

Supramolecular Side-Chain Poly[2]pseudorotaxanes Formed by Orthogonal Coordination-Driven Self-Assembly and Crown-Ether-Based Host-Guest Interactions

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1. Materials and methods

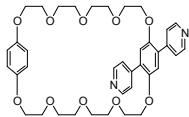
Compounds **3**,^{S1} **4**,^{S2} and **5**^{S3} were synthesized according to literature procedures. All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. NMR spectra were recorded with a Bruker Avance DMX 500 spectrophotometer with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. 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. The melting point was collected on a SHPSIC WRS-2 automatic melting point apparatus. UV-vis spectroscopy was performed on a Shimadzu UV-2550 instrument at room temperature. Dynamic light scattering (DLS) was carried out on a Malvern Nanosizer S instrument at room temperature. The crystal data was collected on an Oxford Diffraction Xcalibur Atlas Gemini ultra. The crystal structures were solved by SHELXS-97^{S4} and refined by SHELXL-97.^{S5} Cyclic voltammetric measurements were carried out in an electrolyte solution consisting of 0.02 M tetrabutylammonium hexafluorophosphate using a Pt working electrode, an auxiliary Pt electrode, and an Ag/AgCl reference electrode. The acetone solutions were degassed and filled up with nitrogen. Cyclic voltammograms were recorded on a Solartron SI 1287 potentiostat controlled by a LabView program at a rate of 0.100 V/s.

Chemical reaction scheme showing the synthesis of compound **1** from compound **5** and 4-pyridylboronic acid.

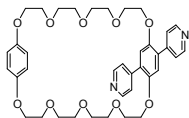
Compound **5** (a macrocyclic ether with two bromophenyl groups) reacts with 4-pyridylboronic acid ($\text{HO-B(OH)-C}_6\text{H}_4\text{-N}$) in the presence of $\text{Pd(PPh}_3)_4$ and K_2CO_3 to yield compound **1** (a macrocyclic ether with two 4-pyridylphenyl groups).

The reaction conditions are: $\text{Pd(PPh}_3)_4$, K_2CO_3 , and the yield is 36%.

S3



-152.90
 -150.48
 -149.63
 -145.43
 -129.05
 -124.33
 -115.43
 -115.29
 -71.00
 -70.80
 -70.73
 -70.66
 -69.67
 -69.62
 -69.17
 -67.99



S4

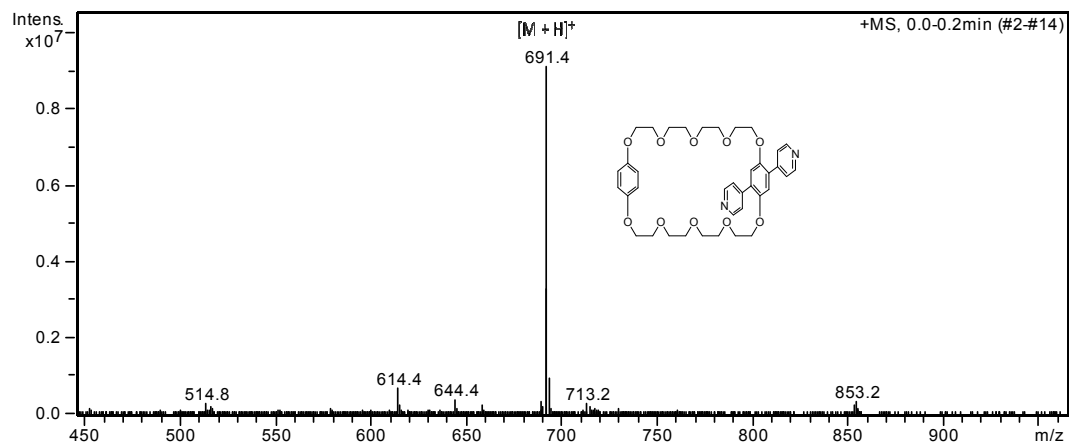


Figure S3. LRESI mass spectrum of **1**.

3. Job plots of **1**↔**2** and **1**↔**3** based on UV-vis spectroscopy data in acetone

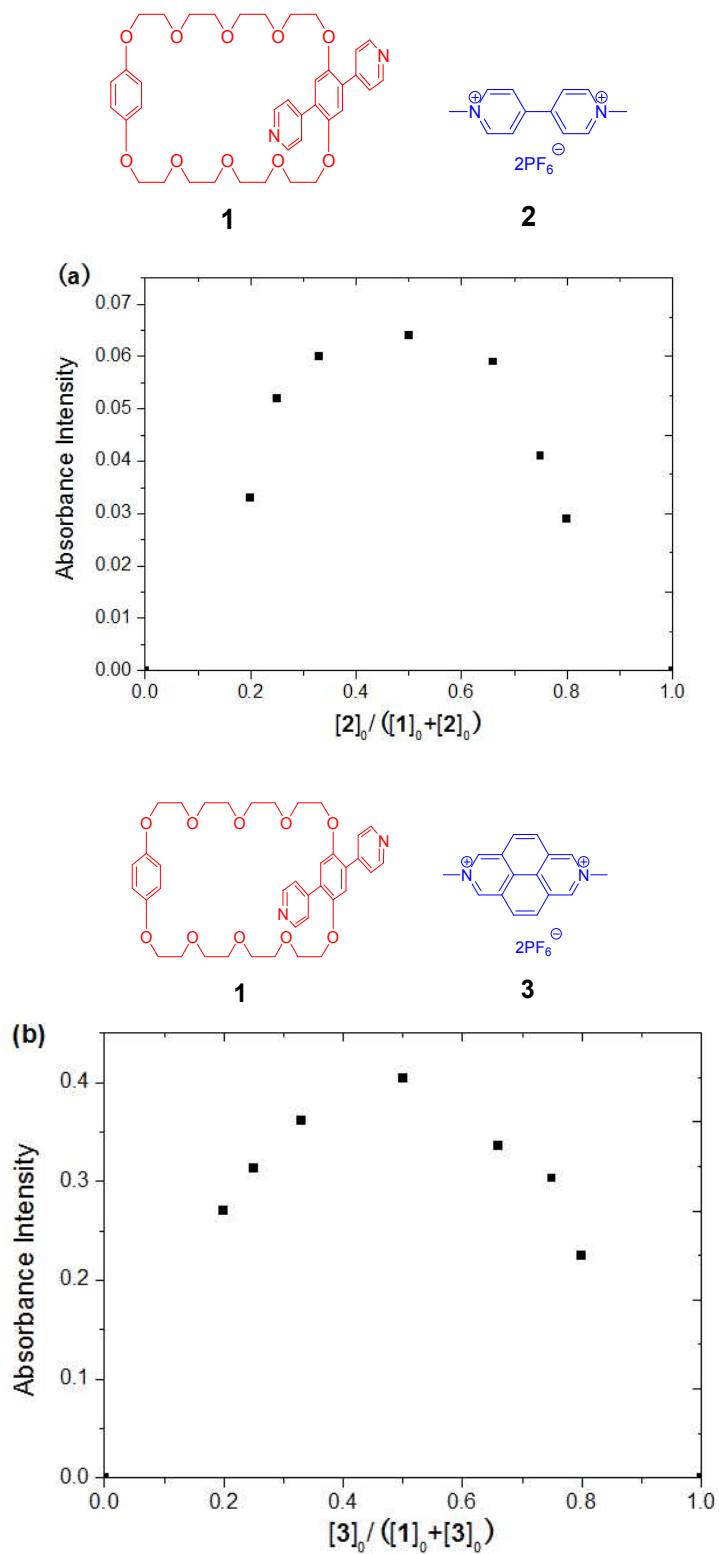


Figure S4. Job plots showing the 1:1 stoichiometries of the complexes between **1** and **2** (a), **1** and **3** (b) in acetone: (a) $[1]_0 + [2]_0 = 1.00$ mM; (b) $[1]_0 + [3]_0 = 1.00$ mM. $[1]_0$, $[2]_0$, and $[3]_0$ are the initial concentrations of **1**, **2**, and **3**, respectively.

4. Electrospray ionization mass spectra of host **1** with guests **2** and **3** in acetonitrile

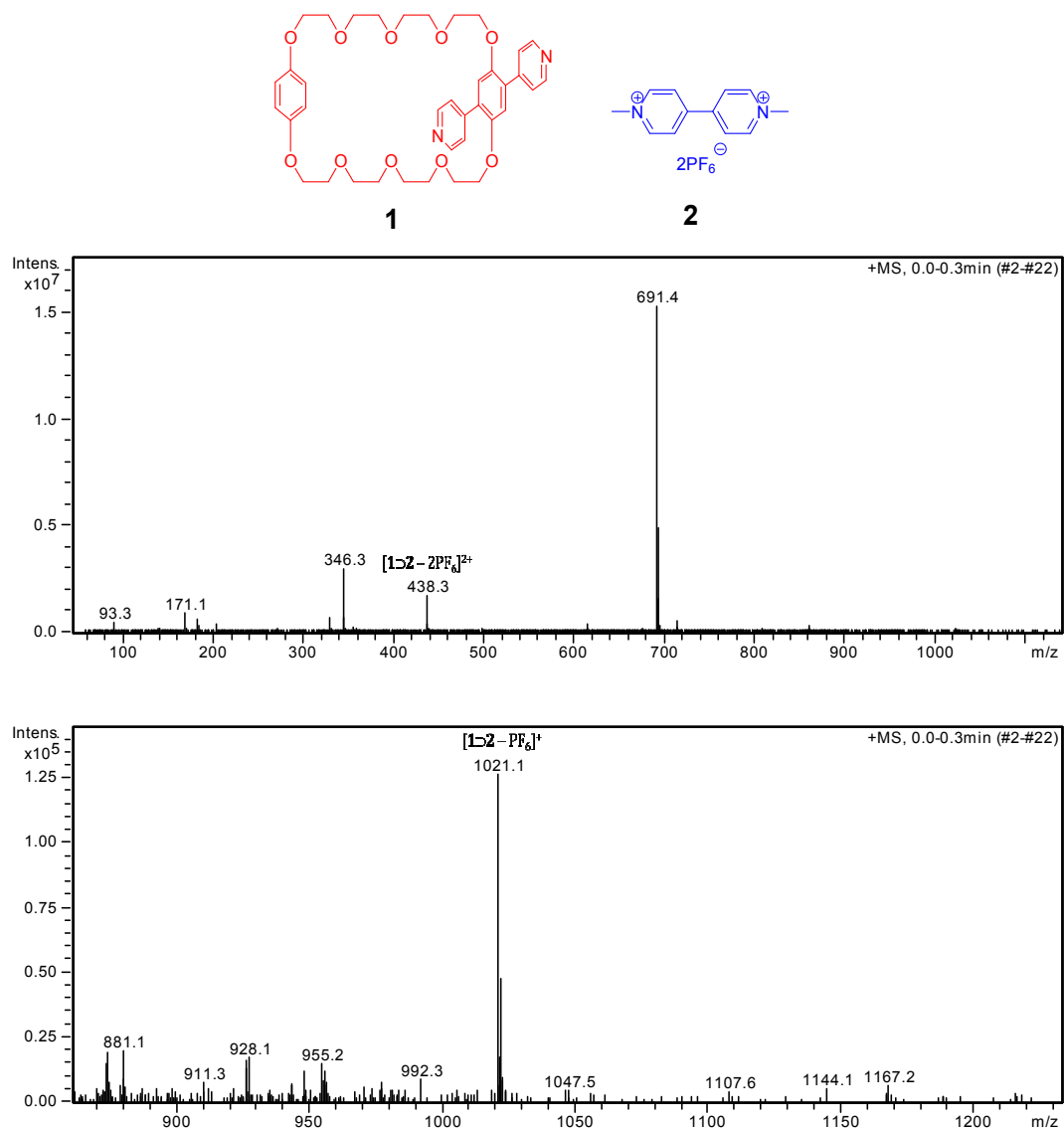


Figure S5. The positive electrospray ionization mass spectrum of an equimolar mixture of **1** and **2** in acetonitrile. Mass fragments at m/z 1021.1 for $[\mathbf{1} \supset \mathbf{2} - \text{PF}_6]^+$ and m/z 438.3 for $[\mathbf{1} \supset \mathbf{2} - 2\text{PF}_6]^{2+}$ confirmed the 1:1 complexation stoichiometry between **1** and **2**. Mass fragment at m/z 691.4 corresponds to host **1**.

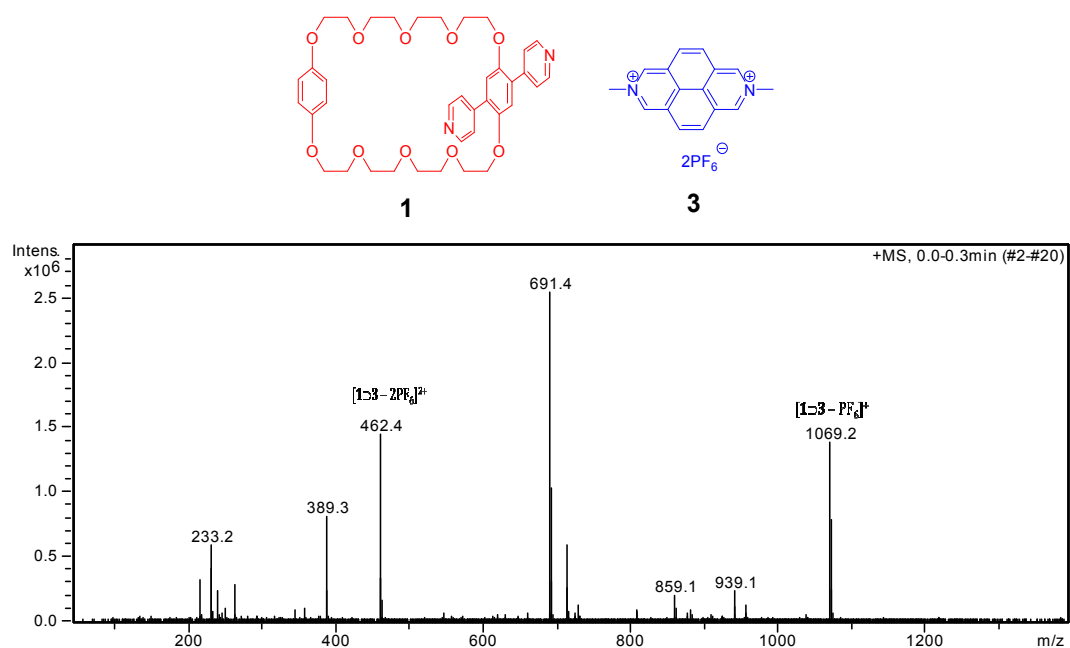


Figure S6. The positive electrospray ionization mass spectrum of an equimolar mixture of **1** and **3** in acetonitrile. Mass fragments at m/z 1069.2 for $[1\div 3 - PF_6]^+$ and m/z 462.4 for $[1\div 3 - 2PF_6]^{2+}$ confirmed the 1:1 complexation stoichiometry between **1** and **3**. Mass fragment at m/z 691.4 corresponds to host **1**.

5. Determination of association constants of complexes **1**⊃**2** and **1**⊃**3** in acetone

The association constants (K_a) of complexes **1**⊃**2** and **1**⊃**3** were determined by probing the charge-transfer bands of the complexes by UV-vis spectroscopy and employing a titration method. Progressive addition of an acetone solution with high guest concentration and low host concentration to an acetone solution with the same host concentration 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 constants (K_a): $7.04 \times 10^2 \text{ M}^{-1}$ for **1**⊃**2** and $2.70 \times 10^3 \text{ M}^{-1}$ for **1**⊃**3**.

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

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

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 initial concentration of the guest.

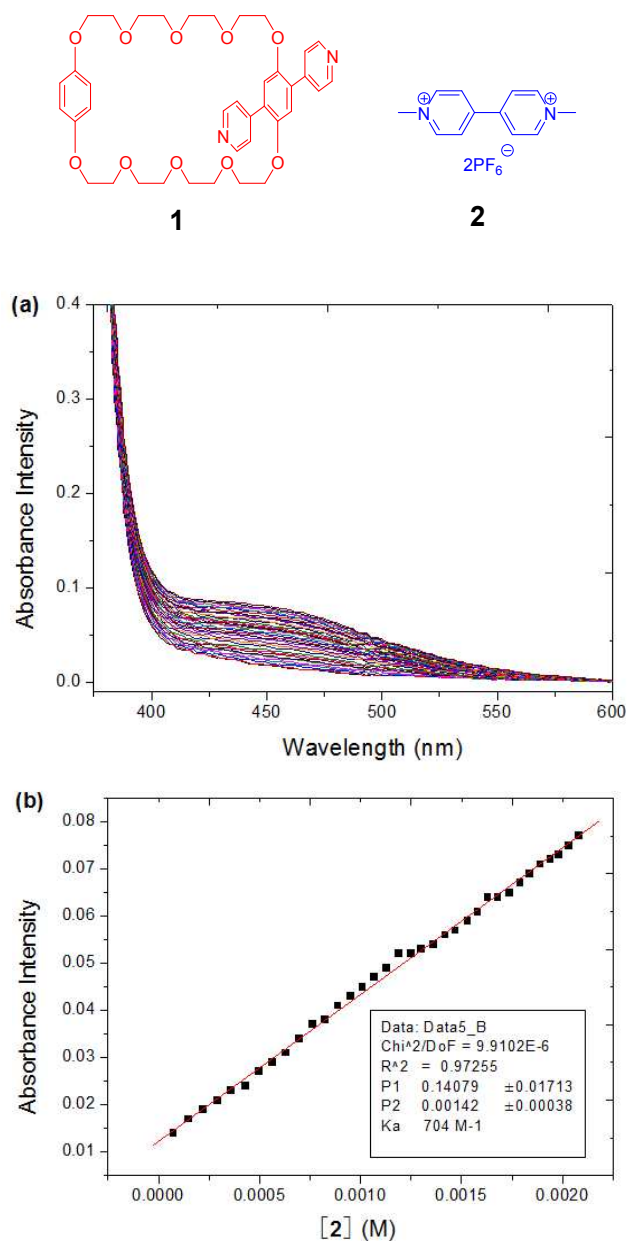


Figure S7. (a) The absorption spectral changes of **1** (1.00 mM) upon addition of **2** and (b) the absorbance intensity changes at $\lambda = 450$ nm upon addition of **2** (from 0 to 2.08 mM). The red solid line was obtained from the non-linear curve-fitting using Eq. S1.

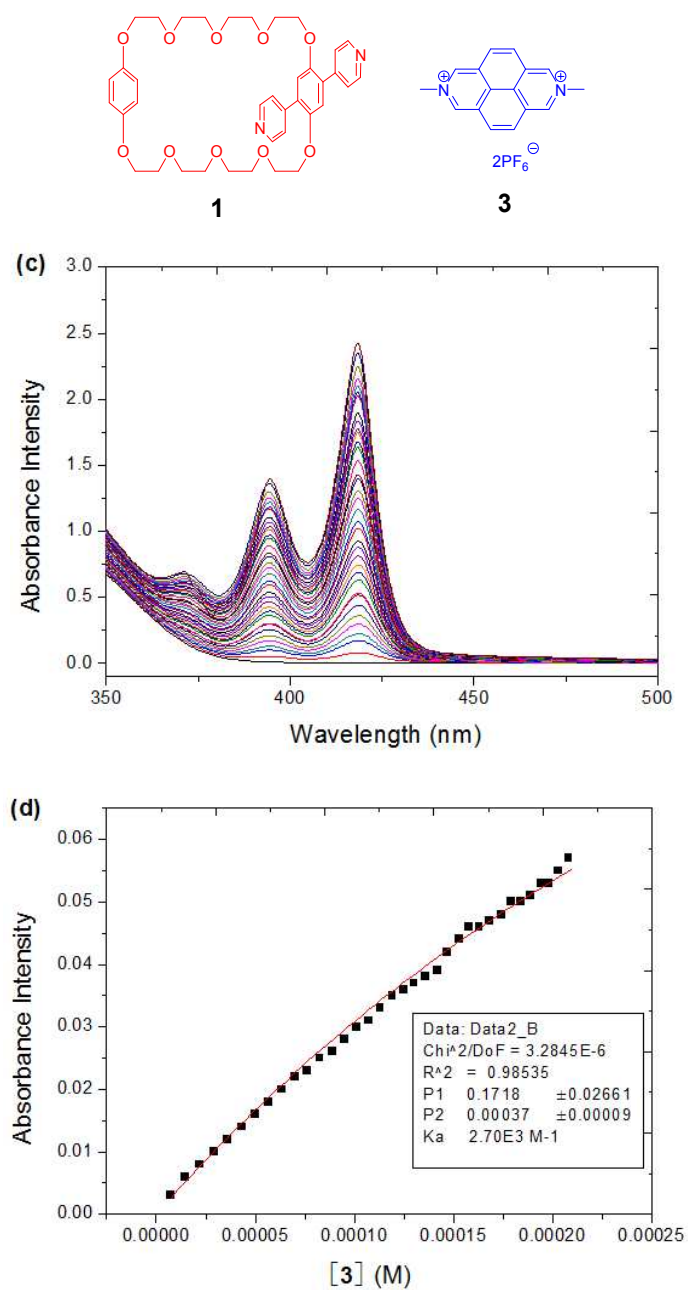


Figure S8. (c) The absorption spectral changes of **1** (0.100 mM) upon addition of **3** and (d) the absorbance intensity changes at $\lambda = 450$ nm upon addition of **3** (from 0 to 0.208 mM). The red solid line was obtained from the non-linear curve-fitting using Eq. S1.

6. Partial DOSY NMR of **1** and **1** + **4**

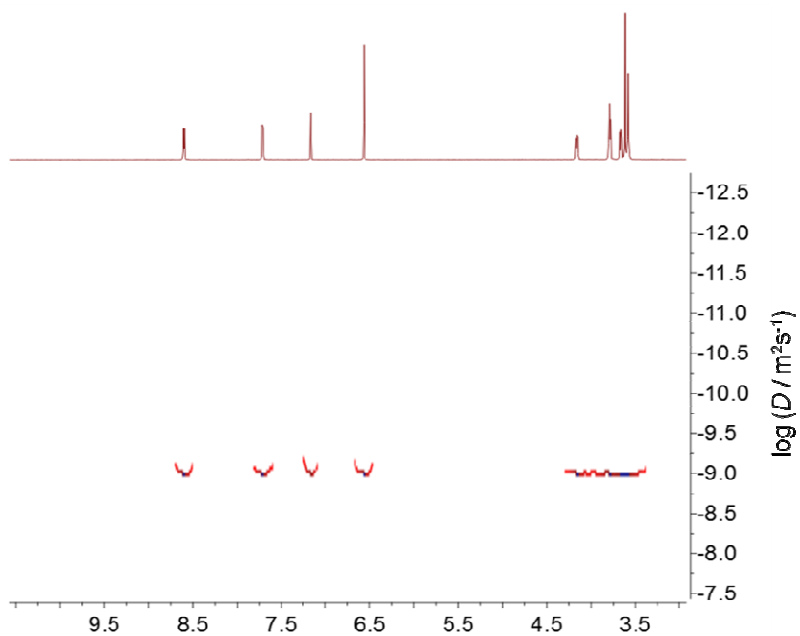


Figure S9. Partial DOSY NMR spectrum (500 MHz, acetone-*d*₆, 293 K) of **1** at 5.00 mM.

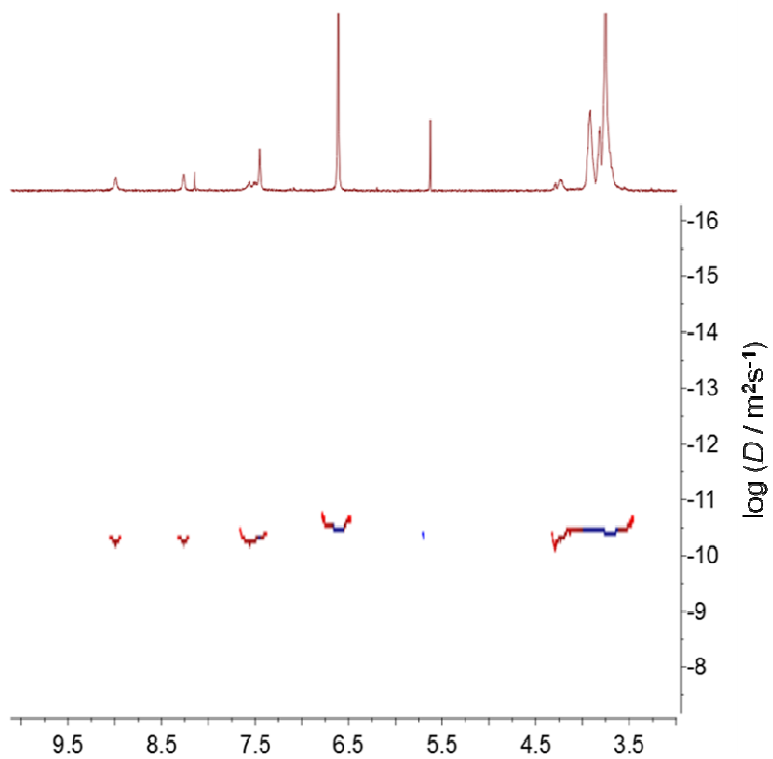


Figure S10. Partial DOSY NMR spectrum (500 MHz, acetone-*d*₆, 293 K) of **1** + **4** at 5.00 mM.

7. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of acceptor **4** and assemblies

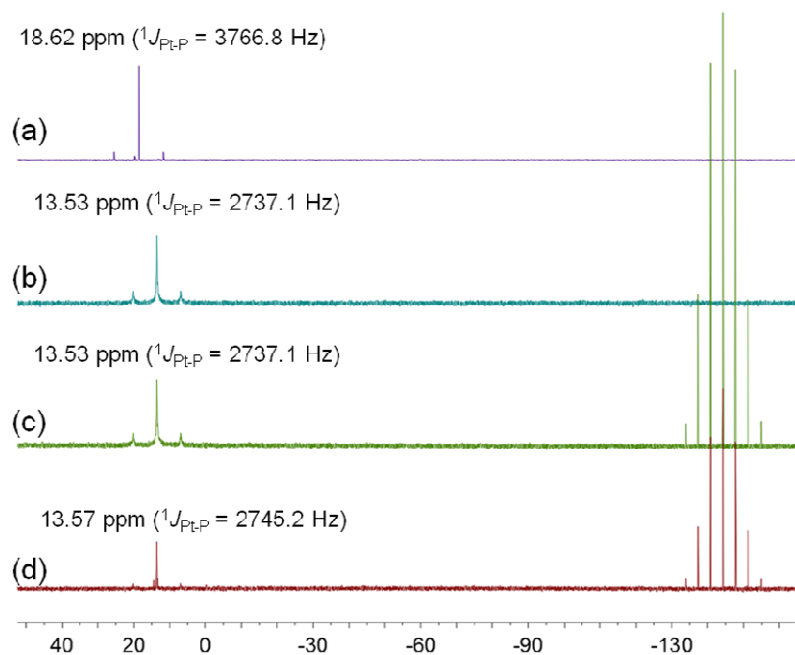


Figure S11. Partial $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (500 MHz, acetone- d_6 , 293 K): (a) **4**; (b) **1** + **4**; (c) **1** + **2** + **4**; (d) **1** + **2** + **4** + **3**. $c = 5.00$ mM.

8. X-ray analysis data for **1**⊃**2**

Crystallographic data: block, yellow, $0.32 \times 0.26 \times 0.20 \text{ mm}^3$, $\text{C}_{53}\text{H}_{64.50}\text{N}_{5.50}\text{O}_{10}\text{F}_{12}\text{P}_2$, FW 1228.54, orthorhombic, space group $Pbcn$, $a = 10.9871(5)$, $b = 15.0321(6)$, $c = 19.4495(9) \text{ \AA}$, $\alpha = 67.410(4)^\circ$, $\beta = 87.040(4)^\circ$, $\gamma = 85.923(4)^\circ$, $V = 2957.3(2) \text{ \AA}^3$, $Z = 2$, $D_c = 1.380 \text{ g cm}^{-3}$, $T = 170 \text{ K}$, $\mu = 0.170 \text{ mm}^{-1}$, 5075 measured reflections, 18454 independent reflections, 705 parameters, 0 restraints, $F(000) = 1278.0$, $R_1 = 0.1081$, $wR_1 = 0.2627$ (all data), $R_2 = 0.0839$, $wR_2 = 0.2402$ [$I > 2\sigma(I)$], max. residual density $1.344 \text{ e} \cdot \text{\AA}^{-3}$, and goodness-of-fit (F^2) = 1.114. CCDC 982064.

9. Size distributions of **1** + **4**, **1** + **2** + **4** and **1** + **3** + **4** in acetone

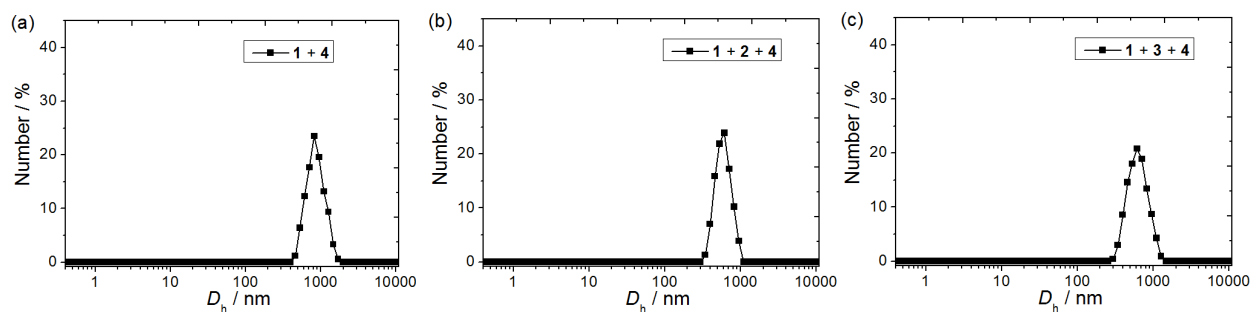


Figure S12. Size distributions of **1** + **4** (a), **1** + **2** + **4** (b) and **1** + **3** + **4** (c) in acetone. $c = 5.00 \text{ mM}$.

10. Cyclic voltammograms of **2**, **1 + 4** and **1 + 2 + 4**

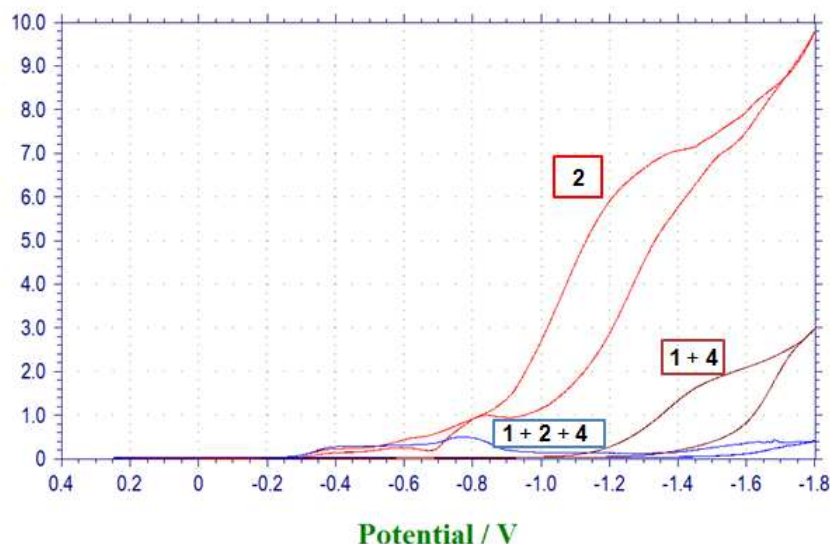


Figure S13. Cyclic voltammograms (acetone, 298 K, scan rate 100 mV/s) of **2**, **1 + 4** and **1 + 2 + 4**. $c = 1.00$ mM.

we conducted cyclic voltammetry experiments of paraquat **2**, metallosupramolecular polymer **1 + 4**, and side-chain poly[2]pseudorataxane **1 + 2 + 4** (Figure S13). It was found that our metallosupramolecular polymer (**1 + 4**) has electrochemical activity. Moreover, when the paraquat was recognized by metallosupramolecular polymer (**1 + 4**) to form side-chain poly[2]pseudorataxane (**1 + 2 + 4**), the electrochemical activity of paraquat decreased significantly due to the inclusion complexation. These findings provide a foundation for the design of supramolecular polymer-based electrochemical sensors.

11. References:

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