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

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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.


![Scheme S1 Synthetic route to pillar[6]arene $I$.](image_url)


$\textit{per}$-Hydroxylated pillar[6]arene $3$ (0.500 g, 0.682 mmol) was dissolved in CH$_3$CN (50 mL). K$_2$CO$_3$ (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$_2$Cl$_2$. The resultant solution was
washed with H₂O and brine. The organic phase was collected, dried over anhydrous Na₂SO₄ and concentrated to give a crude solid. Column chromatography (silica gel; CH₂Cl₂ : CH₃OH = 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, CDCl₃, 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 ¹³C NMR spectrum of pillar[6]arene 1 is shown in Figure S2. ¹³C NMR (100 MHz, CDCl₃, room temperature) δ (ppm): 150.63, 128.38, 115.66, 71.43, 68.24, 58.93, 30.74. LRMS: m/z 1451.1 [M + Na]⁺ (100%). HRMALDIMS: m/z calcd. for [M + Na]⁺ C₇₈H₁₀₈O₂₄Na, 1451.7128, found 1451.7124, error –0.3 ppm.

**Fig. S1** ¹H NMR spectrum (400 MHz, CDCl₃, 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) Å³, 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 > 2σ(I)], max. residual density 0.948 e·Å⁻³, and goodness-of-fit (R^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:  
\[ A = (A_\infty/[H]_0) \left( 0.5[G]_0 + 0.5 ([H]_0 + 1/K_a) - (0.5 ([(G)_0^2] + (2[G]_0(1/K_a - [H]_0)) + (1/K_a + [G]_0^2)^{0.5}) \right) \]  
(Eq S1)

Where A is the absorption intensity of the charge-transfer band at [G]_0, A_\infty 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.
$R^2 = 0.9975$

$K_a = (2.5 \pm 0.2) \times 10^5 \text{ M}^{-1}$

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.

\[ R^2 = 0.9948 \]

\[ K_a = (3.9 \pm 0.1) \times 10^5 \text{ M}^{-1} \]
6. Electrospray ionization mass spectrometry of an equimolar mixture of 1 and 4.

![Electrospray ionization mass spectrometry spectrum](image)

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

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

![Color change photos](image)

**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.

Fig. S9 Partial $^1$H NMR spectra (400 MHz, CD$_3$CN, 22 °C): (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$_3$CN, 22 °C): (a) 1.00 mM 1; (b) 0.500 mM 1 and diquat 4; (c) 1.00 mM diquat 4.
References:

