Electronic Supplementary Material (ESI) for RSC Advances

Inclusion [2]complexes based on a pillar[5]arene with mono(ethylene oxide) substituents and vinylogous viologens

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Electronic Supplementary Information (17 pages)

1. Materials and methods:

Pillar[5]arene **1**[S1] was 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 or 600 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. Isothermal titration calorimetric (ITC) measurements were performed on a VP-ITC micro-calorimeter (Microcal, USA). The crystal data were collected on an Oxford Diffraction Xcalibur Atlas Gemini ultra. The crystal structure was solved by SHELXS-97[S2] and refined by SHELXL-97.[S2]

*2. X-ray crystal data of **1**⊃**2***

Crystal data of **1**⊃**2**: block, yellow, $C_{83}H_{112}F_{12}N_4O_{20}P_2$, *FW* 1775.71, monoclinic, space group *P*–1, a = 12.8518(4), b = 16.4858(6), c = 22.2701 (7) Å, α = 78.660(3)°, β = 73.634(3)°, γ = 82.764(3)°, V = 4426.4(3) Å^3, Z = 2, D_c = 1.332 g cm^{-3}, T = 170 K, μ = 0.662 mm^{-1}, 15539 measured reflections, 12289 independent reflections, 1104 parameters, 3 restraints, F(000) = 1280.0, R_1 = 0.0834, wR_2 = 0.0687 (all data), R_1 = 0.1912, wR_2 = 0.1797 [$I > 2\sigma(I)$], max. residual density 0.948 e·Å^{-3}, and goodness-of-fit (F^2) = 1.066. CCDC-953961.

*3. ITC experiments of **1**⊃**2**, **1**⊃**3**, **1**⊃**4** and **1**⊃**5** in acetonitrile*

Isothermal titration calorimetric measurements were performed on a VP-ITC micro calorimeter (Microcal, USA), which is composed of a reference cell and a sample cell of 1.43 mL. Stock solutions of host (0.100 mM, 10.0 mL) and guest (2.00 mM, 5.00 mL) in acetonitrile were prepared using volumetric glassware. Before each titration, all

the solutions were degassed and kept constant temperature. In a typical run, a 250 μL syringe was full of the guest solution (2.00 mM) and the cell was loaded with the host solution (0.100 mM, 1.43 mL). The titration of the host with the guest was carried out at 298 K with a constant rate of 307 rpm, 29 injections of 3.3 μL, a time interval of 240 s and a duration of 2 s per μL. The enthalpy change per mole of each added guest in the sample cell was recorded continuously. The control titrations of the guest into acetonitrile were also completed under the same conditions. The enthalpy changes of the titrations of the blank test were subtracted from the original titration. All the data were analyzed with Microcal Origin 7.0 software provided by the manufacturer. The final integration data obtained from the titration were fitted by the one set of binding site model.

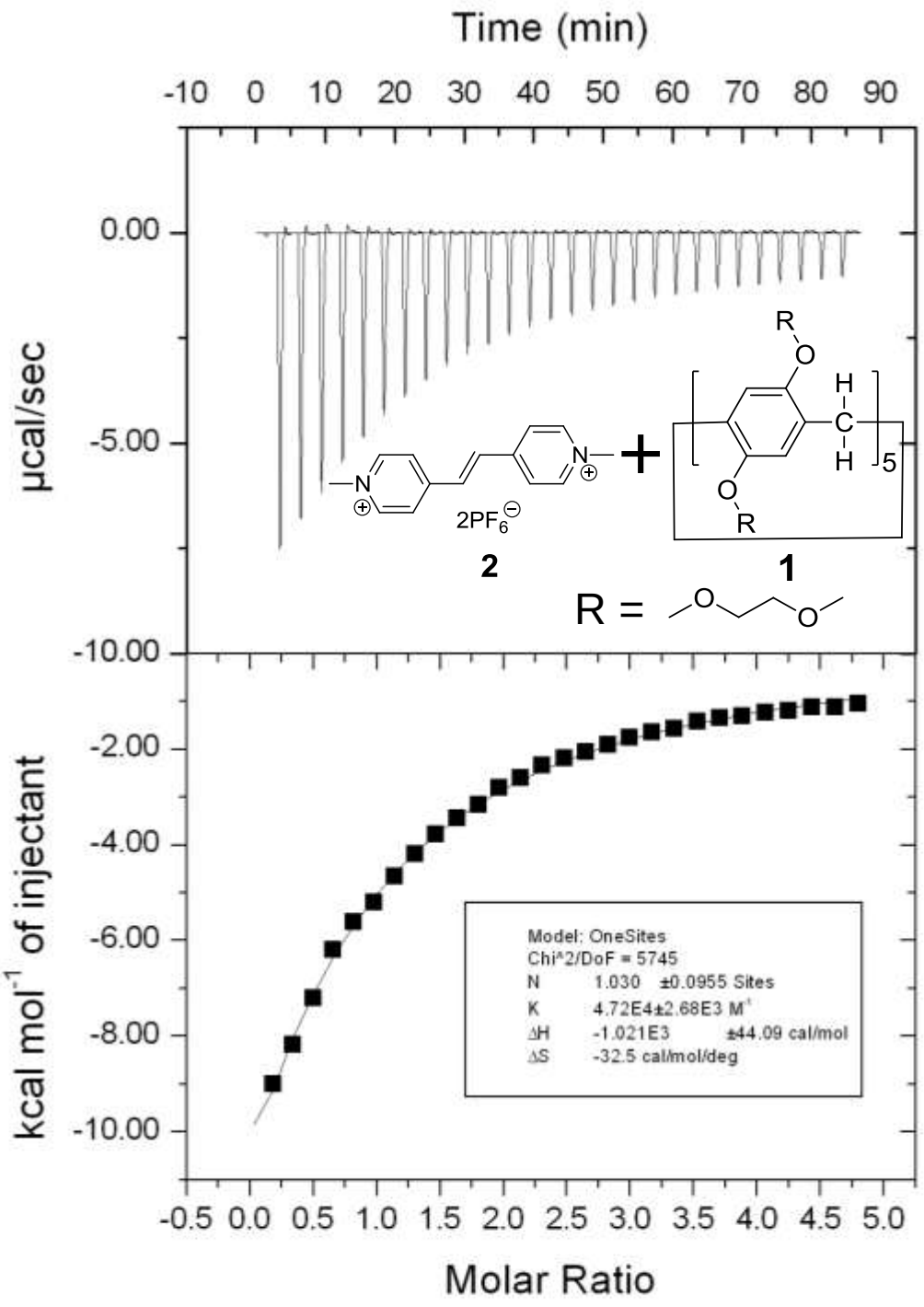


Fig. S1 Titration of **1** (0.100 mM) with **2** (2.00 mM) in acetonitrile at 298 K.

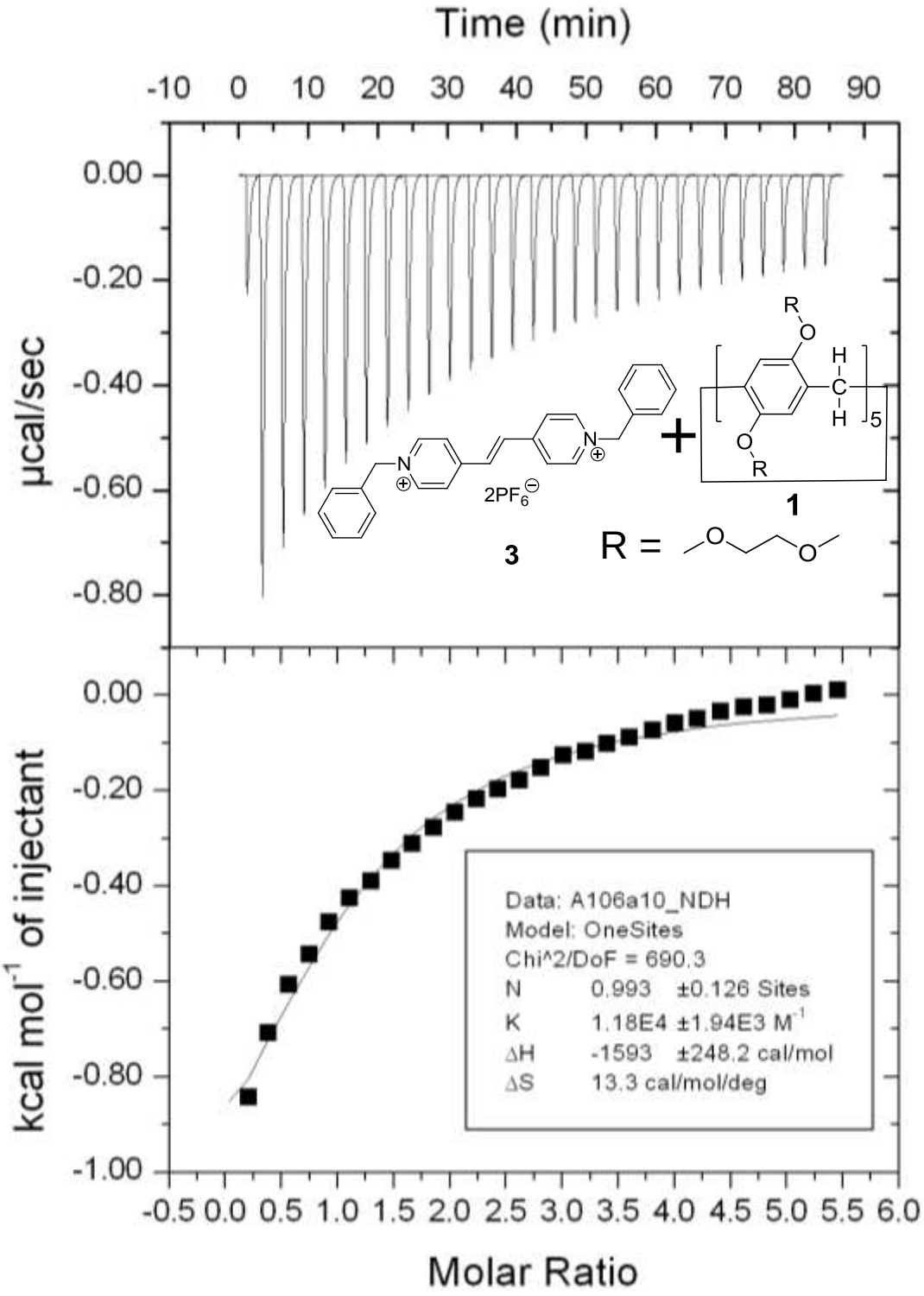


Fig. S2 Titration of **1** (0.100 mM) with **3** (2.00 mM) in acetonitrile at 298 K.

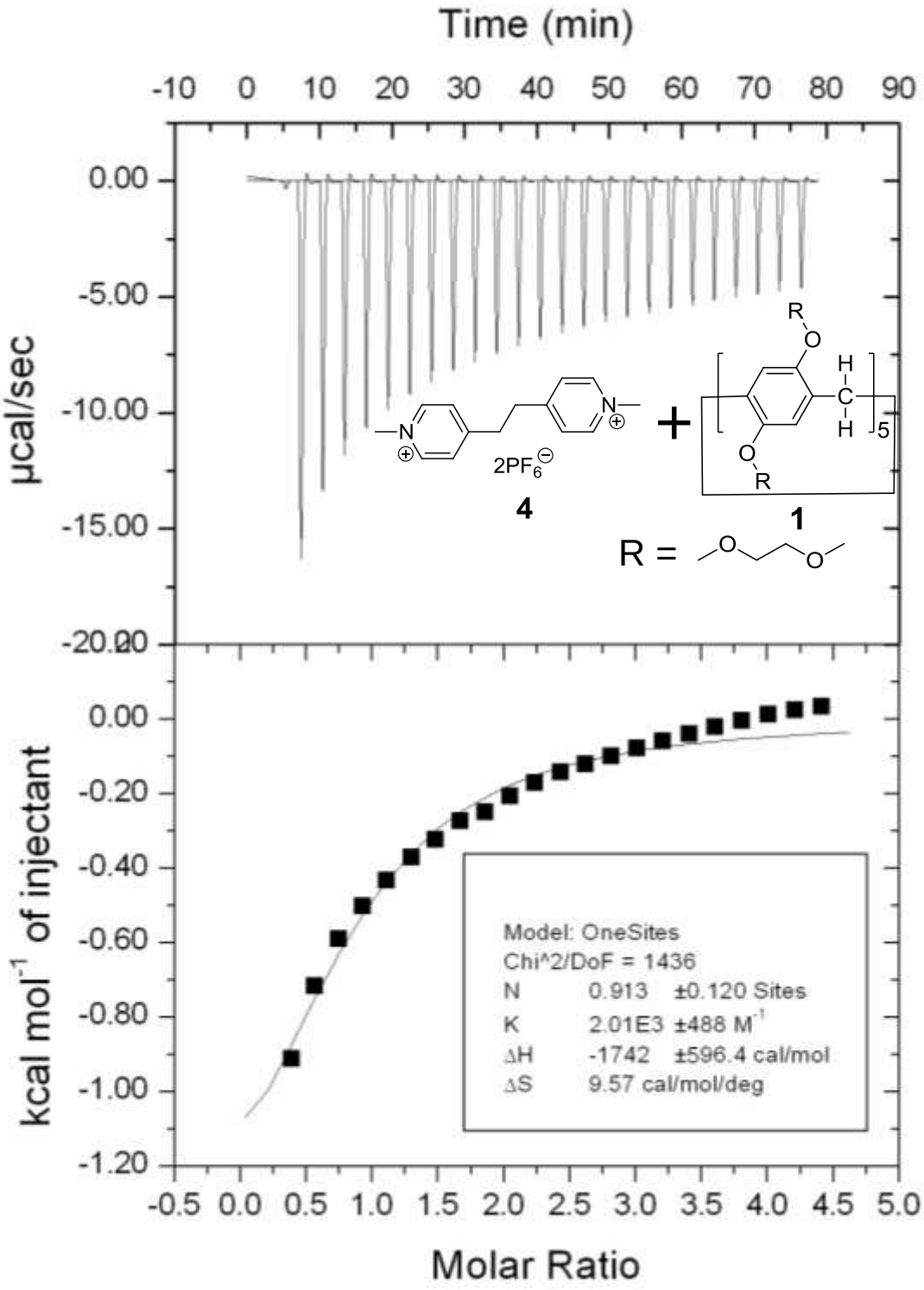


Fig. S3 Titration of **1** (0.100 mM) with **4** (2.00 mM) in acetonitrile at 298 K.

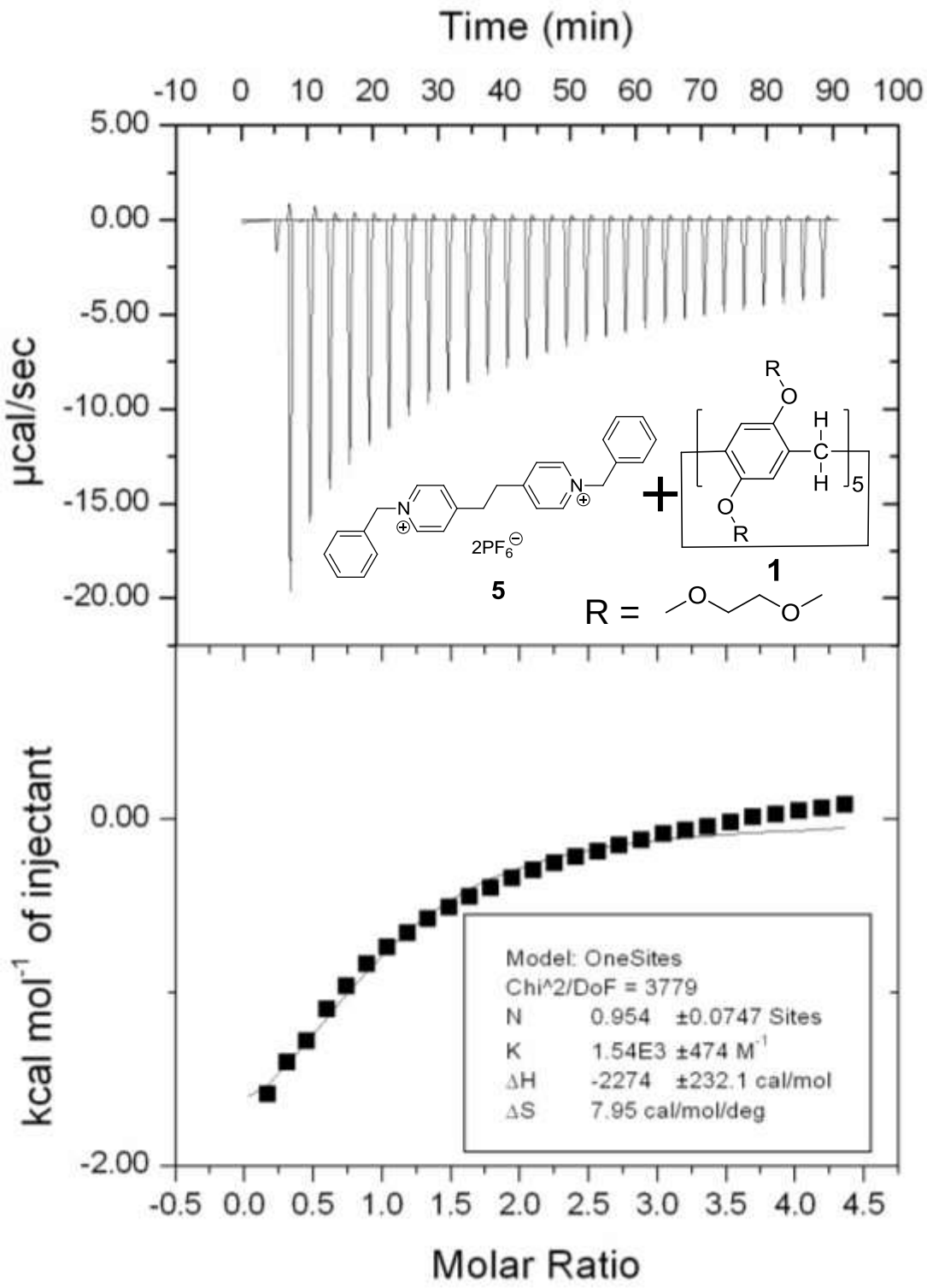


Fig. S4 Titration of **1** (0.100 mM) with **5** (2.00 mM) in acetonitrile at 298 K.

*4. Electrospray ionization mass spectra of equimolar solutions of **1** with **2–5***

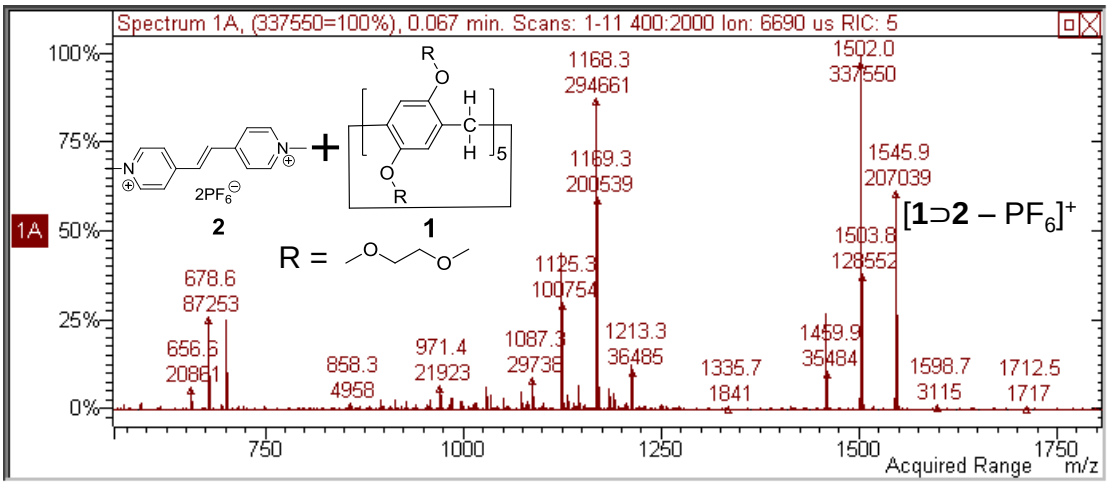


Fig. S5 Electrospray ionization mass spectrum of an equimolar solution of **1** with **2**.

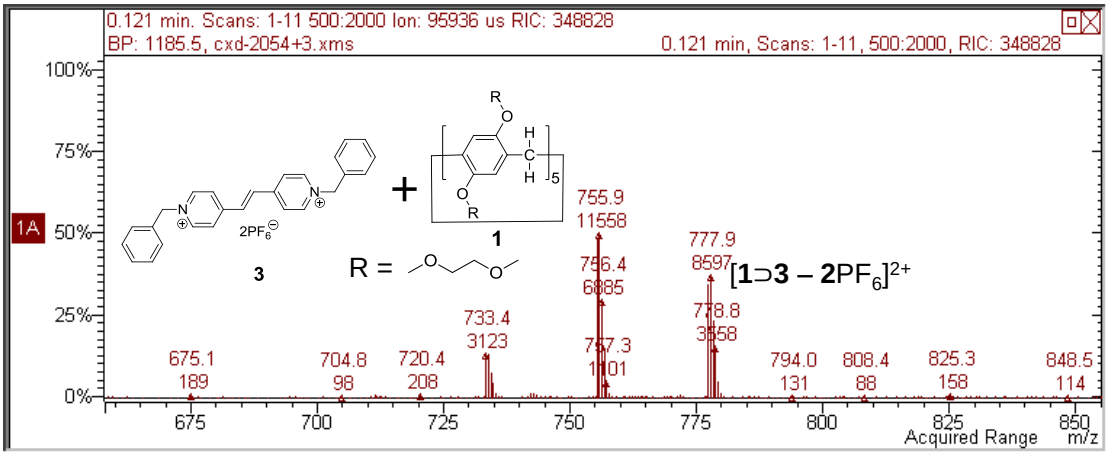


Fig. S6 Electrospray ionization mass spectrum of an equimolar solution of **1** with **3**.

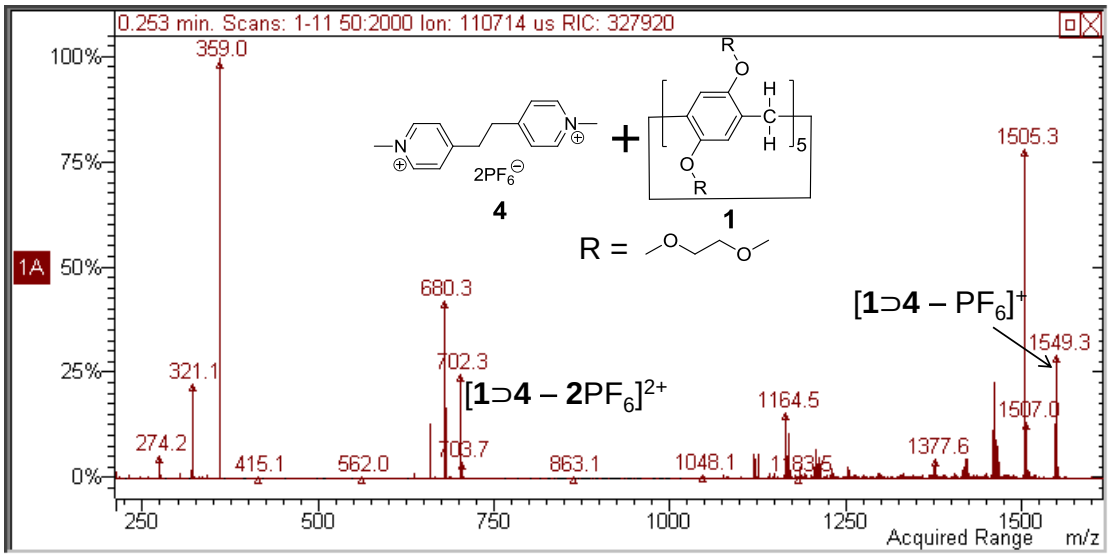


Fig. S7 Electrospray ionization mass spectrum of an equimolar solution of **1** with **4**.

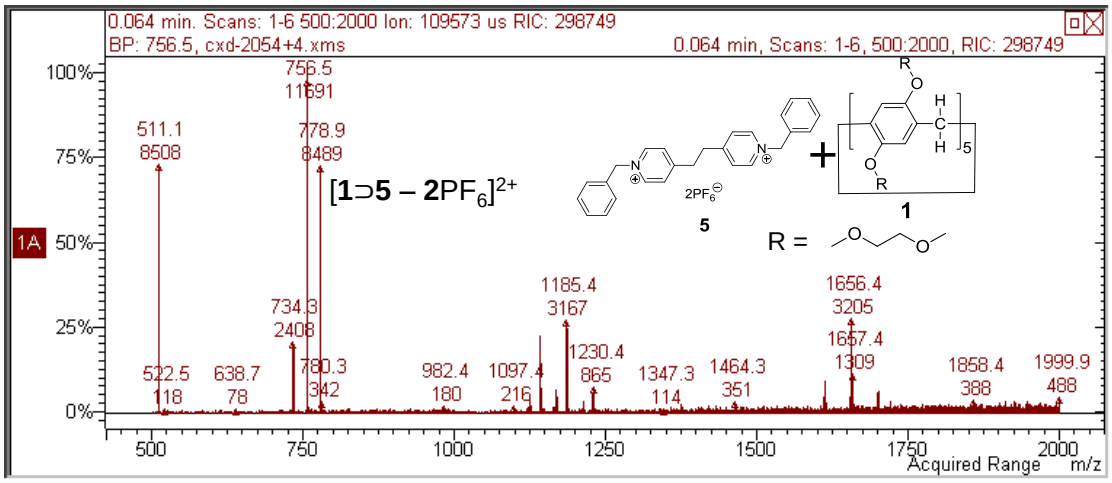
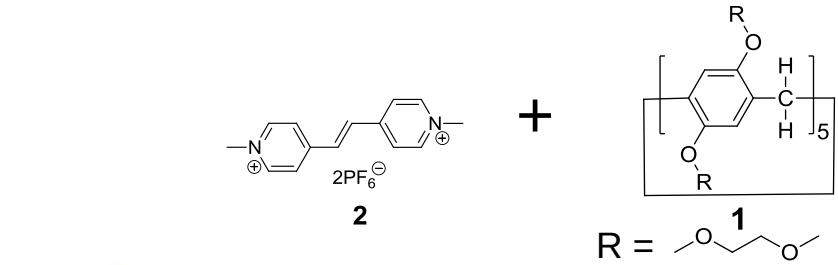
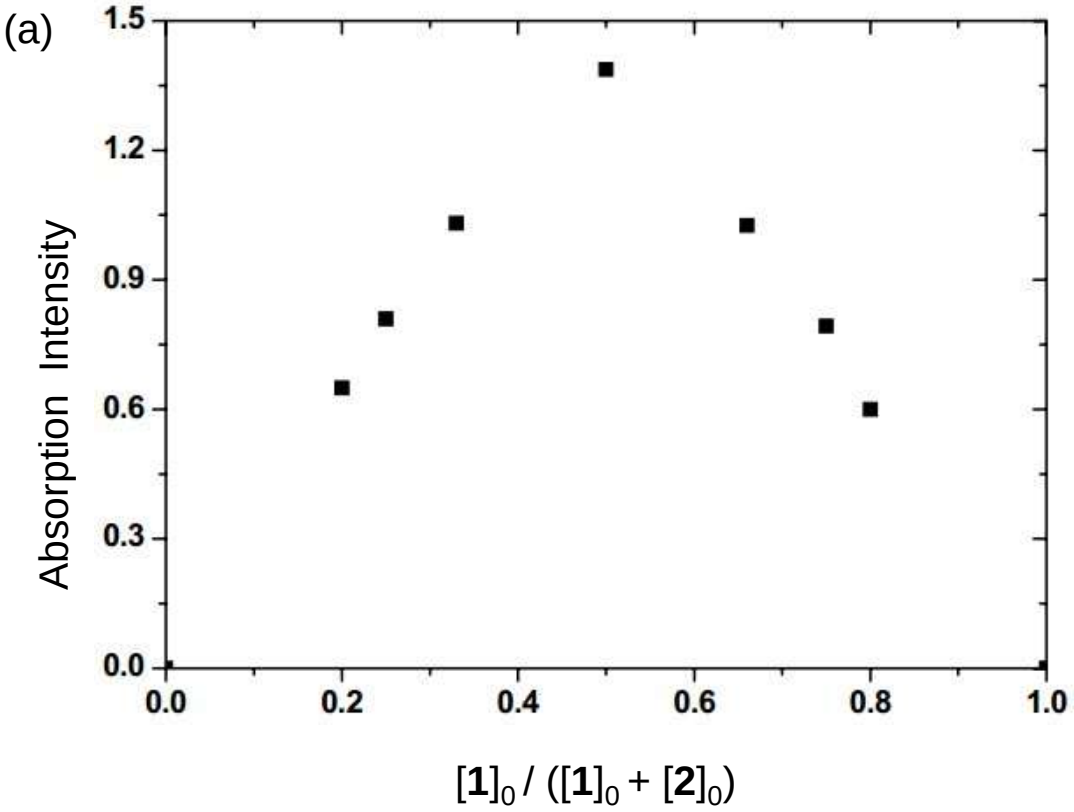
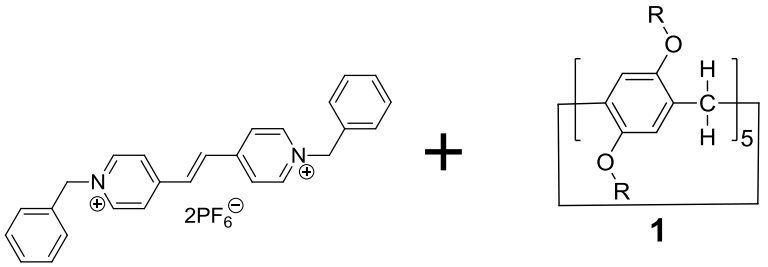


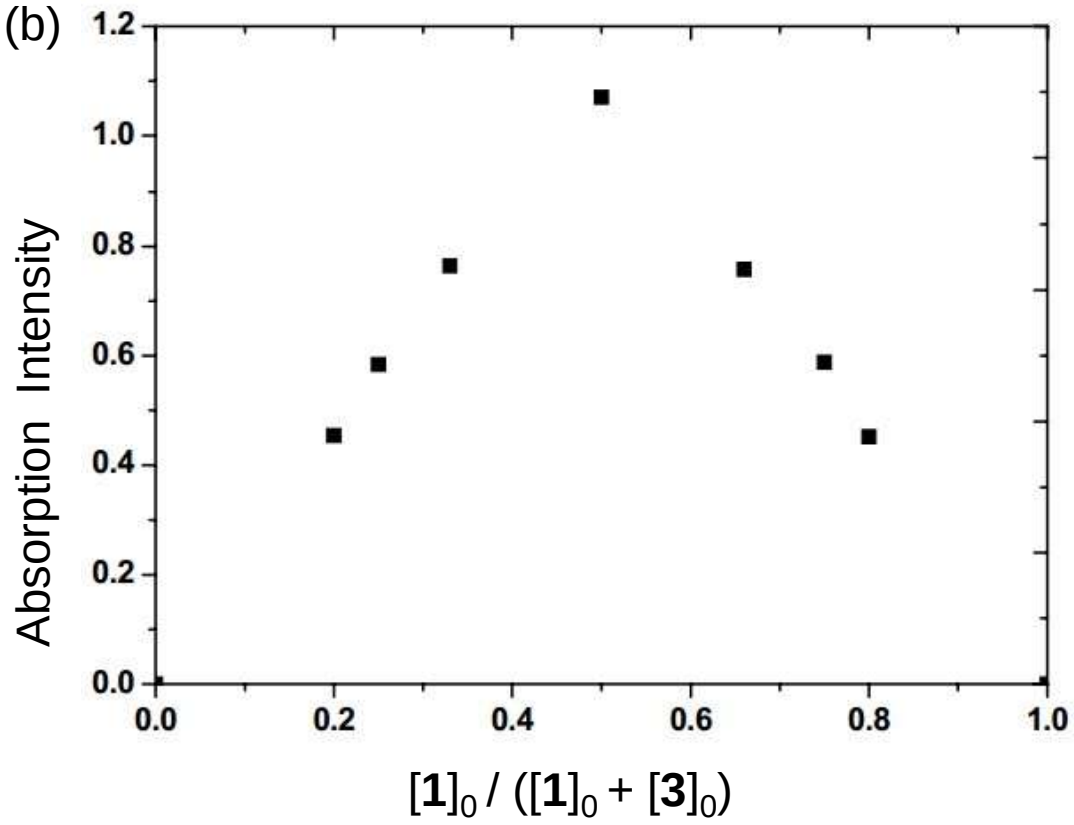
Fig. S8 Electrospray ionization mass spectrum of an equimolar solution of **1** with **5**.

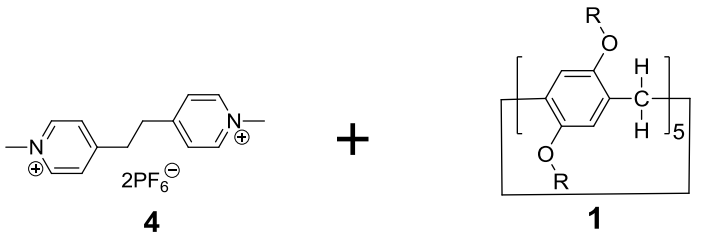
5. Job plots of ***1***⊃***2***, ***1***⊃***3***, ***1***⊃***4*** *and* ***1***⊃***5*** *based on UV-vis spectroscopy data in acetonitrile*



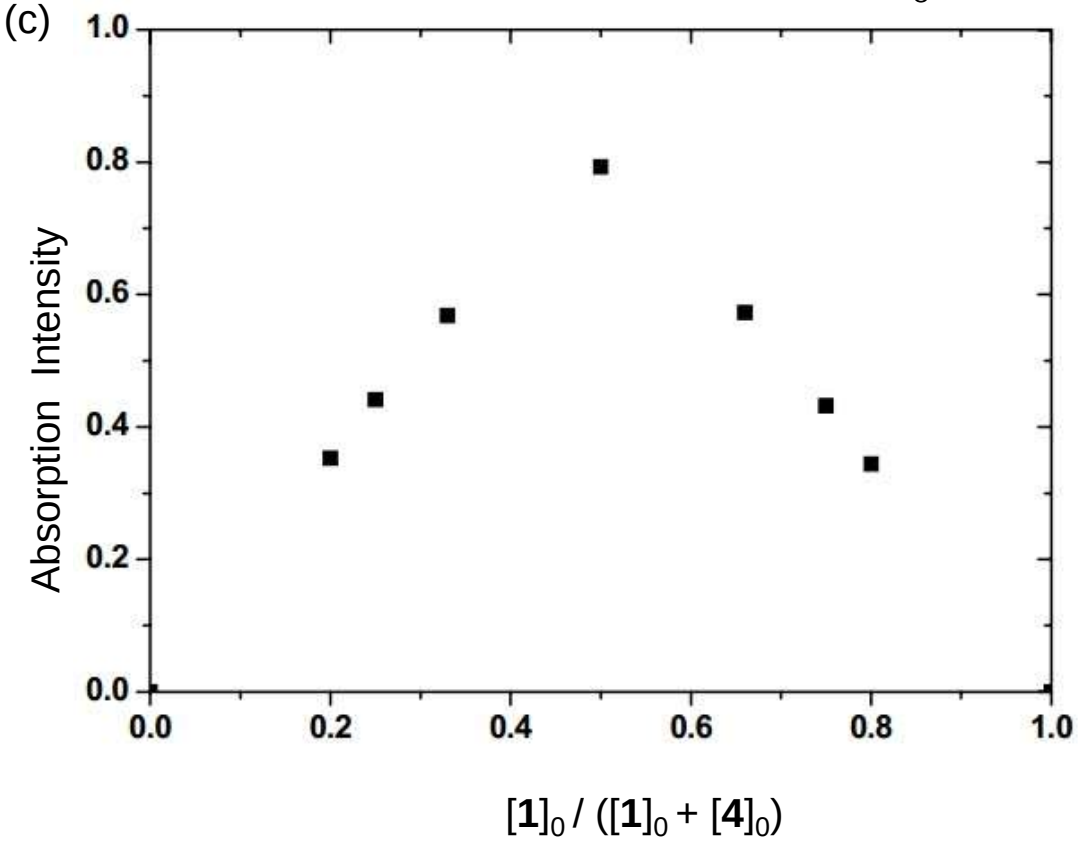








(c)



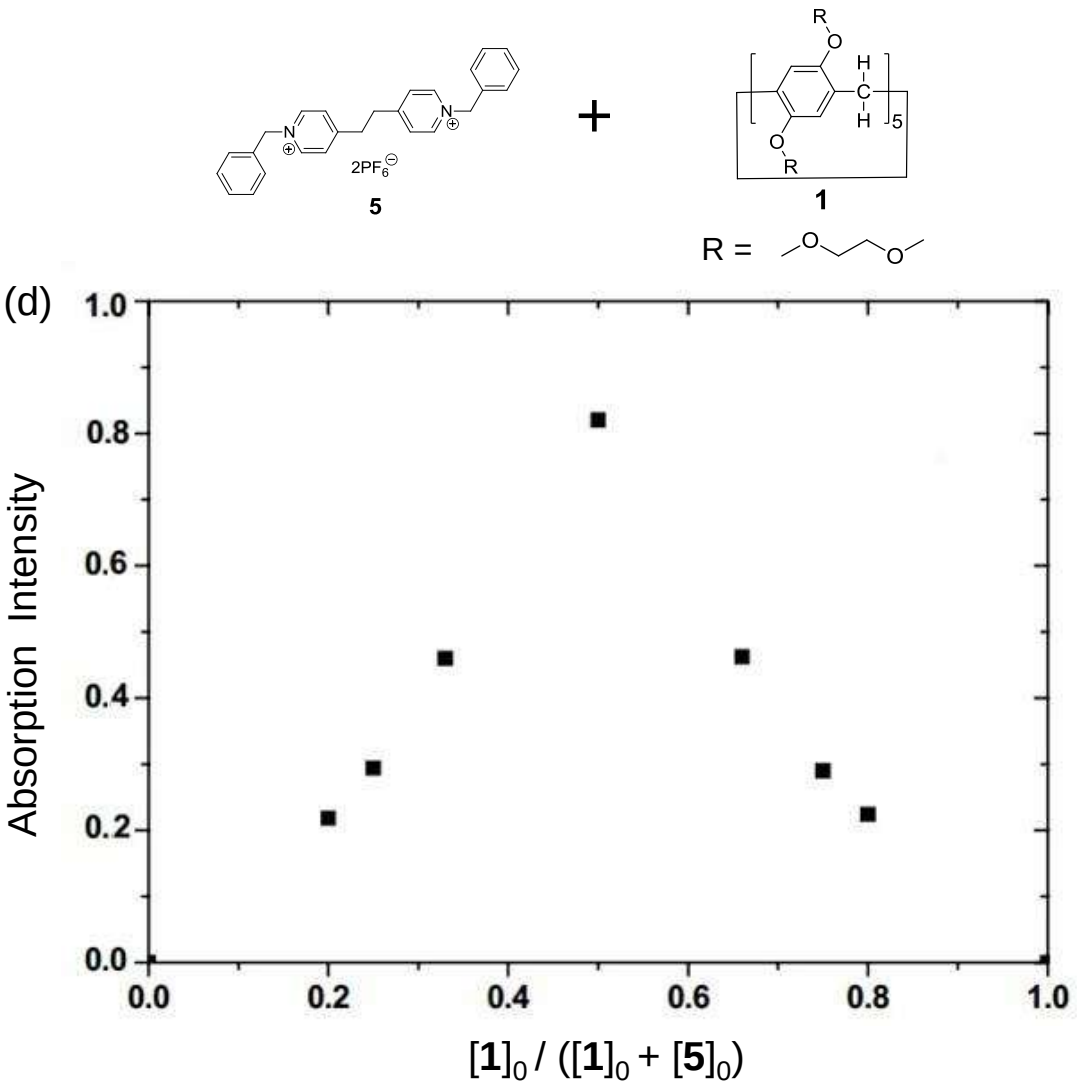


Fig. S9 Job plots showing the 1:1 stoichiometries of the complexations between **1** and **2** (a), between **1** and **3** (b), between **1** and **4** (c), and between **1** and **5** (d) in acetonitrile: (a) $[\mathbf{1}]_0 + [\mathbf{2}]_0 = 2.00$ mM; (b) $[\mathbf{1}]_0 + [\mathbf{3}]_0 = 2.00$ mM; (c) $[\mathbf{1}]_0 + [\mathbf{4}]_0 = 2.00$ mM; (d) $[\mathbf{1}]_0 + [\mathbf{5}]_0 = 2.00$ mM. $[\mathbf{1}]_0$, $[\mathbf{2}]_0$, $[\mathbf{3}]_0$, $[\mathbf{4}]_0$, and $[\mathbf{5}]_0$ are the initial concentrations of **1**, **2**, **3**, **4**, and **5**, respectively.

*6. Investigation on the complexation between pillar[5]arene **1** and salt guests **3–5***

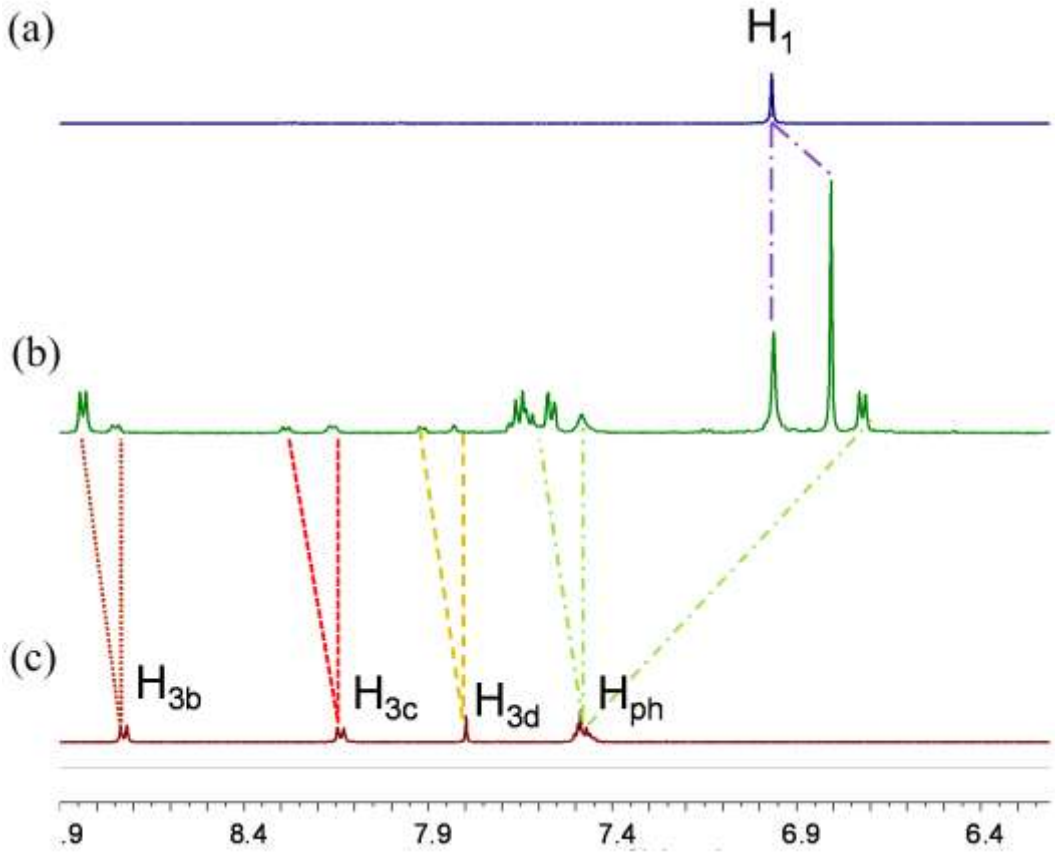


Fig. S10 Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 22 °C): (a) 2.00 mM **1**; (b) 2.00 mM **1** and vinylogous viologen **3**; (c) 2.00 mM vinylogous viologen **3**.

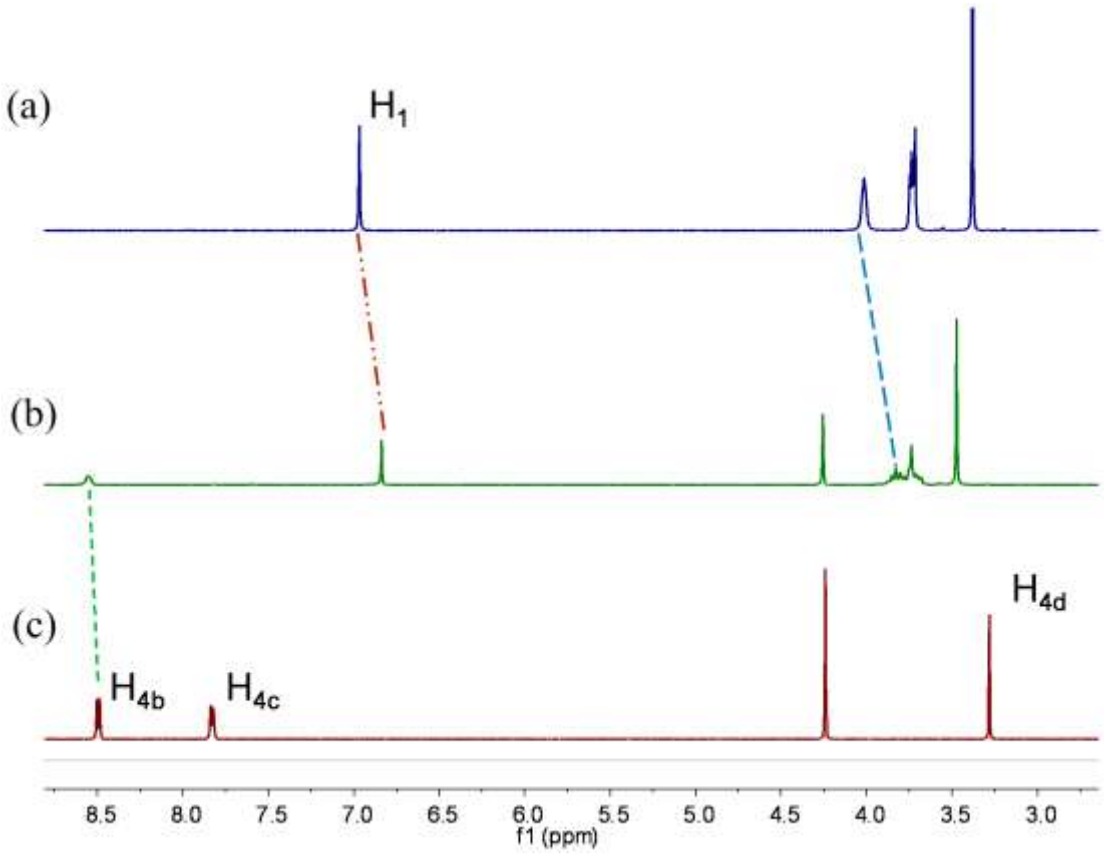


Fig. S11 Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 22 °C): (a) 2.00 mM **1**; (b) 2.00 mM **1** and **4**; (c) 2.00 mM **4**.

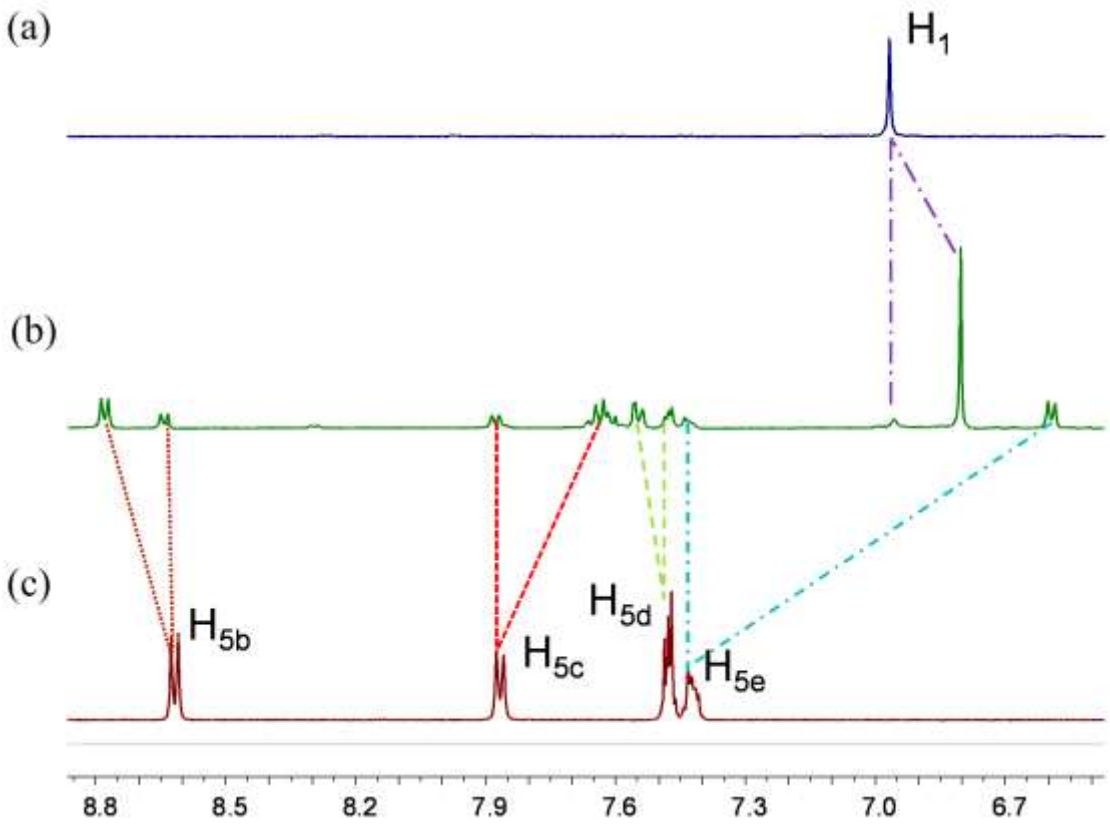


Fig. S12 Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 22 °C): (a) 2.00 mM **1**; (b) 2.00 mM **1** and **5**; (c) 2.00 mM **5**.

References:

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

S2. G. M. Sheldrick, *SHELXS-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.