Electronic Supplementary Material (ESI) for Chemical Communications

A pillar[6]arene with mono(ethylene oxide) substituents: synthesis and complexation with diquat

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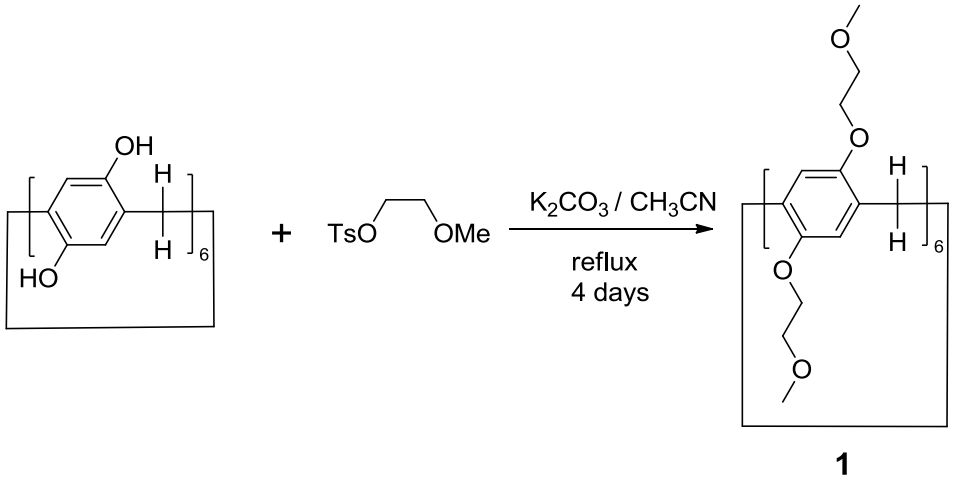
Electronic Supplementary Information (12 pages)

1. Materials and methods:

Pillar[5]arene **2**[S1] and *per*-hydroxylated pillar[6]arene **3**[S2] were synthesized according to literature procedures. Solvents were either employed as purchased or dried according to procedures described in the literature. ^{1}H NMR spectra were collected on a temperature-controlled 400 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 an ESI interface and an ion trap analyzer. High-resolution mass spectrometry experiments were performed with a Bruker Daltonics Apex III spectrometer. UV-vis spectroscopy was performed on a Shimadzu UV-2550 instrument at room temperature.

*2. Synthetic route to pillar[6]arene **1***



1

Scheme S1 Synthetic route to pillar[6]arene **1**.

*3. Synthesis of pillar[6]arene **1***

per-Hydroxylated pillar[6]arene **3** (0.500 g, 0.682 mmol) was dissolved in CH_3CN (50 mL). K_2CO_3 (2.25 g, 16.3 mmol) was added and the reaction mixture was stirred. Then 2-methoxyethyl *p*-toluenesulfonate (4.10 g, 21.3 mmol) was added and the reaction mixture was stirred under N_2 at reflux for 4 days. The solvent was evaporated and the residue was dissolved in CH_2Cl_2. The resultant solution was

washed with H_2O and brine. The organic phase was collected, dried over anhydrous Na_2SO_4 and concentrated to give a crude solid. Column chromatography (silica gel; CH_2Cl_2 : CH_3OH = 20 : 1) afforded a light yellow solid (195 mg, 20%). M.p. 90.2–92.8 °C. The ^1H NMR spectrum of pillar[6]arene **1** is shown in Figure S1. ^1H NMR (400 MHz, $CDCl_3$, room temperature) δ (ppm): 6.74 (s, 12H), 3.92 (t, J = 8.0 Hz, 24H), 3.81 (s, 12H), 3.61 (t, J = 8.0 Hz, 24H), 3.35 (s, 36H). The ^{13}C NMR spectrum of pillar[6]arene **1** is shown in Figure S2. ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ (ppm): 150.63, 128.38, 115.66, 71.43, 68.24, 58.93, 30.74. LRESIMS: m/z 1451.1 $[M + Na]^+$ (100%). HRMALDIMS: m/z calcd. for $[M + Na]^+$ $C_{78}H_{108}O_{24}Na$, 1451.7128, found 1451.7124, error –0.3 ppm.

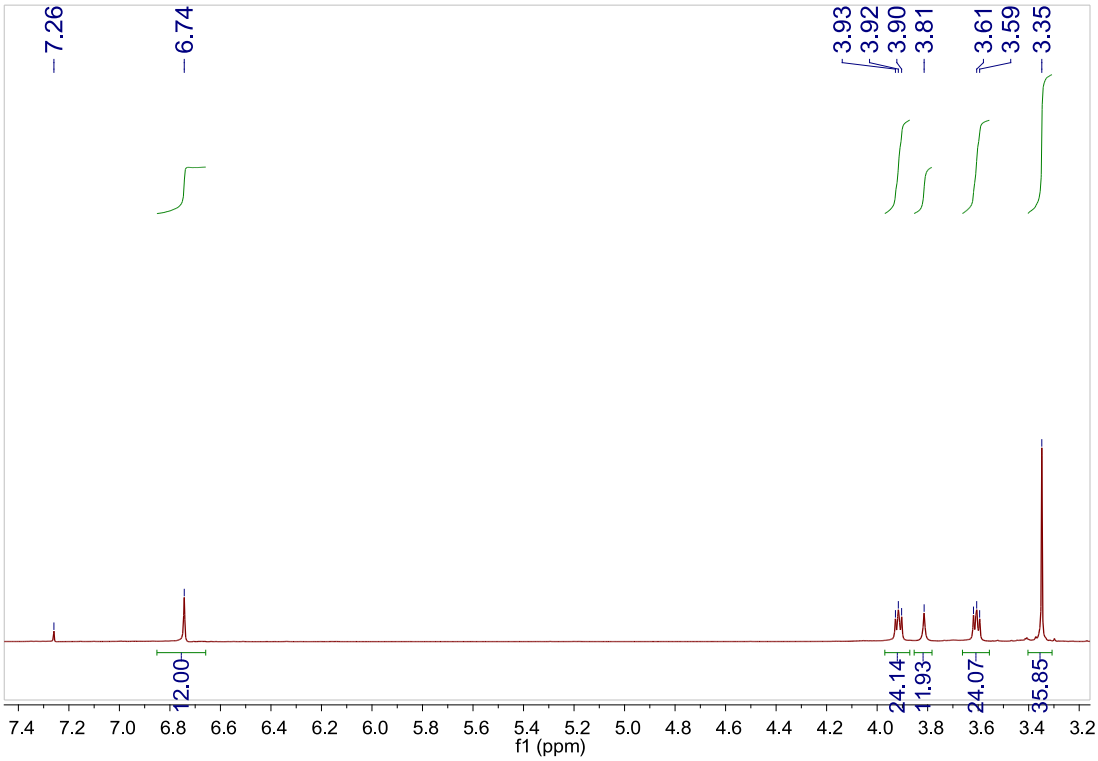


Fig. S1 ^1H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of pillar[6]arene **1**.

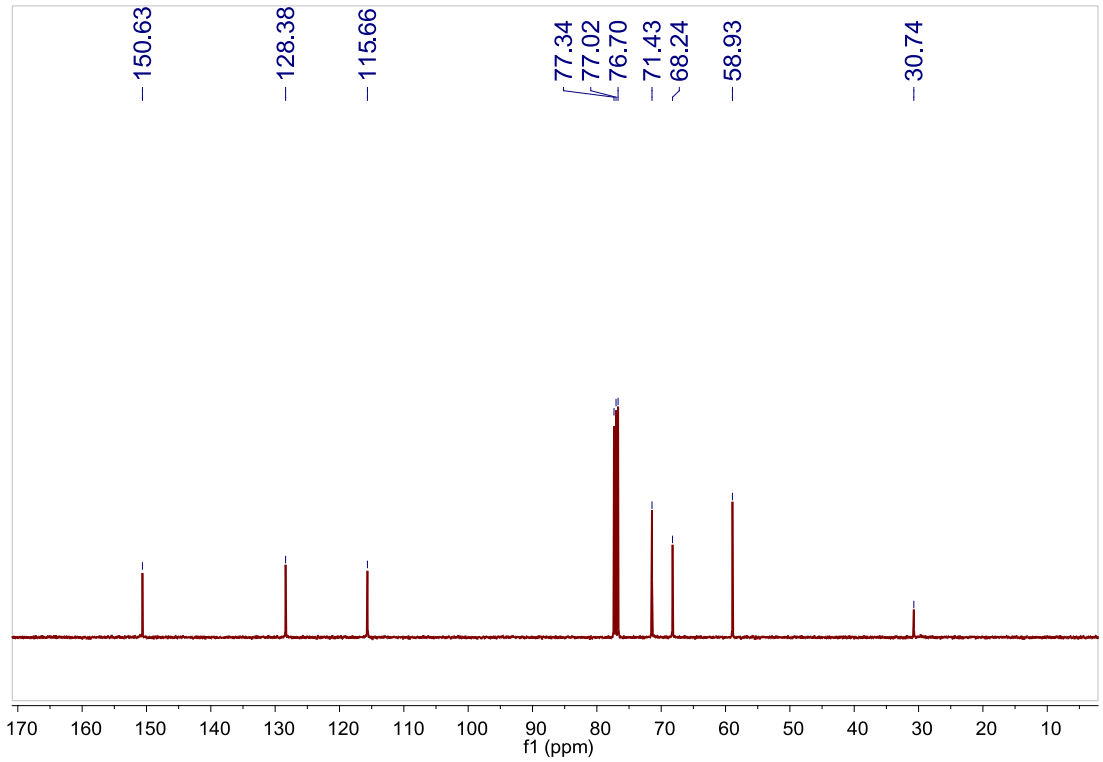


Fig. S2 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of pillar[6]arene **1**.

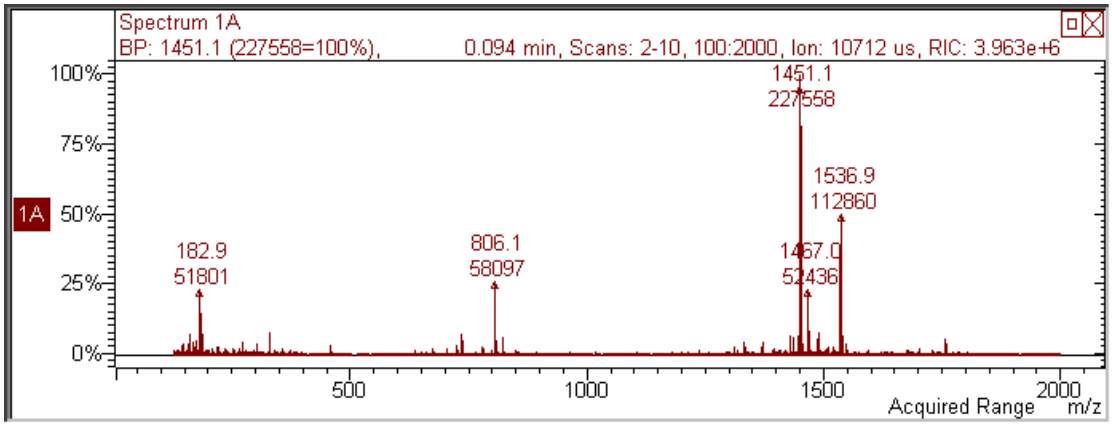


Fig. S3 LRESI mass spectrum of pillar[6]arene **1**. Assignment of the main peak: *m*/*z* 1451.1 $[M + Na]^+$ (100%).

4. X-ray crystal data of ***1⊃4***

Crystal data of **1⊃4**: red, $C_{94}H_{126}F_{12}O_{24}N_4P_2$, *FW* 1985.93, monoclinic, space group *C 2/c*, *a* = 39.5938(13), *b* = 13.3342(3), *c* = 38.3519(8) Å, α = 90.00°, β = 100.616(3)°, γ = 90.00°, *V* = 19901.3(9) Å^3, *Z* = 8, D_c = 1.326 g cm^{-3}, *T* = 140(2) K, μ = 1.216 mm^{-1}, 35832 measured reflections, 16879 independent reflections, 384 parameters, 3 restraints, *F*(000) = 8384.0, R_1 = 0.0891, wR_2 = 0.0730 (all data), R_1 = 0.2282, wR_2 = 0.2097 [$I > 2\sigma(I)$], max. residual density 0.948 e·Å^{-3}, and goodness-of-fit (F^2) = 1.037. CCDC-946929.

5. Stoichiometry and association constant determination for the complexation between ***1*** *and* ***4***

The association constant of complex **1⊃4** was determined by probing the charge-transfer band of the complex by UV/Vis spectroscopy and employing a titration method. Progressive addition of a solution with high guest concentration (5.0 × 10^{-3} M) and low host **1** concentration (2.0 × 10^{-4} M) to a solution with the same concentration of host **1** resulted in an increase of the intensity of the charge-transfer band of the complex. Treatment of the collected absorbance data with a non-linear curve-fitting program afforded the corresponding association constant (K_a).

The non-linear curve-fitting was based on the equation:[S3]

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

Where A is the absorption intensity of the charge-transfer band at $[G]_0$, A_∞ is the absorption intensity of the charge-transfer band when the host is completely complexed, $[H]_0$ is the fixed initial concentration of the host, and $[G]_0$ is the varying concentration of the guest.

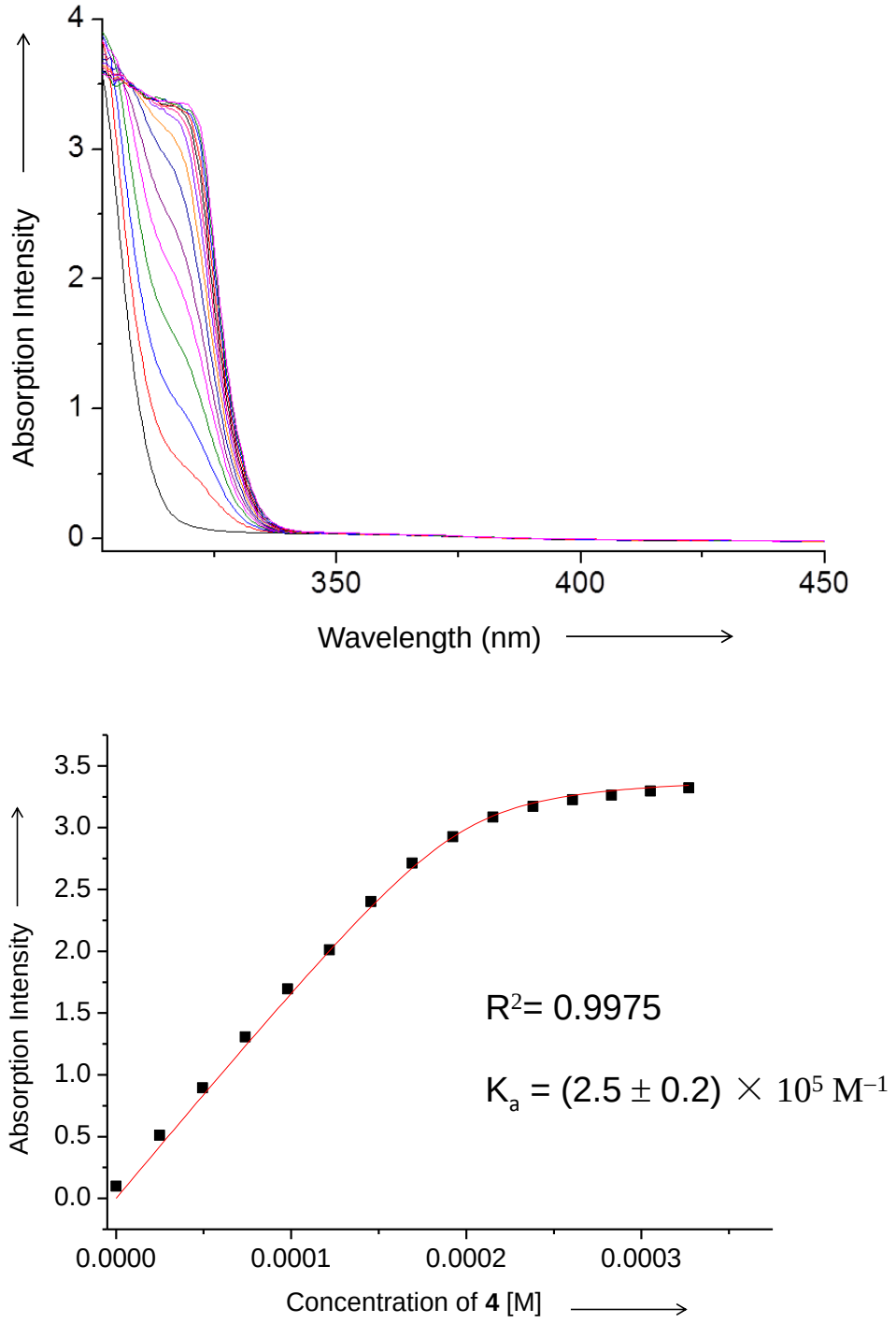


Fig. S4 Titration curve (top) and non-linear fitting curve (bottom) of host **1** and guest **4** in acetonitrile.

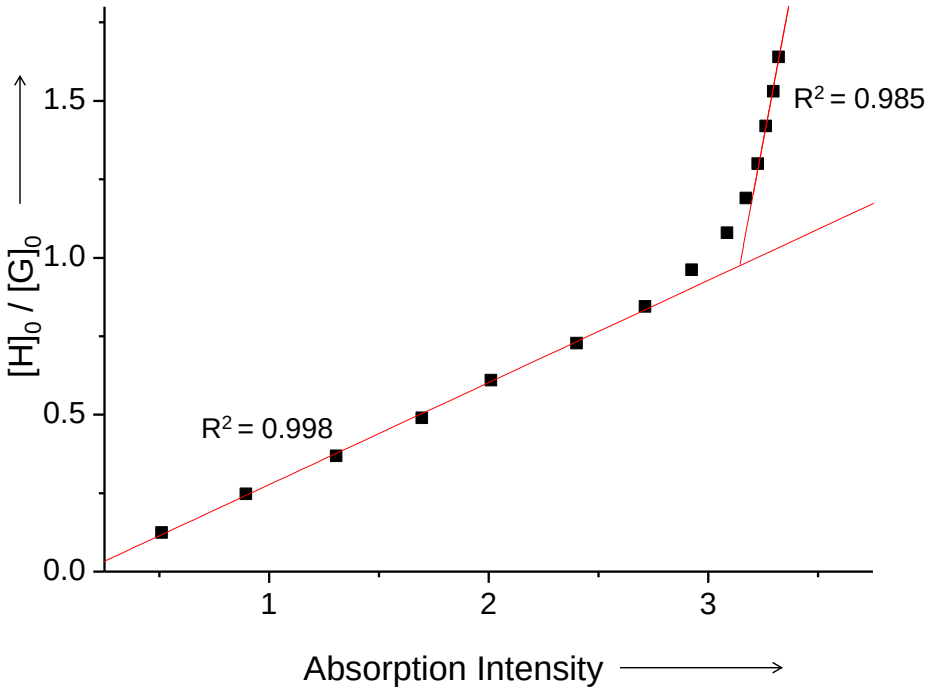


Fig. S5 Mole ratio plot for the complexation between **1** and **4**, indicating a 1:1 stoichiometry.

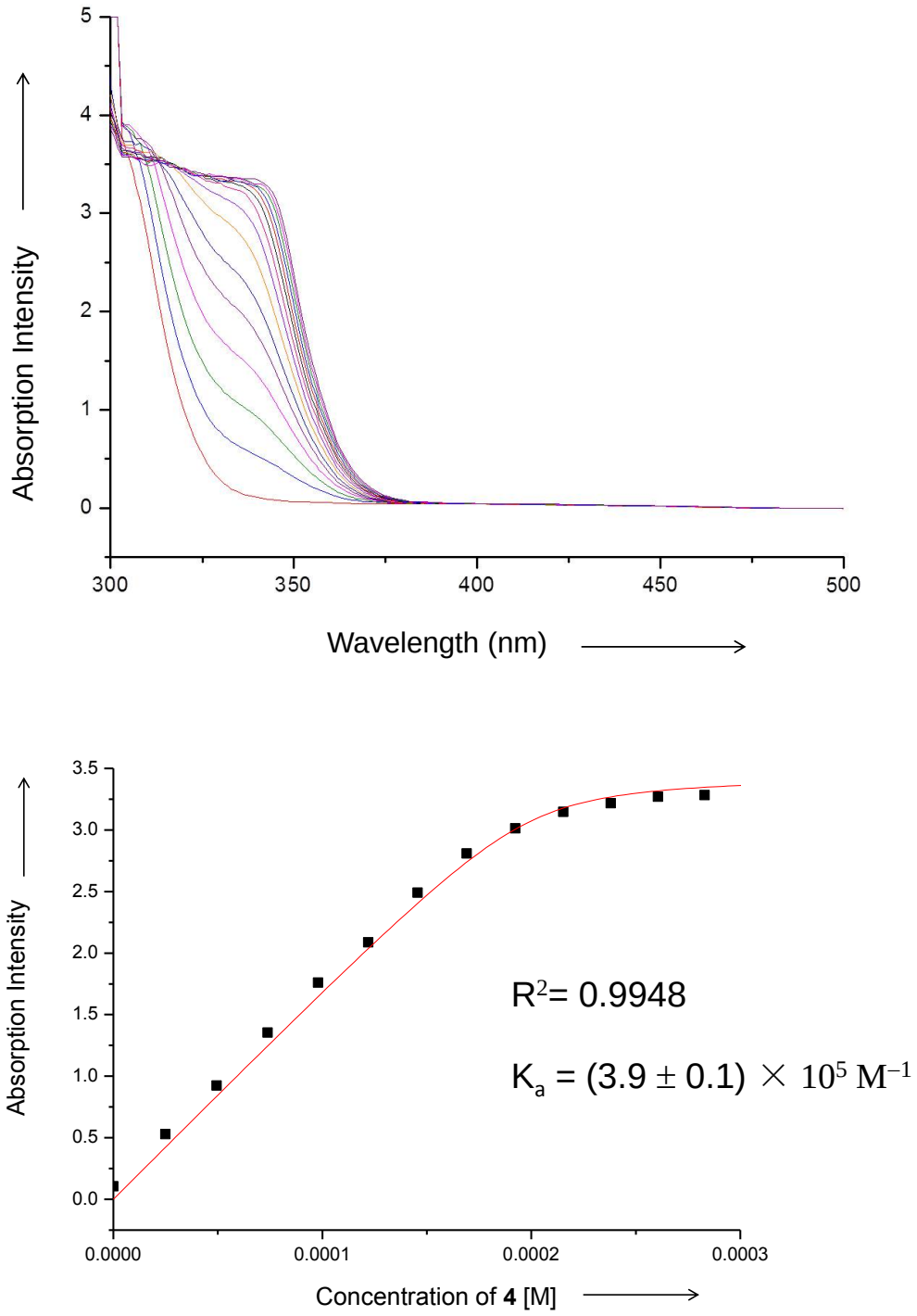


Fig. S6 Titration curve (top) and non-linear fitting curve (bottom) of host **1** and guest **4** in acetone.

*6. Electrospray ionization mass spectrometry of an equimolar mixture of **1** and **4**.*

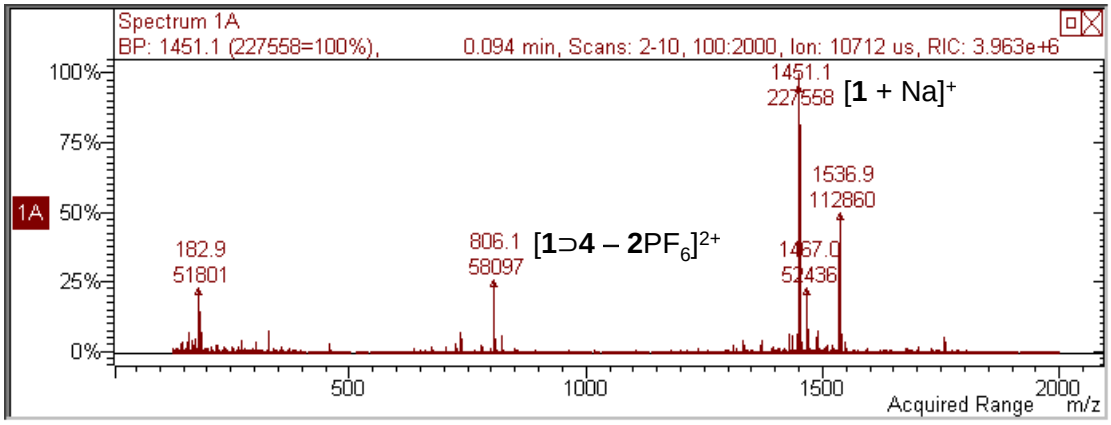


Fig. S7 Electrospray ionization mass spectrometry of an equimolar mixture of **1** and **4**.

7. A photo showing color changes after host–guest complexation

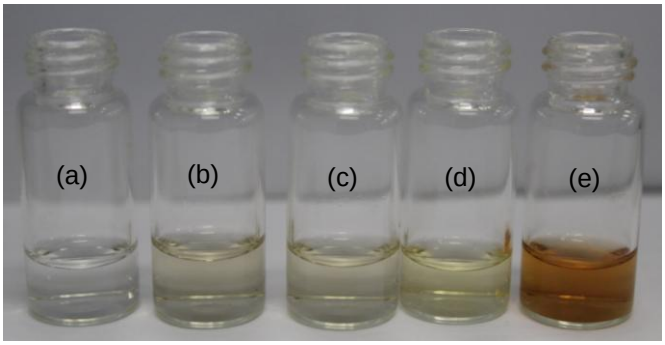


Fig. S8 A photo showing color changes after host–guest complexation in acetonitrile: (a) diquat alone; (b) **2** alone; (c) equimolar mixture of **2** and diquat; (d) **1** alone; (e) equimolar mixture of **1** and diquat.

*8. Investigation on the complexation between pillar[5]arenes **1** and **2** with **4**.*

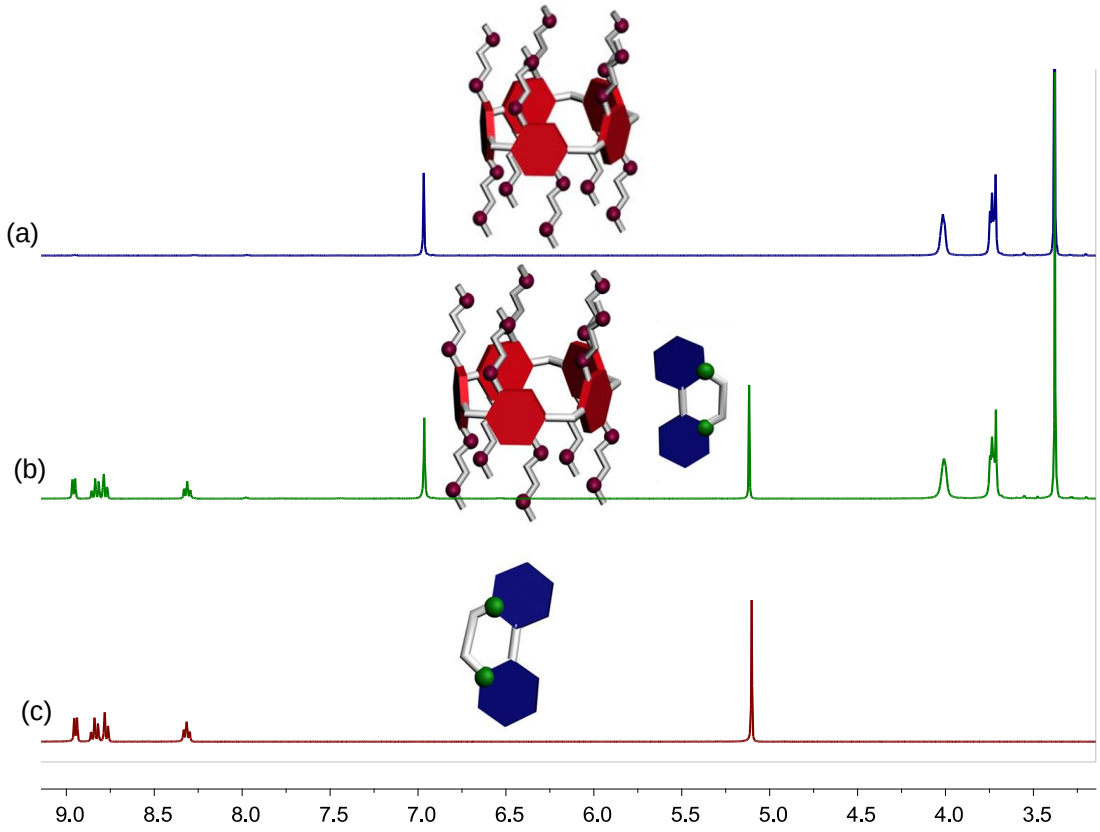


Fig. S9 Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 22 ℃): (a) 2.00 mM **2**; (b) 2.00 mM **2** and diquat **4**; (c) 2.00 mM diquat **4**. After equimolar diquat **4** and pillar[5]arene **2** were mixed in acetonitrile, no chemical shift changes were observed, indicating that no host-guest complexation occurred between **4** and **2**.

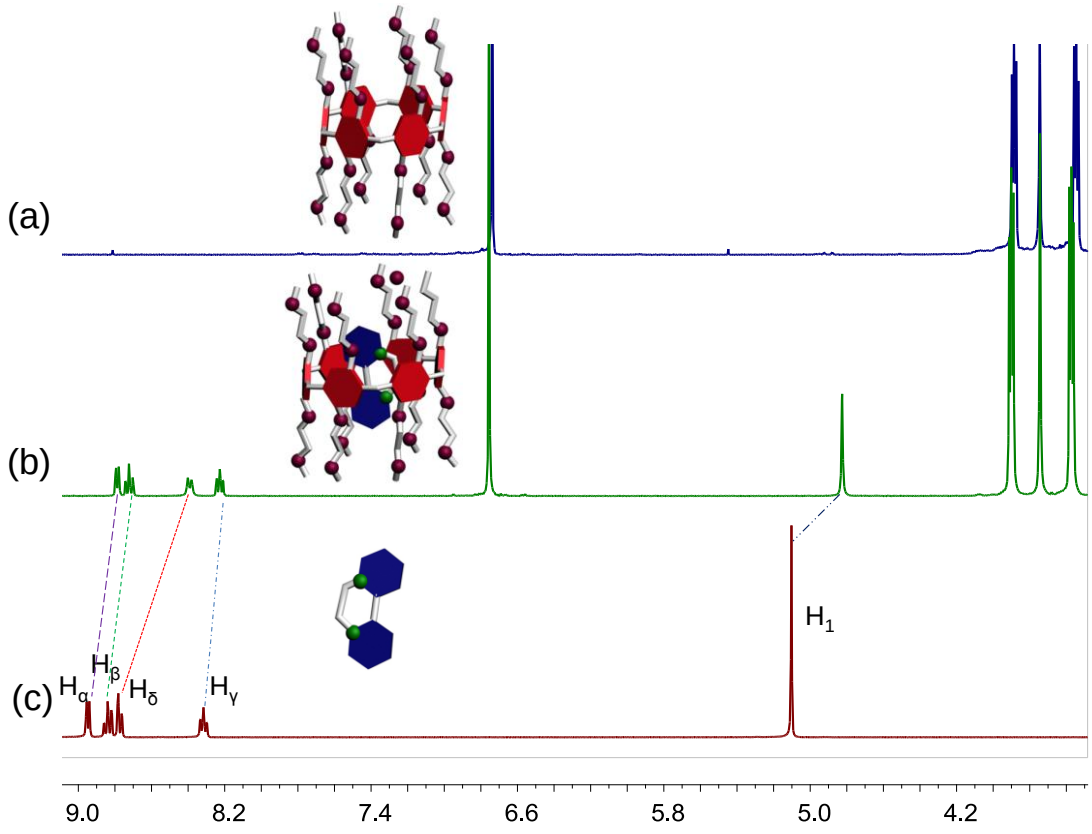


Fig. S10 Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 22 ℃): (a) 1.00 mM **1**; (b) 0.500 mM **1** and diquat **4**; (c) 1.00 mM diquat **4**.

References:

S1. T. Ogoshi, R. Shiga and T. Yamagishi, *J. Am. Chem. Soc.*, 2012, **134**, 4577–4580.

S2. Y. Ma, X. Chi, X. Yan, J. Liu, Y. Yao, W. Chen, F. Huang and J.-L. Hou, *Org. Lett.*, 2012, **14**, 1532–1535.

S3. K. A. Connors, *Binding Constants*; Wiley: New York, 1987; P. S. Corbin, 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 and D. J. Williams, *J. Am. Chem. Soc.*, 1996, **118**, 4931–4951.