S1: NMR and MS spectra of the corresponding complexes

Supporting Information

for

Templated versus non-templated synthesis of benzo-21-crown-7 and the influence of substituents on its complexing properties

Wei Jiang and Christoph A. Schalley*

Address: Institut für Chemie und Biochemie, Freie Universität Berlin, Takustraße 3, 14195 Berlin, Germany

E-mail: Christoph A. Schalley - christoph@schalley-lab.de

* Corresponding author

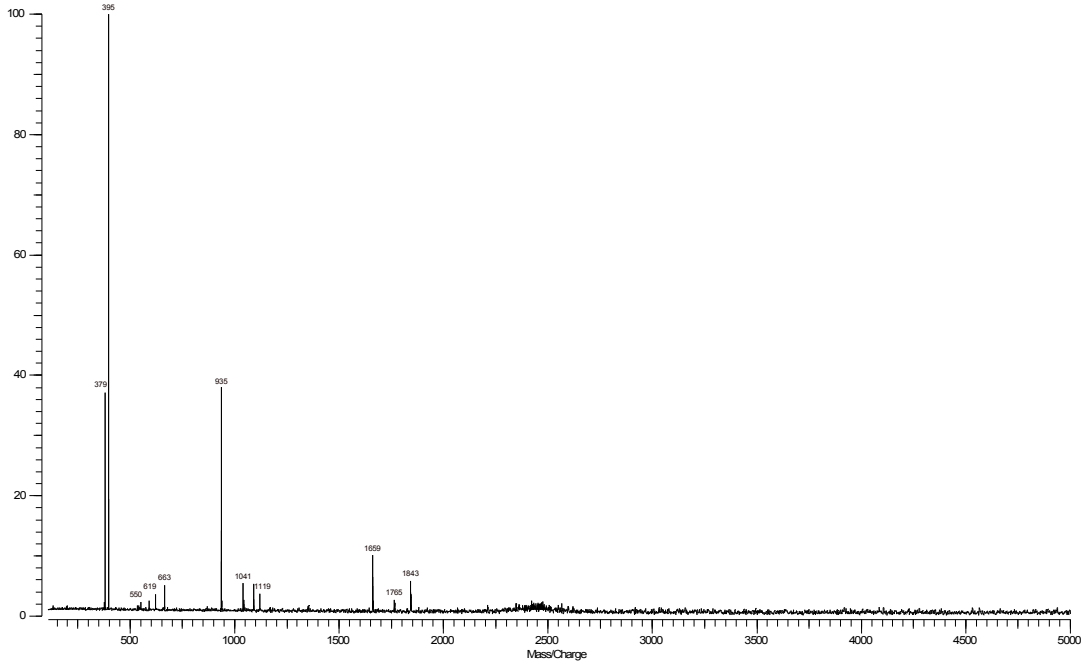

Figure S1: ESI-FTICR Mass spectrum of (**C7**+KPF_6) sprayed from DCM. The peaks at *m/z* 379, 395, and 935 are assigned to [**C7**+Na]$^+$, [**C7**+K]$^+$, and [2**C7**+K+KPF_6]$^+$, respectively. Since we didn't deliberately add KPF_6 into this solution, KPF_6 should be from the template used in the reaction which could not be removed after extraction and column chromatography. This result is in agreement with NMR results.

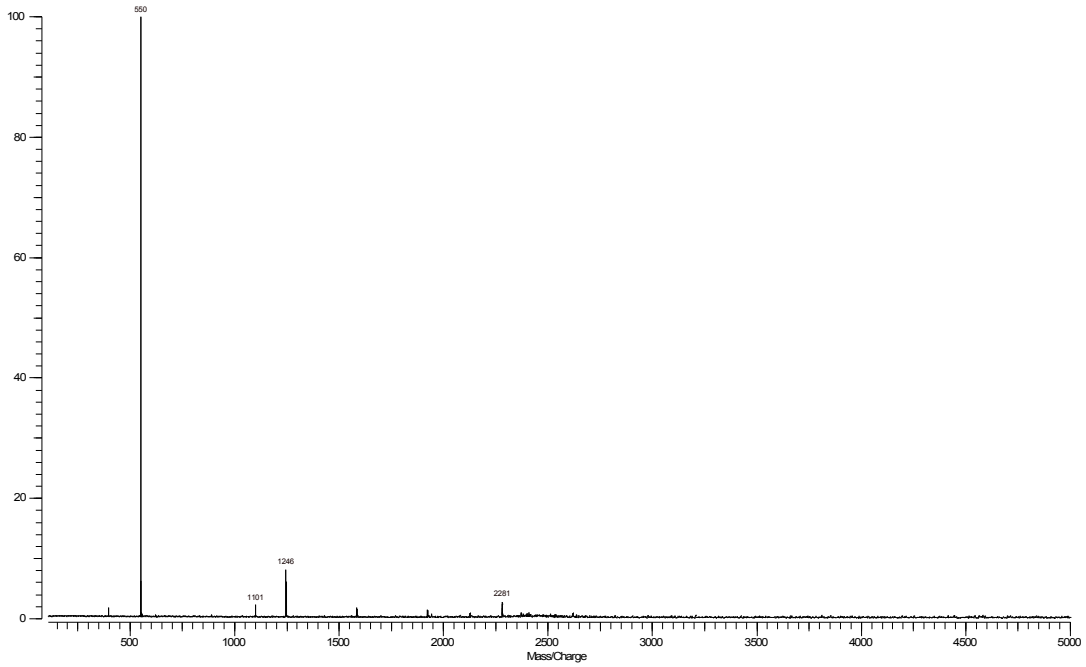

Figure S2: ESI-FTICR Mass spectrum of (**C7**+KPF_6) in the presence of **6**-H·PF_6. The peak at *m/z* 550 is assigned to [**6**-H@**C7**]$^+$. The only intense peak suggests that **C7** is the dominant organic compound in (**C7**+KPF_6) and **6**-H·PF_6 fits better to **C7** than KPF_6.

The association constants which were calculated by single-point method:

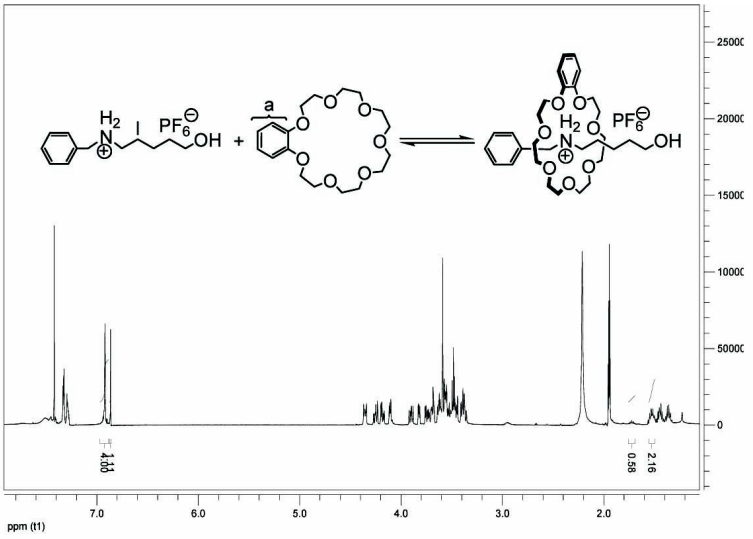

Figure S3: ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$:CD_3CN = 2:1, 1.0 mM) of the equimolar mixture of **6**-H·PF_6 and **C7**. From complexed and uncomplexed H_a of **C7**, $K_a(H_a)$ = [(4.00/5.11) × 1.0 × 10^{-3}] / [(1.11/5.11) × 1.0 × 10^{-3}]^2 M^{-1} = 16590 M^{-1}; From complexed and uncomplexed H_l of **6**-H·PF_6, $K_a(H_l)$ = [(2.16/2.74) × 1.0 × 10^{-3}] / [(0.58/2.74) × 1.0 × 10^{-3}]^2 M^{-1} = 17590 M^{-1}. Finally, K_a = (16590+17590)/2 = 17090 (±500) M^{-1}.

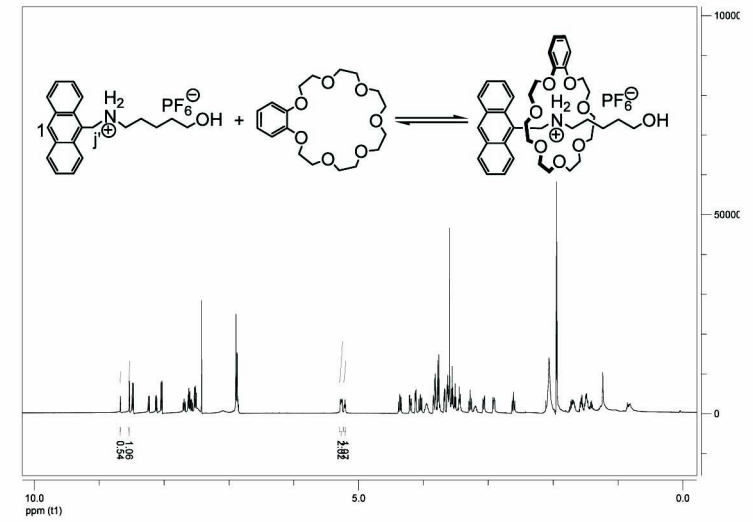

Figure S4: ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$:CD_3CN = 2:1, 1.0 mM) of the equimolar mixture of **7**-H·PF_6 and **C7**. From complexed and uncomplexed H_1 of **7**-H·PF_6, $K_a(H_1)$ = [(1.06/1.60) × 1.0 × 10^{-3}] / [(0.54/1.60) × 1.0 × 10^{-3}]^2 M^{-1} = 5820 M^{-1}; From complexed and uncomplexed $H_{j'}$ of **7**-H·PF_6, $K_a(H_{j'})$ = [(2.02/3.09) × 1.0 × 10^{-3}] / [(1.07/3.09) × 1.0 × 10^{-3}]^2 M^{-1} = 5450 M^{-1}. Finally, K_a = (5820+5450)/2 = 5640 (±190) M^{-1}.

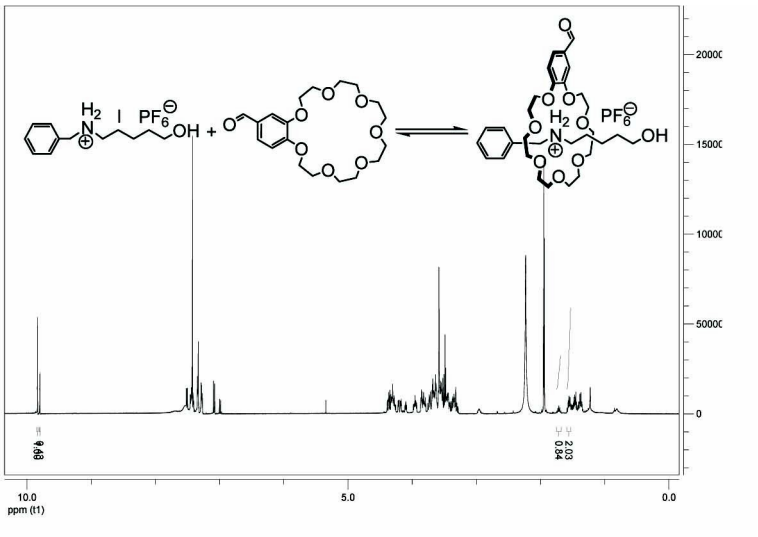

Figure S5: ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$:CD_3CN = 2:1, 1.0 mM) of the equimolar mixture of **6**-H·PF_6 and **4**. From complexed and uncomplexed CHO of **4**, K_a(CHO) = [(1.00/1.43) × 1.0 × 10^{-3}] / [(0.43/1.43) × 1.0 × 10^{-3}]^2 M^{-1} = 7730 M^{-1}; From complexed and uncomplexed H_l of **6**-H·PF_6, $K_a(H_l)$ = [(2.03/2.87) × 1.0 × 10^{-3}] / [(0.84/2.87) × 1.0 × 10^{-3}]^2 M^{-1} = 8260 M^{-1}. Finally, K_a = (7730+8260)/2 = 8000 (±270) M^{-1}.

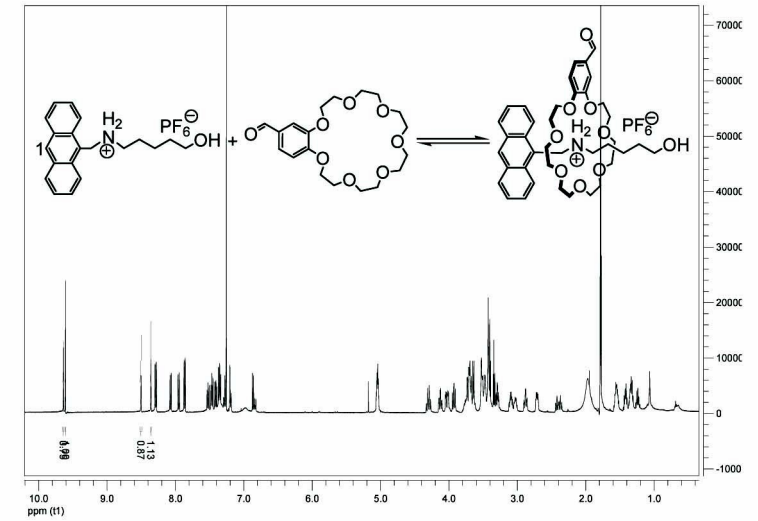

Figure S6: ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$:CD_3CN = 2:1, 1.0 mM) of the equimolar mixture of **7**-H·PF_6 and **4**. From complexed and uncomplexed CHO of **4**, K_a(CHO) = [(1.00/1.75) × 1.0 × 10^{-3}] / [(0.75/1.75) × 1.0 × 10^{-3}]^2 M^{-1} = 3110 M^{-1}; From complexed and uncomplexed H_1 of **7**-H·PF_6, $K_a(H_1)$ = [(1.13/2.00) × 1.0 × 10^{-3}] / [(0.87/2.00) × 1.0 × 10^{-3}]^2 M^{-1} = 2990 M^{-1}. Finally, K_a = (3110+2990)/2 = 3050 (±60) M^{-1}.

^{1}H-^{1}H COSY Spectra:

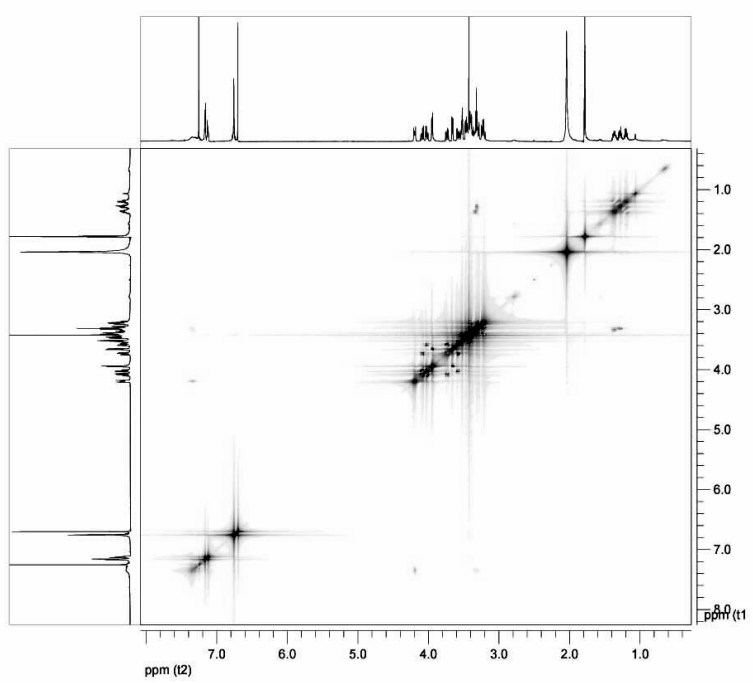

Figure S7: ^{1}H-^{1}H COSY spectrum (500 MHz, 298 K, $CDCl_3$:CD_3CN = 2:1, 10.0 mM) of the equimolar mixture of **6-**H·PF_6 and **C7**. The COSY spectrum supports the assignments of the peaks in Figure 5b.

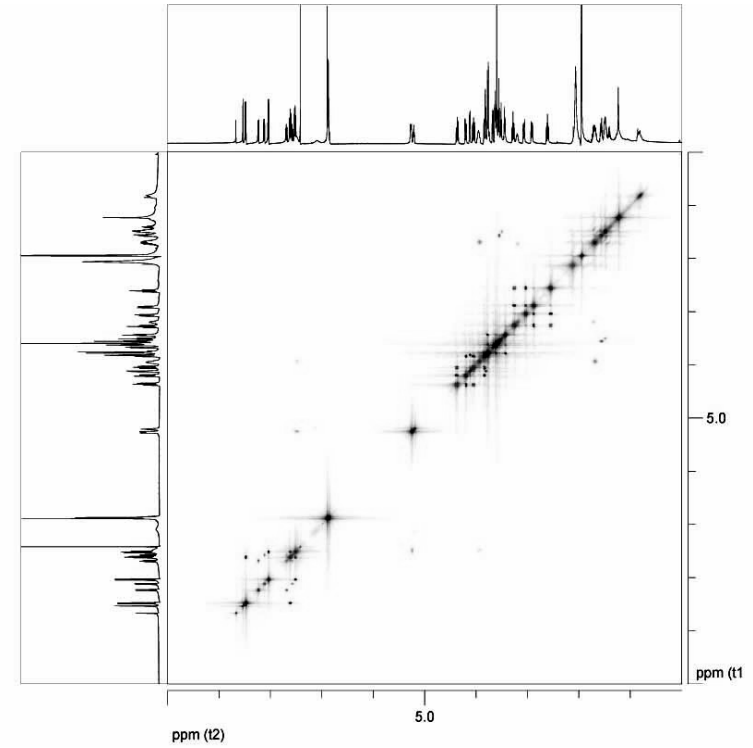

Figure S8: ^{1}H-^{1}H COSY spectrum (500 MHz, 298 K, $CDCl_3$:CD_3CN = 2:1, 10.0 mM) of the equimolar mixture of **7-**H·PF_6 and **C7**. The COSY spectrum supports the assignments of the peaks in Figure 5e.

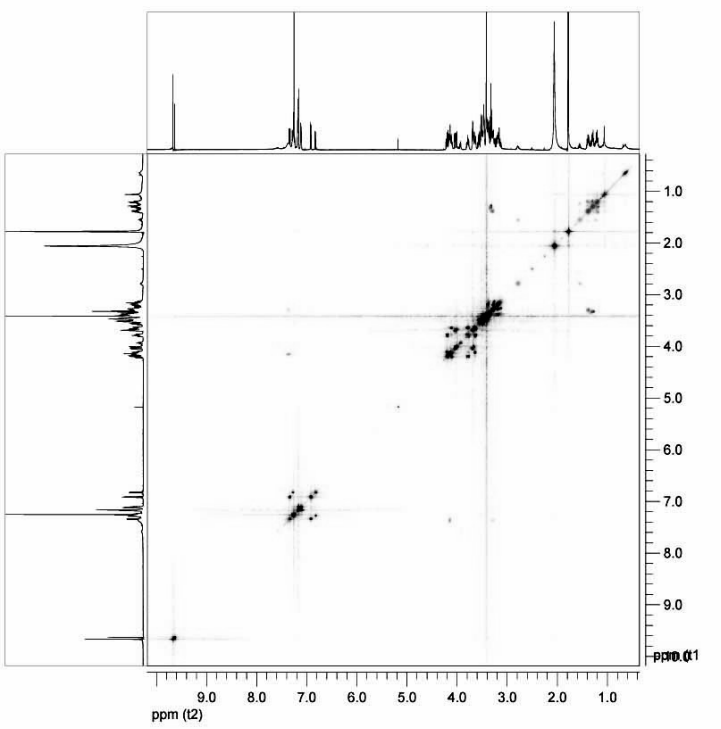

Figure S9: ^{1}H-^{1}H COSY spectrum (500 MHz, 298 K, $CDCl_3$:CD_3CN = 2:1, 10.0 mM) of the equimolar mixture of **6**-H·PF_6 and **4**. The COSY spectrum supports the assignments of the peaks in Figure 5c.

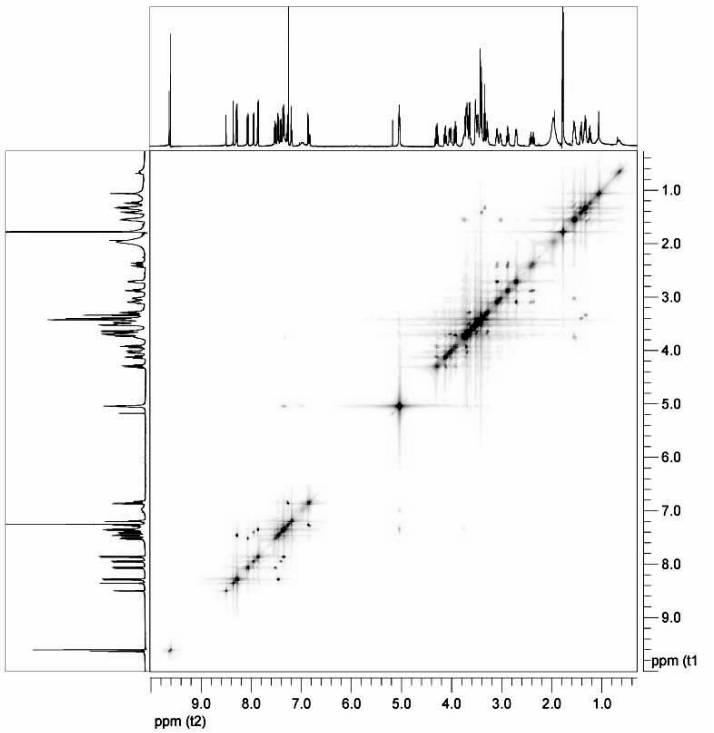

Figure S10: ^{1}H-^{1}H COSY spectrum (500 MHz, 298 K, $CDCl_3$:CD_3CN = 2:1, 10.0 mM) of the equimolar mixture of **7**-H·PF_6 and **4**. The COSY spectrum supports the assignments of the peaks in Figure 5d.

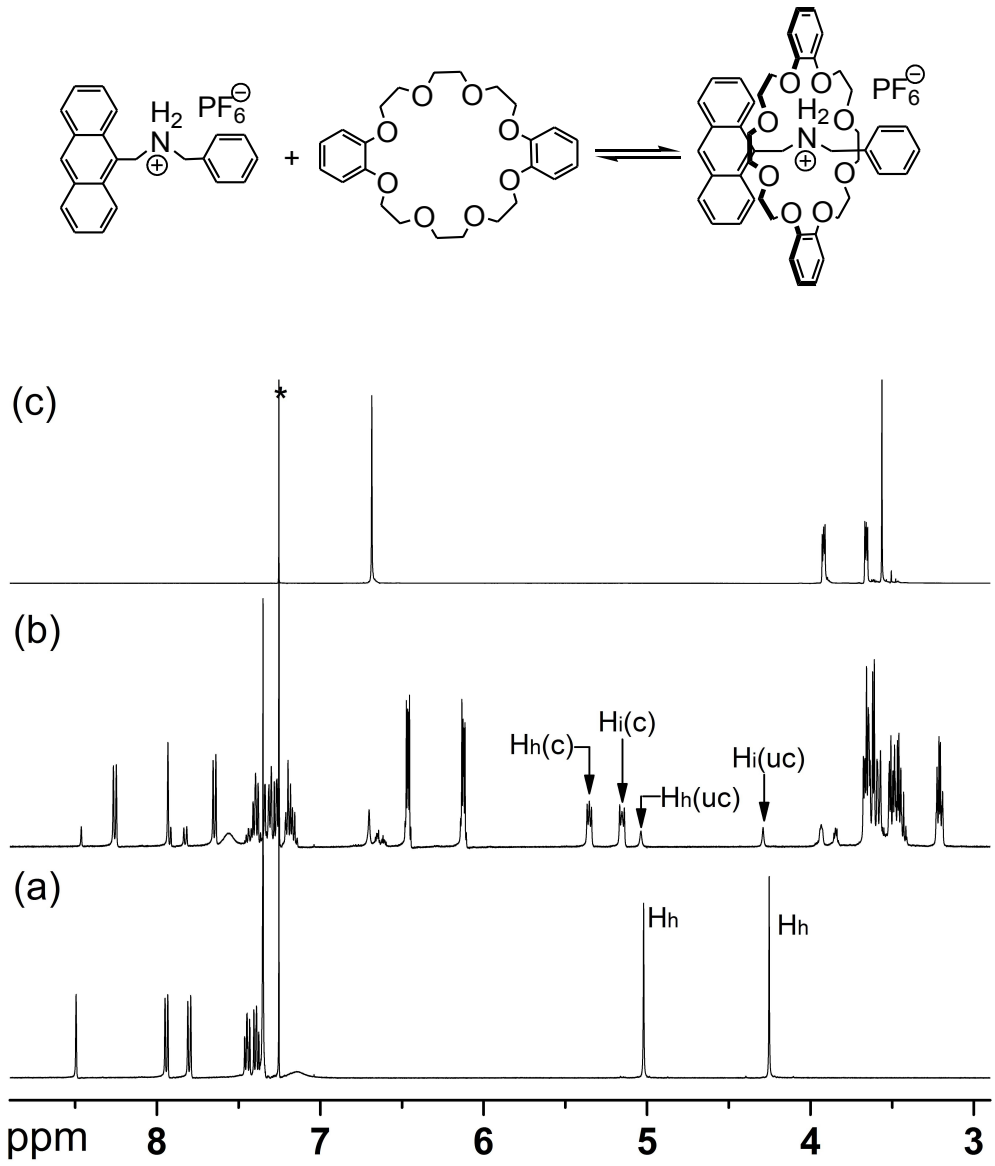

Figure S11: Top: complexation of **5**-H·PF_6 and DB24C8; Bottom: ^{1}H NMR spectra (500 MHz, 298 K, $CDCl_3$:CD_3CN = 2:1, 10.0 mM) of (a) **5**-H·PF_6, (c) DB24C8, and (b) the equimolar mixture of **5**-H·PF_6 and DB24C8. Asterisk = residual solvent. The descriptors "c" and "uc" in the parentheses denote signals arising from protons that are complexed and uncomplexed, respectively. After complexation with DB24C8, H_h and H_i of **5**-H·PF_6 are shifted by +0.90 and +0.34 ppm, respectively, indicating DB24C8 is flexible enough to complex H_h and experiences no obvious hindrance from anthracene of **5**-H·PF_6.