**The First [2]Pseudorotaxane and the First Pseudocryptand-Type
Poly[2]pseudorotaxane based on Bis(*meta*-phenylene)-32-Crown-10 and
Paraquat derivatives**

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1. Materials and methods

Carbazole, sodium hydride (NaH) and ammonium hexafluorophosphate were reagent grade and used as received. The bis(*meta*-phenylene)-32-crown-10 BMP32C10 dibromide was prepared according to a literature procedure.¹ Solvents were either used as purchased or dried according to literature procedures. ¹H-NMR spectra were obtained on a JEOL ECLIPSE-500 spectrometer with internal standard TMS. ¹³C-NMR spectra were collected on a JEOL ECLIPSE-500 spectrometer at 125 MHz. HR-MS were obtained by employing an Agilent LC-ESI-TOF.

2. Synthesis of BMP32C10 dicarbazole **1d**

Scheme S1. Synthesis of BMP32C10 dicarbazole **1d**.

NaH (56.5 mg, 1.41 mmol) was suspended in THF (40 mL, anhydrous). The suspension was stirred at room temperature for 5 min under N₂. Carbazole (171 mg, 1.02 mmol) was added and the mixture was stirred at room temperature for 30 minutes, then refluxed for another 30 minutes, and cooled to room temperature. BMP32C10 dibromide (170 mg, 0.231 mmol) was added and the mixture was stirred at room temperature for 30 min. and then refluxed for 24 h. DI water (3 mL) was added into the resulting pink suspension to quench the excess NaH. Solvent was removed and a pink solid was obtained. The solid was redissolved in dichloromethane (DCM) and the solution was washed with DI water (x 3). After solvent was removed, a pink solid was again obtained. A silica gel column (gradient elution: dichloromethane, then dichloromethane : methanol = 96 : 4) was employed to purify the crude product. A pale yellow solid was obtained (207 mg, 100%, mp = 185-186 °C). ¹H-NMR (CDCl₃, 500 MHz) (Figure S1): δ : 8.08 (d, ³J = 8 Hz, 4.0 H), 7.39 (t, ³J = 8 Hz, 4.1 H), 7.30 (d, ³J = 8 Hz, 4.1 H), 7.22 (t, ³J = 8 Hz, 4.0 H), 6.26 (m, 6.2 H), 5.33 (s, 4.0 H), 5.30 (s, DCM), 3.85 (t, ³J = 8 Hz, 8.0 H), 3.68 (t, ³J = 8 Hz, 8.1 H), 3.59 (s, 17 H). ¹³C-NMR (CDCl₃, 126 MHz) (Figure S2): δ (ppm): 160.36, 140.75, 139.71, 125.92, 123.06, 120.40, 119.26, 108.97,

105.56, 99.81, 70.84, 70.80, 69.55, 67.45, 46.67. HR-ESIMS (Figure S3): calcd for $[M+H]^+$: 895.4164, found m/z , 895.4163 $[M + H^+]$, error: -0.11 ppm.

Figure S1. ^1H -NMR (CDCl_3 , 500 MHz, room temperature) of BMP32C10 dicarbazole **1d**.

Figure S2. ^{13}C -NMR (CDCl_3 , 125 MHz, room temperature) of BMP32C10 dicarbazole **1d**.

Figure S3. Electrospray ionization mass spectrum of BMP32C10 dicarbazole **1d**.

3. Job plot between **1d** and **2**

Figure S4. Job plot showing the 1:1 stoichiometry of the complex between **1d** and **2** in $CDCl_3/CD_3CN = 1/1$ $\langle v/v \rangle$. $[1d]_0 + [2]_0 = 2.00$ mM.

4. Determination of Δ_0 of **1d·2**

Figure S5. Determination of Δ_0 of **1d·2** in $CDCl_3/CD_3CN = 1/1$ $\langle v/v \rangle$. $[1d]_0 = 0.176$ mM.

4. Determination of Δ_0 of **1d·3**

Figure S6. Determination of Δ_0 of **1d·3** in $\text{CDCl}_3/\text{CD}_3\text{CN} = 1/1$ <v/v>. $[\mathbf{1d}]_0 = 0.416$ mM.

5. Mass spectrum of **1d·2**

Figure S7. Electrospray ionization mass spectrum of **1d·2**.

6. Mass spectrum of **1d·3**

Figure S8. Electrospray ionization mass spectrum of **1d·3**. m/z 1285.51 [**1d·3**-PF₆]⁺.

7. Crystal Structure of **1d·3**

a

b

Figure S9. (a) and (b): Two views of the X-ray structure of **1d·3**. **1d** is red. **3** is blue. Solvent molecules, minor disordered carbon and hydrogen atoms, one PF₆ ion and hydrogen atoms except the ones involved in hydrogen bonding have been omitted for clarity. Hydrogen bonds in (b) were omitted for clarity. Selected hydrogen-bond parameters: H···O(F) distances (Å), C···O(F) distances (Å), C-H···O(F) angles (deg): o 2.641, 3.582, 159.0; p 2.714, 3.625, 153.32; q 2.109, 2.943, 171.4; r 2.496, 3.406, 160.5; s 2.674, 3.574, 151.4; t 2.479, 3.338, 142.7; Off-set face-to-face π -stacking parameters: centroid-centroid distances (Å) and dihedral angles (deg): aromatic rings of **1d** and pyridinium rings of paraquat **3**: 3.771, 3.828 and 1.58, 7.84.

References

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