Electronic supplementary information

Host-guest Complexation of Pillar[6]arene towards Neutral Nitrile Guests

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Contents

Materials and methods.

All of the guests were commercially available and used as received. EtP6A[S1] host was prepared according to literature procedures. ^{1}H NMR, ^{13}C NMR and 2D NOESY spectra were recorded on a Bruker AV500 instrument.

X-ray crystal data of 5⊂EtP6A complex.

Crystallographic data: colorless, $C_{76}H_{92}N_2O_{12}$, FW 1225.51, Monoclinic, space group P 21/n, a=11.966 (3), b=12.944 (4), c=21.641 (6), α =90°, β =90.390 (5)°, γ =90°, V=3351.9 (16) Å^3; Z=2, D_c=1.214 g cm^{-3}; T=173(2) K, μ =0.081 mm^{-1}; 12619 measured reflections, 5823 independent reflections, 412 parameters, 0 restraint, F(000)=1316, R1=0.1072, *wR*2 =0.2138 (all data), R1=0.0632, *wR*2 =0.1735 [I＞2σ(*I*)], max. residual density 0.465 e·Å^{-3}; and goodness-of-fit (F^2) =1.025. CCDC 1417657.

Copy of ^{1}H NMR and ^{13}C NMR spectra of EtP6A host.

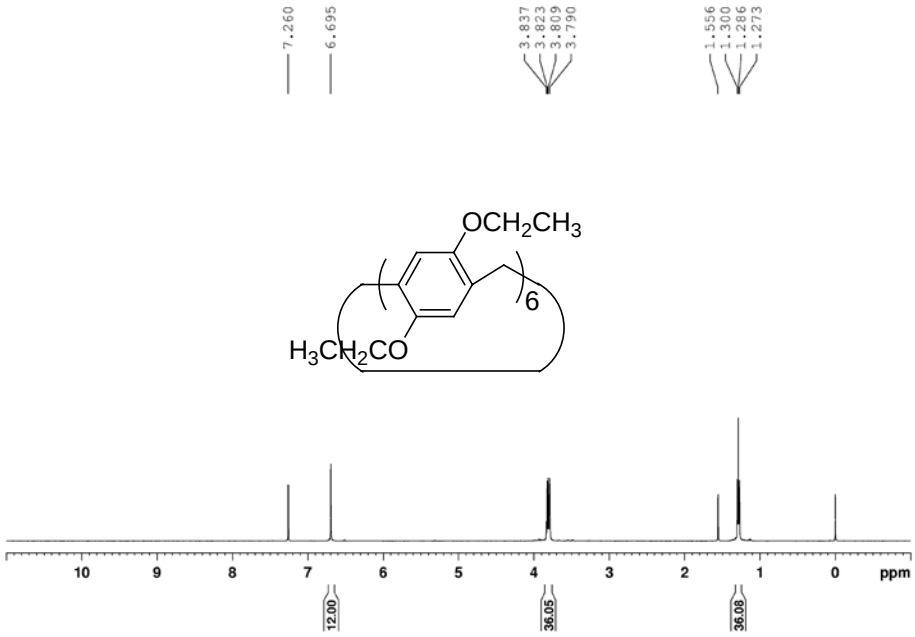

Figure S1. ^{1}H NMR spectrum (500MHz) of EtP6A in $CDCl_3$.

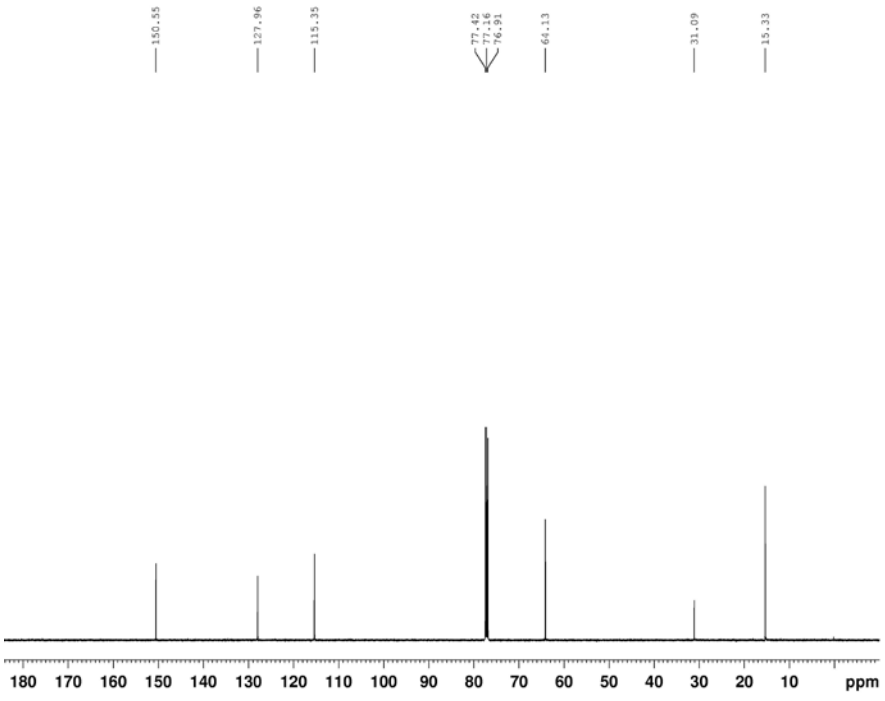

Figure S2. ^{13}C NMR spectrum (125MHz) of EtP6A in $CDCl_3$.

^{1}H NMR spectra of guests in the absence and presence of EtP6A.

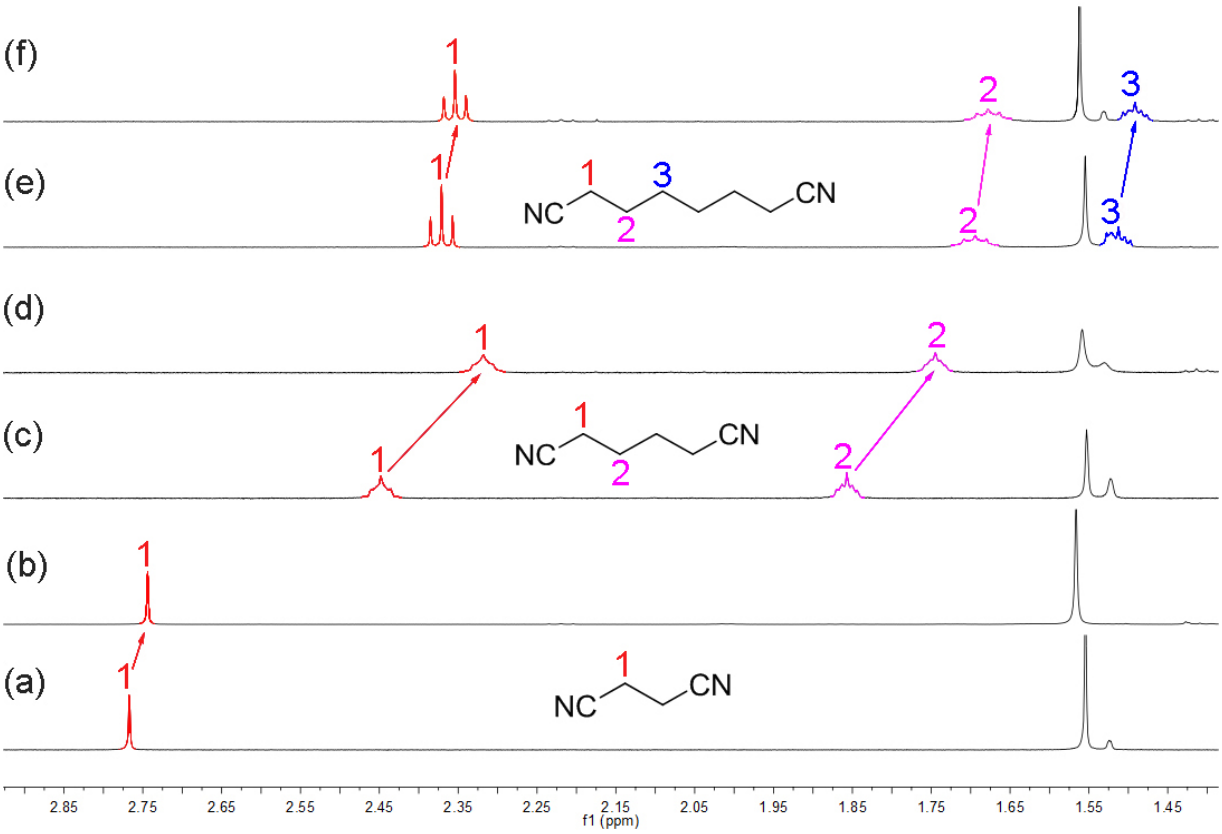

Figure S3. ^{1}H NMR spectra (500 MHz) of (a) **1**, (b) **1**+EtP6A, (c) **2**, (d) **2** + EtP6A, (e) **3**, and (f) **3** + EtP6A in $CDCl_3$ at 4.5−5.0 mM.

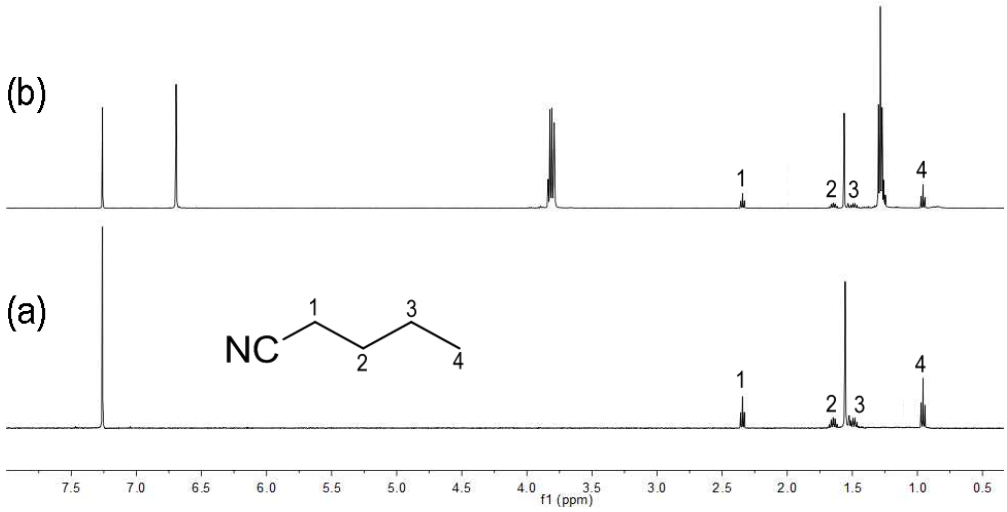

Figure S4. ^{1}H NMR spectra (500 MHz) of (a) **4** and (b) **4** + EtP6A in $CDCl_3$ at 4.4−4.7 mM.

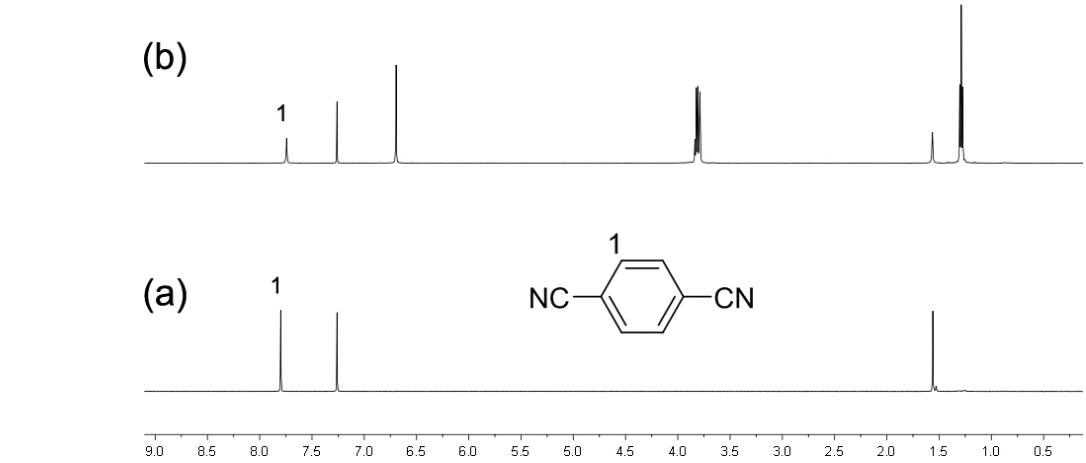

Figure S5. ^{1}H NMR spectra (500 MHz, 298 K) of (a) **7** and (b) **7**+ EtP6A in $CDCl_3$ at 4.6−5.0 mM.

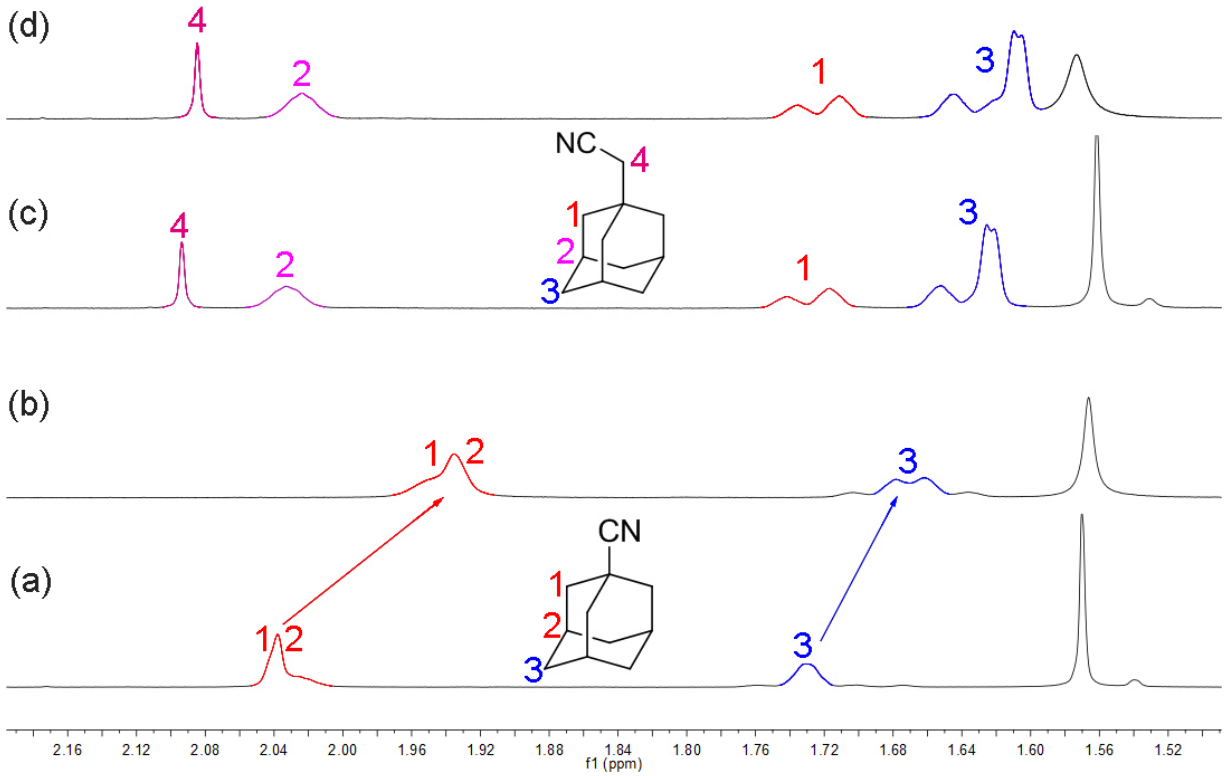

Figure S6. ^{1}H NMR spectra (500 MHz) of (a) **10**, (b) **10** + EtP6A, (c) **11**, and (d) **11** + EtP6A in $CDCl_3$ at 4.4−4.9 mM.

UV-*vis* spectra.

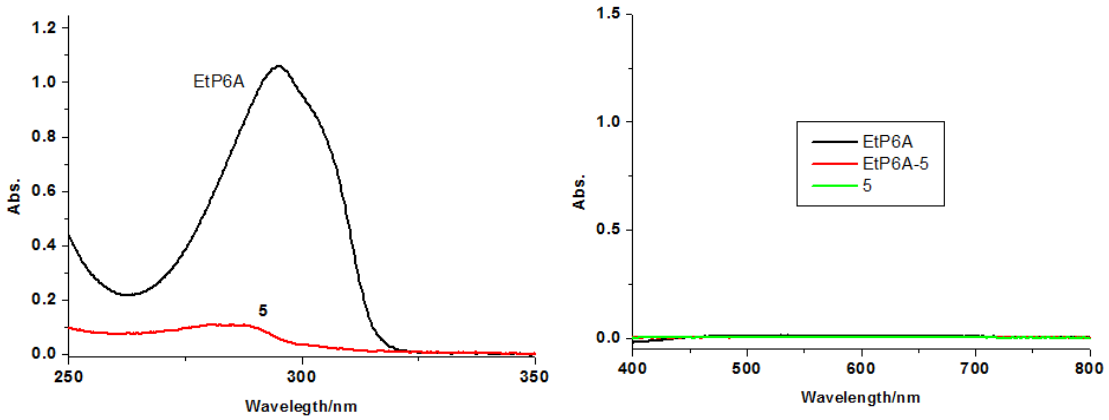

Figure S7. UV-*vis* spectra of EtP6A, guest **5**, and 1:1 mixture of EtP6A and **5** in $CHCl_3$. Left: The concentration is 3.0×10^{-5} mol/L for the left graph, and 3.0×10^{-3} mol/L for the right one.

Crystal structure of 5⊂EtP6A complex and the C−H···N(O, π) parameters.

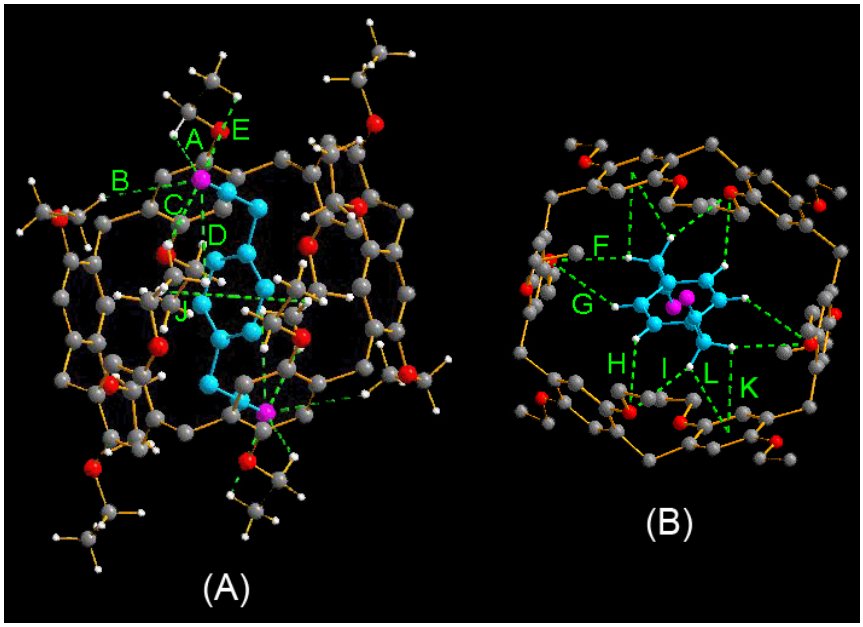

Figure S8. Crystal structure of the inclusion complex **5**⊂EtP6A. EtP6A is gray, guest **5** is sky blue, oxygens are red, and nitrogens are pink. Dashes represent C−H···N(O) hydrogen bonds or C−H···π interactions. C−H···N hydrogen bonds parameters: H···N distances (Å), C−H···N angles (deg) A, 3.284, 110.620; B, 3.475, 132.178; C, 2.732, 133.608; D, 3.477, 82.125; E, 3.417, 110.620. C−H···O hydrogen-bond parameters: H···O distances (Å), C−H···O angles (deg) F, 2.756, 164.078; G, 3.403, 141.262; H, 3.312, 142.022; I, 2.726, 153.420. C−H···π parameters: H···ring centre distance (Å), C−H···ring angles (deg) J, 3.142, 146.474; K, 3.148, 98.270; L, 2.902, 114.405.

Determination of the association constants.

To determine the association constant (K_a), NMR titrations were done with solutions which had a constant concentration of EtP6A and varying concentrations of guest. Using the nonlinear curve-fitting method, the association constant was obtained for the host-guest combination from the following equation[S2]:

$$A = (A_\infty/[\text{EtP6A}]_0)\ (0.5[G]_0 + 0.5([\text{EtP6A}]_0+1/K_a) - (0.5\ ([G]_0^2+(2[G]_0(1/K_a - [\text{EtP6A}]_0)) + (1/K_a + [\text{EtP6A}]_0)^2)^{0.5}))$$

Where A is the chemical shift change of the aromatic protons on EtP6A host at $[G]_0$, A_∞ is the chemical shift change of the aromatic protons when the host is completely complexed, $[\text{EtP6A}]_0$ is the fixed initial concentration of the host, and $[G]_0$ is the initial concentration of guest.

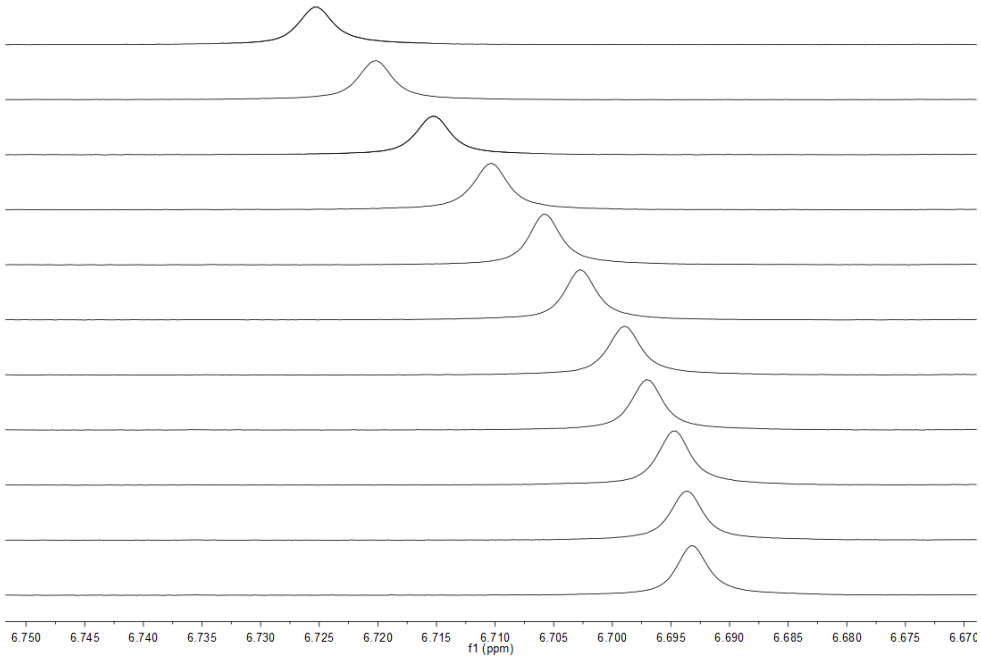

Figure S9. Partial ^{1}H NMR spectra (500 MHz, in $CDCl_3$ at 296 K) of EtP6A at a concentration of 1.01 mM upon addition of **5**. From bottom to top, the concentration of **5** was 0, 0.85, 2.5, 5.7, 8.7, 14, 19, 27, 37, 49 and 66 mM.

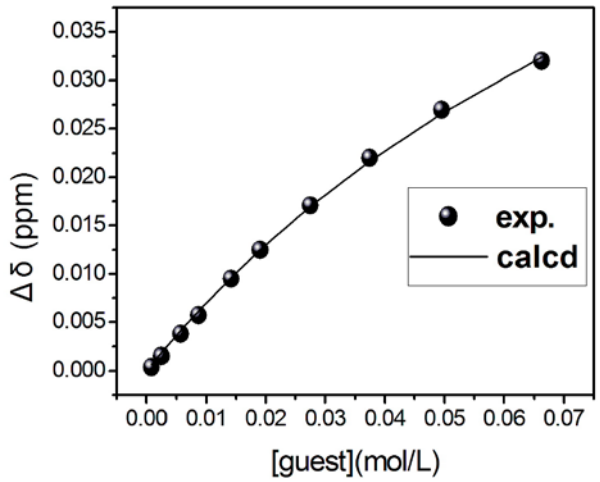

Figure S10. The non-linear curve-fitting (NMR titrations) for the complexation of EtP6A host (1.0 mM) with **5** in $CDCl_3$ at 296 K. The concentration of **5** was 0.85, 2.5, 5.7, 8.7, 14, 19, 27, 37, 49 and 66 mM.

References.

[S1] (a) D. Cao, Y. Kou, J. Liang, Z. Chen, L. Wang and H. Meier, *Angew. Chem., Int. Ed.*, **2009**, *48*, 9721; (b) X.-B. Hu, Z. Chen, L. Chen, L. Zhang, J.-L. Hou and Z.-T. Li *Chem. Commun.*, **2012**, *48*, 10999; (c) Y. Ma, X. Chi, X. Yan, J. Liu, Y. Yao, W. Chen, F. Huang, and J.-L. Hou, *Org. Lett.*, **2012**, *14*, 1532.

[S2] (a) K. A. Connors, Binding Constants; Wiley: New York, **1987**. Corbin, P. S. Ph.D. Dissertation, University of Illinois at Urbana-Champaign, Urbana, IL, 1999; (b) R. P. 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; (c) Y. Inoue, K. Yamamoto, T. Wada, S. Everitt, X.-M. Gao, Z.-J. Hou, L.-H. Tong, S.-K. Jiang, H.-M. Wu, *J. Chem. Soc., Perkin Trans. 2*, **1998**, 1807.