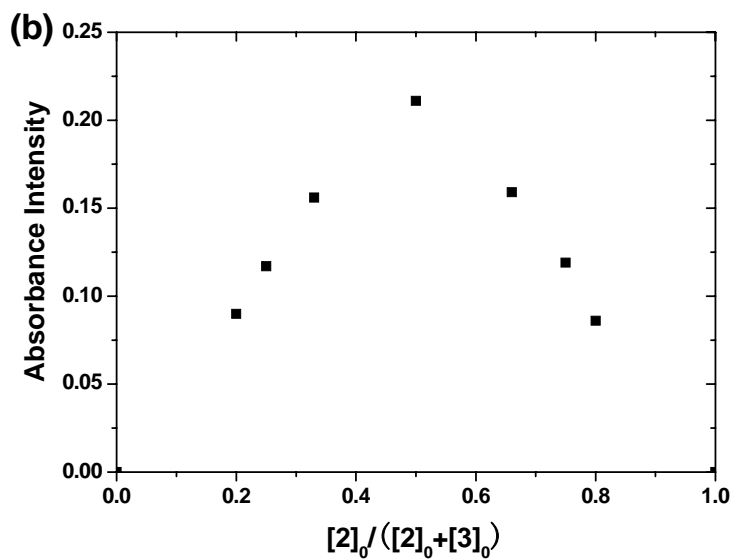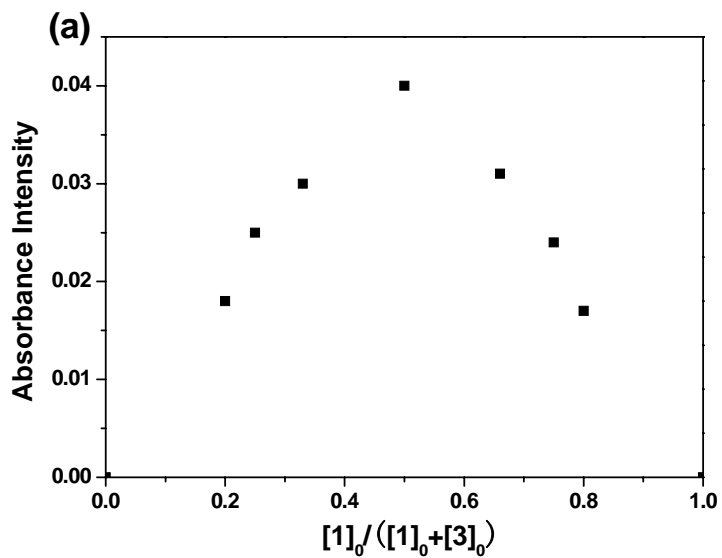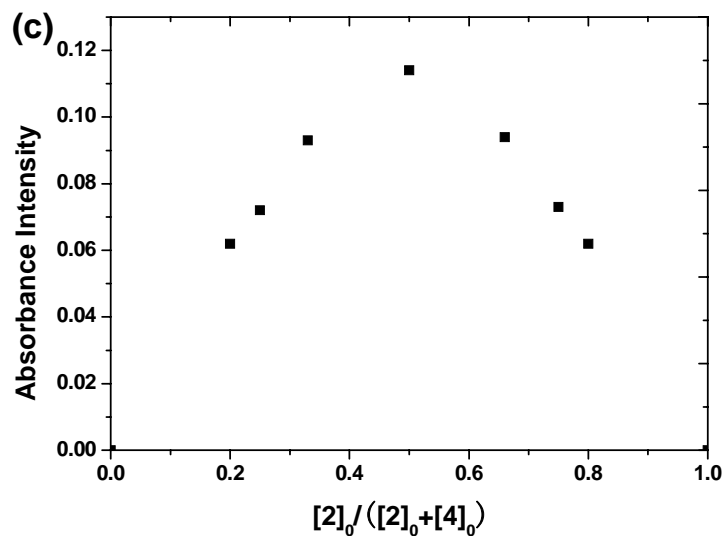
Figure S7. Job plots showing the 1:1 stoichiometries of the complexes between **1** and **3** (a), between **2** and **3** (b), and between **2** and **4** (c) in acetone: (a) $[1]_0 + [3]_0 = 1.00$ mM; (b) $[2]_0 + [3]_0 = 1.00$ mM; (c) $[2]_0 + [4]_0 = 1.00$ mM. $[1]_0$, $[2]_0$, $[3]_0$, and $[4]_0$ are the initial concentrations of **1**, **2**, **3**, and **4**, respectively.

4. Determination of association constants of 1⊃3, 2⊃3, and 2⊃4 [S2]

The association constants of complexes *1⊃3, 2⊃3, and 2⊃4* were determined by probing the charge-transfer band of the complexes by UV-vis spectroscopy and employing a titration method. Progressive addition of an acetone solution with high guest **3** (or **4**) concentration and low host **1** or **2** concentration to a acetone solution with the same concentration of host **1** or **2** resulted in an increase of the intensity of the charge-transfer band of the complex. Treatment of the collected absorbance data at $\lambda = 403$ nm with a non-linear curve-fitting program afforded the corresponding association constants (K_a): 962 ($\pm$ 55) M^{-1} for **2·3**, and 127 ($\pm$ 16) M^{-1} for **1·3**, and 714 ($\pm$ 78) M^{-1} for **2⊃4**.

The non-linear curve-fitting was based on the equation:

$$A = (A_\infty/[H]_0)\,(0.5[G]_0 + 0.5([H]_0 + 1/K_a) - (0.5\,([G]_0^2 + (2[G]_0(1/K_a - [H]_0)) + (1/K_a + [H]_0)^2)^{0.5})) \qquad \text{(Eq. S1)}$$

Where A is the absorption intensity of the charge-transfer band ($\lambda = 403$ nm) at $[G]_0$, A_∞ is the absorption intensity of the charge-transfer band ($\lambda = 403$ nm) when the host is completely complexed, $[H]_0$ is the fixed initial concentration of the host, and $[G]_0$ is the initial concentration of the guest.

Figure S8. (a) The absorption spectral changes of **1** upon addition of **3** and (b) the absorbance intensity changes upon addition of **3**. The red solid line was obtained from the non-linear curve-fitting using Eq. S1.

(c)

(d)

Chi^2/DoF   = 0.00004
R^2 = 0.99938

P1 = 1.75322 ±0.04298
P2 = 0.00104 ±0.00006
Ka = 962 ± 55

Figure S9. (c) The absorption spectral changes of **2** upon addition of **3** and (d) the absorbance intensity changes upon addition of **3**. The red solid line was obtained from the non-linear curve-fitting using Eq. S1.

(e)

(Absorption spectral changes plot: Absorbance Intensity vs Wavelength (nm), 360–500 nm)

(f)

(Plot: Absorbance Intensity vs [4] (M))

Chi^2/DoF = 0.00003
R^2 = 0.99779

P1   0.8882   ±0.0466
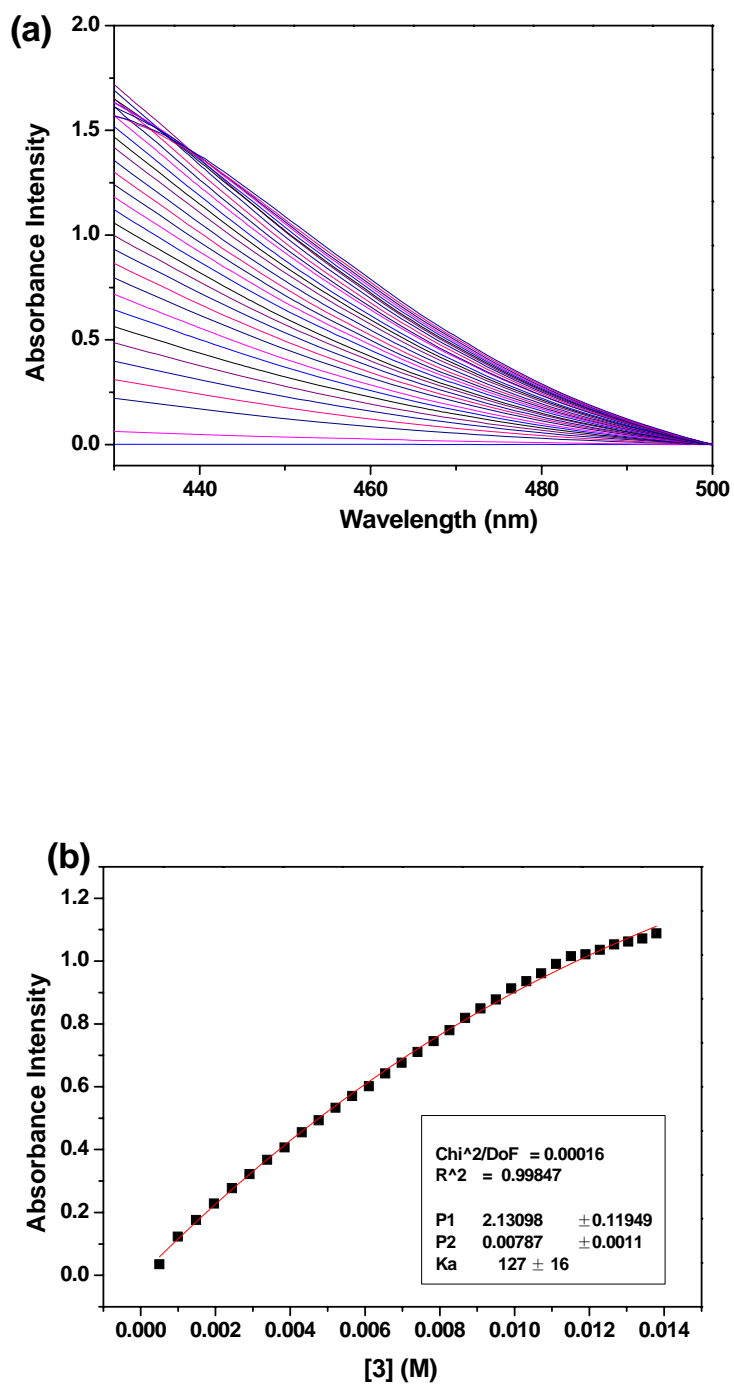P2   0.0014   ±0.00015
Ka   714   ± 78

Figure S10. (e) The absorption spectral changes of **2** upon addition of **4** and (f) the absorbance intensity changes upon addition of **4**. The red solid line was obtained from the non-linear curve-fitting using Eq. S1.
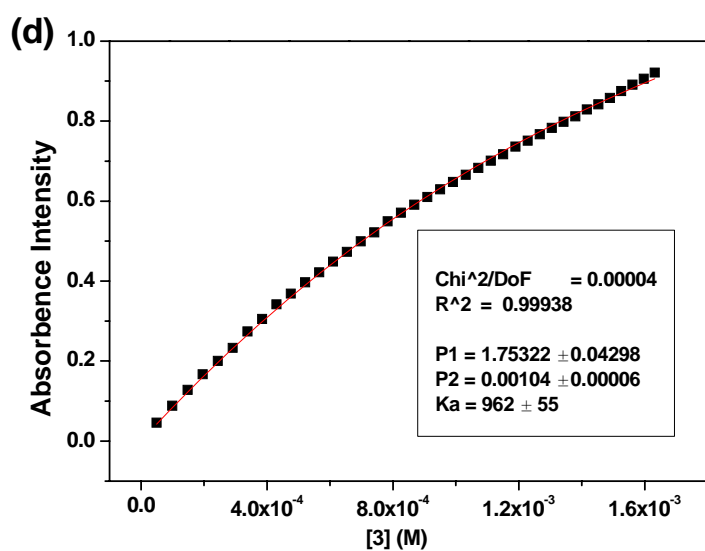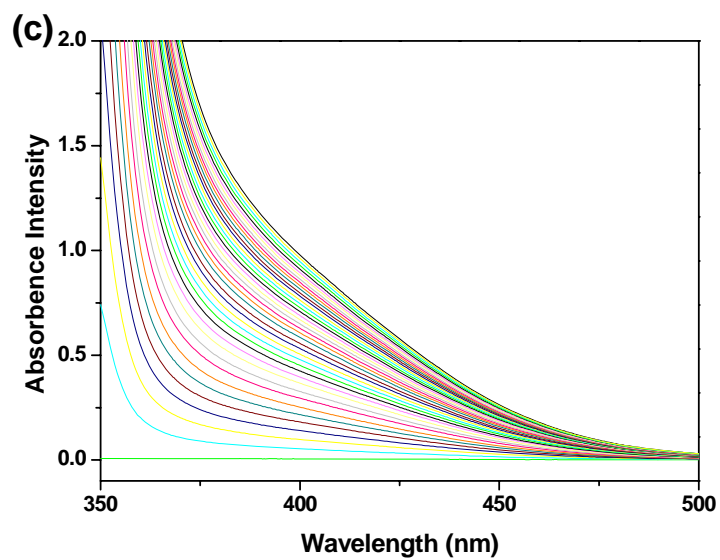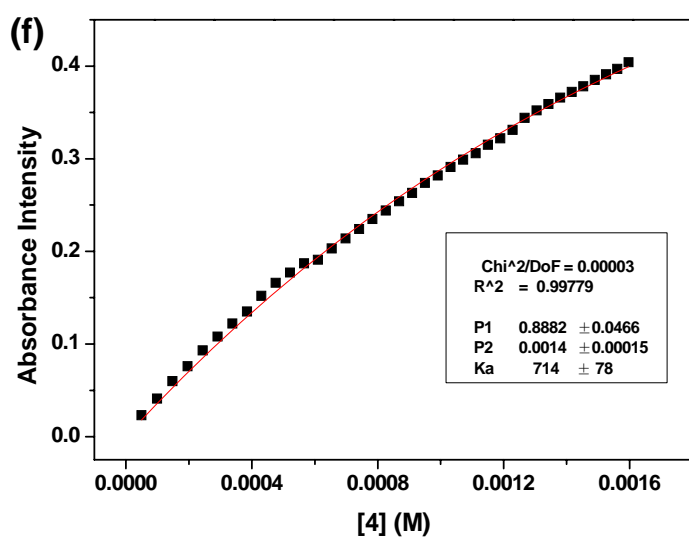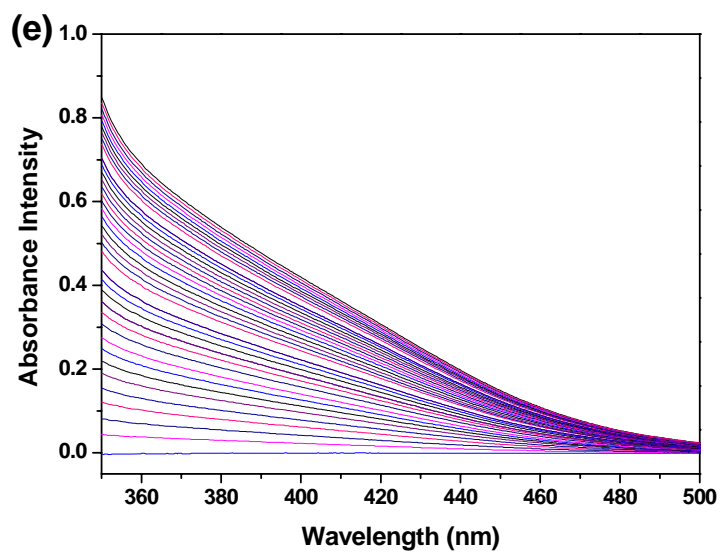
*5. Electrospray ionization mass spectra of equimolar acetone solutions of **2** with either of guests **3** and **4***

Display Report

Analysis Info

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Method	Copy of E3Kp Default.ms		Operator	Administrator
Sample Name	YXZ-HG		Instrument	esquire3000plus
Comment				

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off	
Mass Range Mode	Std/Normal	Scan Begin	104 m/z	Scan End	1800 m/z	
Capillary Exit	280.0 Volt	Skim 1	40.0 Volt	Trap Drive	116.0	
Accumulation Time	393 µs	Averages	5 Spectra	Auto MS/MS	off	

Bruker Daltonics DataAnalysis 3.1   printed: 04/18/11   09:41:06   Page 1 of 1
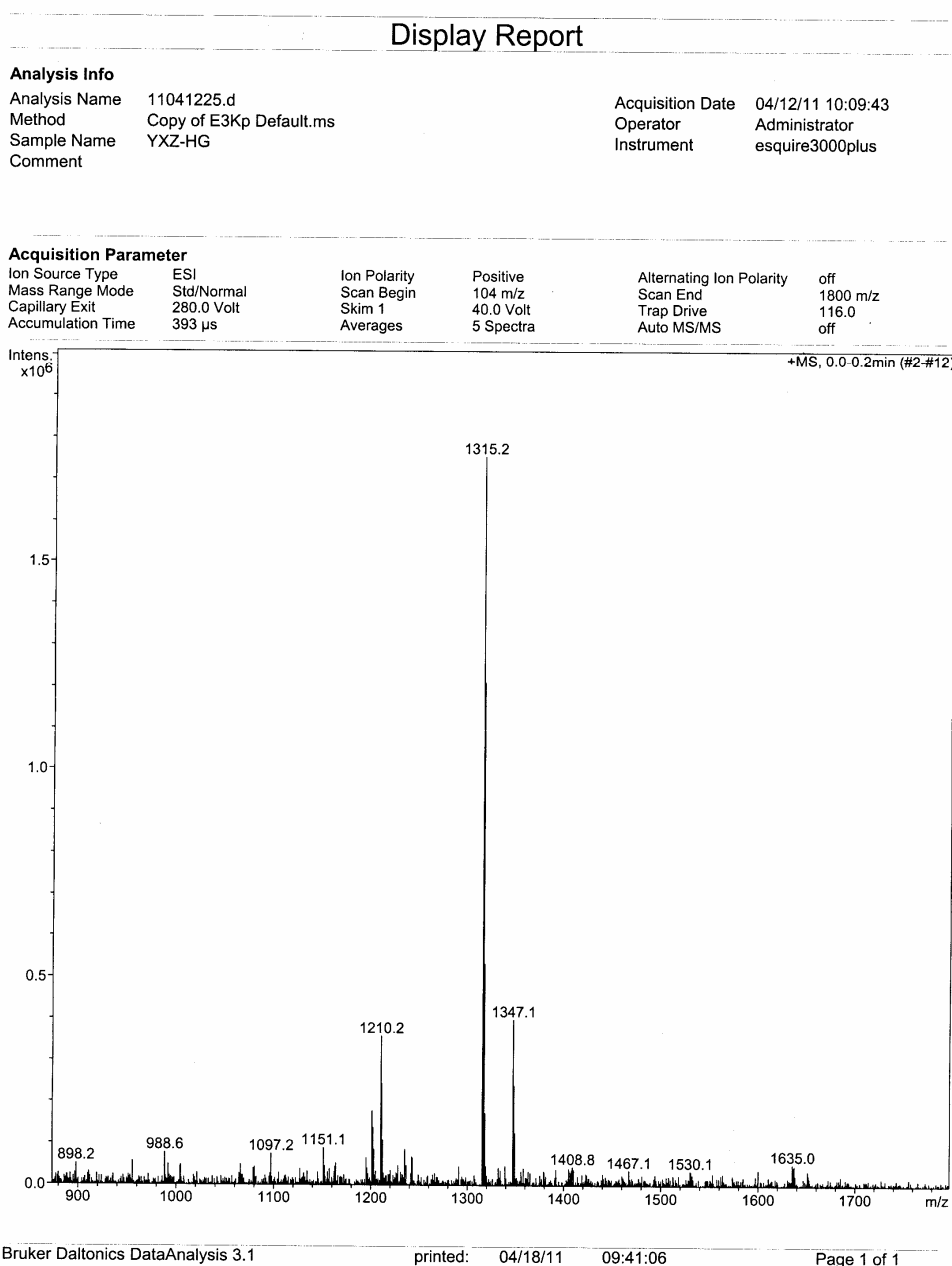
Figure S11. Positive electrospray ionization mass spectrum in acetone of equimolar mixtures of **2** and **3** gave strong mass fragment: 1315.2, which correspond to $[\textbf{2}{\supset}\textbf{3} - \text{PF}_6]^+$, respectively. This result confirmed the 1:1 complexation stoichiometry between **2** and **3**.

S15

Display Report

Analysis Info

Analysis Name	11051904.d	Acquisition Date	05/19/11 18:58:27
Method	Copy of E3Kp Default.ms	Operator	Administrator
Sample Name	YXZ-25	Instrument	esquire3000plus
Comment			

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off	
Mass Range Mode	Std/Normal	Scan Begin	400 m/z	Scan End	1500 m/z	
Capillary Exit	280.0 Volt	Skim 1	40.0 Volt	Trap Drive	89.1	
Accumulation Time	367 µs	Averages	8 Spectra	Auto MS/MS	off	

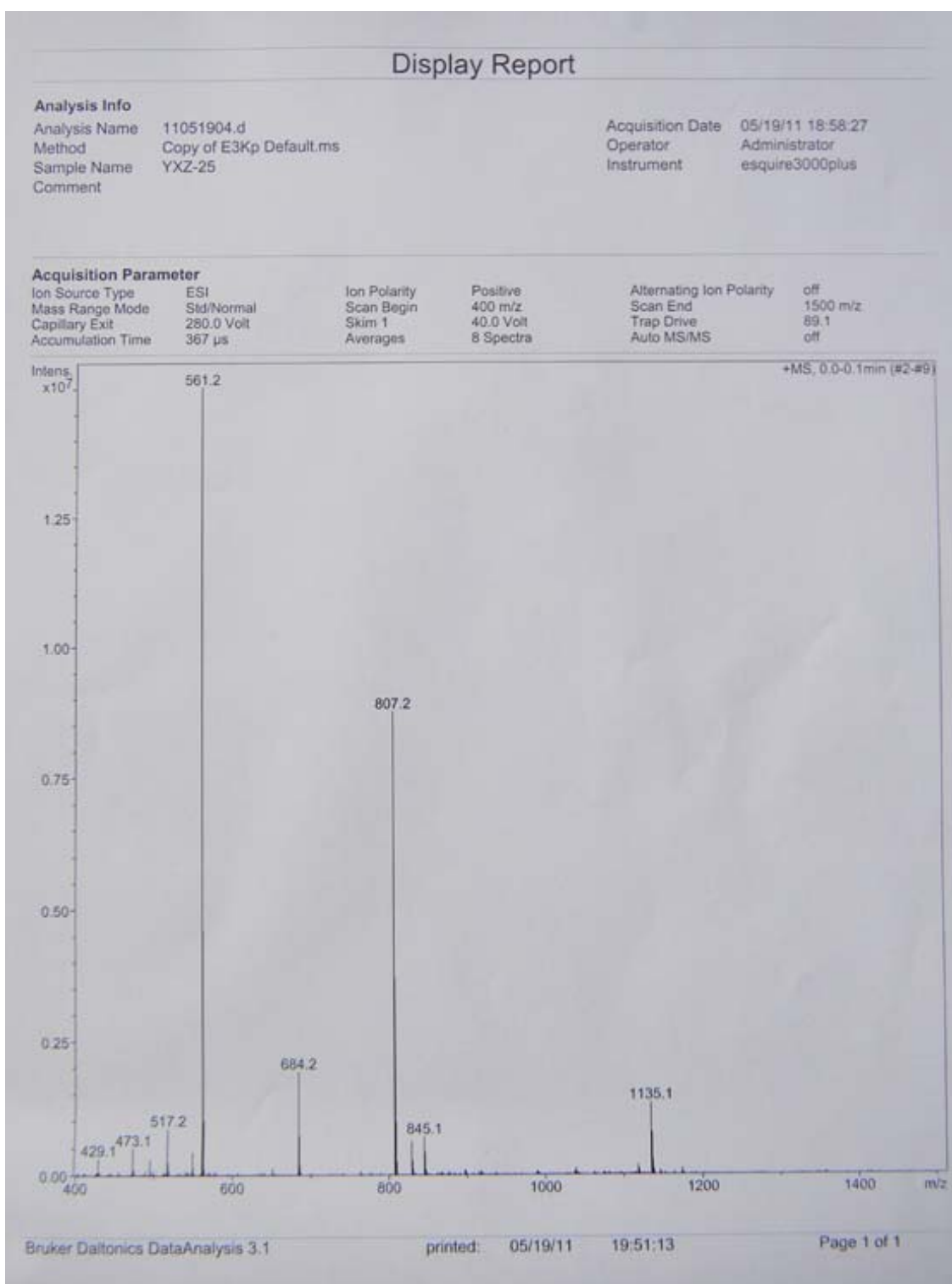Bruker Daltonics DataAnalysis 3.1   printed: 05/19/11   19:51:13   Page 1 of 1

Figure S12. Positive electrospray ionization mass spectrum in acetone of equimolar mixtures of **2** and **4** gave mass fragment: m/z 1135.1, which correspond to $[2 \supset 3 - PF_6]^+$.

6. *Partial ^{1}H NMR spectra of equimolar solutions of either of hosts **1** and **2** with guests **3***
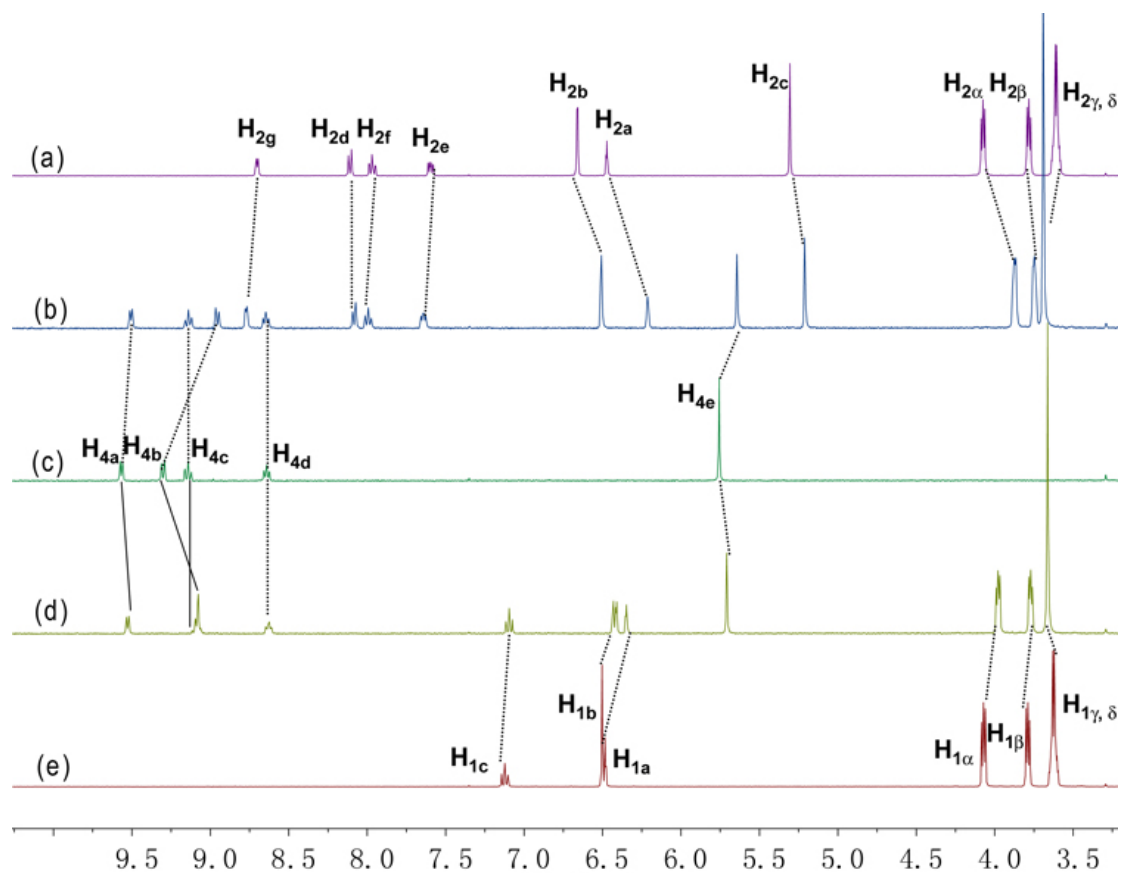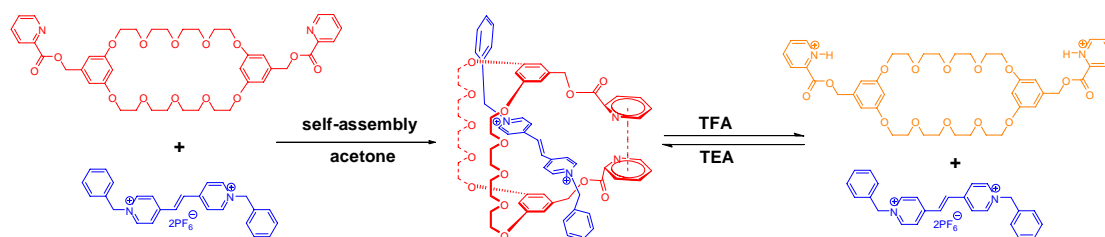

Figure S13. Partial ^{1}H NMR spectra (acetone-d_6, 293 K, 400 MHz) of (a) 2.00 mM **2**; (b) 2.00 mM **2** + 2.00 mM **4**; (c) 2.00 mM **4**; (d) 2.00 mM **1** + 2.00 mM **4**; and (e) 2.00 mM **1**.

7. Schematic representation of reversible control of the formation of [2] pseudorataxane based on a supramolecular cryptand

Scheme S2. Reversible control of the formation of [2] pseudorataxane based on the supramolecular cryptand.

8. X-ray crystal data for 2⊃3

Crystallographic data: block, yellow, $0.35 \times 0.26 \times 0.23$ mm^3, $C_{68}H_{74}F_{12}N_4O_{14}P_2$, *FW* 1461.25, triclinic, space group *P* -1, $a = 10.7621(4)$, $b = 12.8281(5)$, $c = 29.8195(11)$ Å, $\alpha = 85.387(3)°$, $\beta = 84.518(3)°$, $\gamma = 70.803(4)°$, $V = 3864.8(3)$ Å^3, $Z = 2$, $D_c = 1.256$ g cm^{-3}, $T = 100$ (2) K, $\mu = 1.286$ mm^{-1}, 29018 measured reflections, 13386 independent reflections, 901 parameters, 0 restraints, $F(000) = 1520$, $R(\text{int}) = 0.0229$, $R_1 = 0.0689$, $wR_1 = 0.1625$ (all data), $R_2 = 0.0621$, $wR_2 = 0.1573$ [$I > 2\sigma(I)$], max. residual density 1.455 e•Å^{-3}, and goodness-of-fit (F^2) = 1.066. CCDC 829264.

9. X-ray crystal data for 2⊃4

Crystallographic data: block, yellow, $0.28 \times 0.23 \times 0.18$ mm^3, $C_{54}H_{62}F_{12}N_4O_{14}P_2$, *FW* 1281.02, monoclinic, space group *P* 21/c, $a = 10.8701(3)$, $b = 22.6954(6)$, $c = 22.8977(6)$ Å, $\alpha = 90.00°$, $\beta = 100.794(3)°$, $\gamma = 90.00°$, $V = 5549.0(3)$ Å^3, $Z = 4$, $D_c = 1.533$ g cm^{-3}, $T = 100$ (2) K, $\mu = 1.700$ mm^{-1}, 31682 measured reflections, 9701 independent reflections, 775 parameters, 0 restraints, $F(000) = 2656$, $R(\text{int}) = 0.0394$, $R_1 = 0.0543$, $wR_1 = 0.1325$ (all data), $R_2 = 0.0432$, $wR_2 = 0.1224$ [$I > 2\sigma(I)$], max. residual density 0.962 e•Å^{-3}, and goodness-of-fit (F^2) = 1.091. CCDC 829263.

References:

S1. H. W. Gibson, D. S. Nagvekar, *Can. J. Chem.* **1997**, *75*, 1375–1384.

S2. K. A. Connors, *Binding Constants*; Wiley: New York, **1987**. Corbin, P. S. Ph.D. Dissertation, University of Illinois at Urbana-Champaign, Urbana, IL, **1999**. P. R. Ashton, R. Ballardini, V. Balzani, M. Belohradsky, M. T. Gandolfi, D. Philp, L. Prodi, F. M. Raymo, M. V. Reddington, N. Spencer, J. F. Stoddart, M. Venturi, D. J. Williams, *J. Am. Chem. Soc.* **1996**, *118*, 4931–4951.