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Preparation of Bis(*m*-phenylene)-32-crown-10-Based Cryptand/Bisparaquat [3]Rotaxanes with High Efficiency

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Two [3]rotaxanes were synthesized from two bis(*m*-phenylene)-32-crown-10-based cryptands and a bisparaquat derivative by using a threading-followed-by-stoppering method. As a result of strong association and positive cooperative complexation between the cryptands and the bisparaquat derivative, high yields and high selectivities were achieved. No [2]rotaxanes were found during the preparation.

Introduction

In the past decade, mechanically interlocked structures such as rotaxanes have attracted a great deal of attention not only because of their topological importance but also due to their potential applications in molecular devices and material science.[1] Following the development of various template strategies, such as transition-metal–organic-ligand interaction, donor–acceptor interactions, intermolecular hydrogen bonding, and hydrophilic–hydrophobic interaction, these interlocked structures are now becoming much more easily available than before.[1,2] Among them, [*n*]rotaxanes represent a subclass of interesting compounds.[3–6] Whereas the synthesis of 2-component rotaxanes has been well achieved by template-directed protocols,[3] the efficient synthesis of [3]- and higher-order rotaxanes, especially the ones on which no stoppers exist between neighboring rings, still remains a challenging task.[4] Several template strategies have been applied to construct [3]- or higher-order rotaxanes, but only finite protocols could achieve high efficiency.[5,6] Furthermore, during the preparation of [*n*]rotaxanes ($n > 2$) on which no stoppers exist between neighboring rings, usually [2]rotaxanes and other lower-order [*m*]rotaxanes ($n > m > 2$) were also obtained except for [*n*]rotaxanes ($n > 2$) and yields were low.[6,7] For example, during the preparation a bis(*p*-phenylene)-34-crown-10/bisparaquat [3]rotaxane, though 4 molar equiv. of bis(*p*-phenylene)-34-crown-10 were used, the corresponding bis(*p*-phenylene)-34-crown-10/bisparaquat [2]rotaxane was obtained in 5% yield, whereas [3]rotaxane was obtained in only 33% yield.[7] Though the formation of [3]rotaxane without the [2]rotaxane product in the crown ether/ammonium ion recognition system has been reported, the yield was only 10%.[8]

Bis(*m*-phenylene)-32-crown-10-based cryptands have proved to be much better hosts for paraquat derivatives (*N*,*N*′-dialkyl-4,4′-bipyridinium salts), diquat, monopyridinium salts, and diazapyrenium salts than the corresponding simple bis(*m*-phenylene)-32-crown-10 (BMP32C10).[9] On the basis of the strong association between bis(*m*-phenylene)-32-crown-10-based cryptands and a paraquat derivative, we recently reported the synthesis of [2]rotaxanes by using a threading-followed-by-stoppering method.[10] It was demonstrated that the strong association between the cryptands and the paraquat derivative could result in high yields of [2]rotaxanes even in dilute solutions. The high efficiency, mainly brought by the strong association, should be more valuable for the syntheses of [3]- and higher-order rotaxanes.

Moreover, it was proved that bis(*m*-phenylene)-32-crown-10-based cryptand/bisparaquat [3]pseudorotaxane could be formed by positive cooperative complexation.[11] This is also very important for the efficient preparation of [3]- or higher-order rotaxanes, because the yields of [2]rotaxanes and other lower-order rotaxanes should be very low if positive cooperative complexation is involved in the formation of the corresponding [*n*]pseudorotaxanes. Herein, we report the syntheses of two bis(*m*-phenylene)-32-crown-10-based cryptand/bisparaquat [3]rotaxanes. High yields were given even in dilute solutions due to the strong association and cooperative complexation between the two cryptands and the bisparaquat derivative, and no [2]rotaxanes were detected during the preparation of these two [3]rotaxanes.

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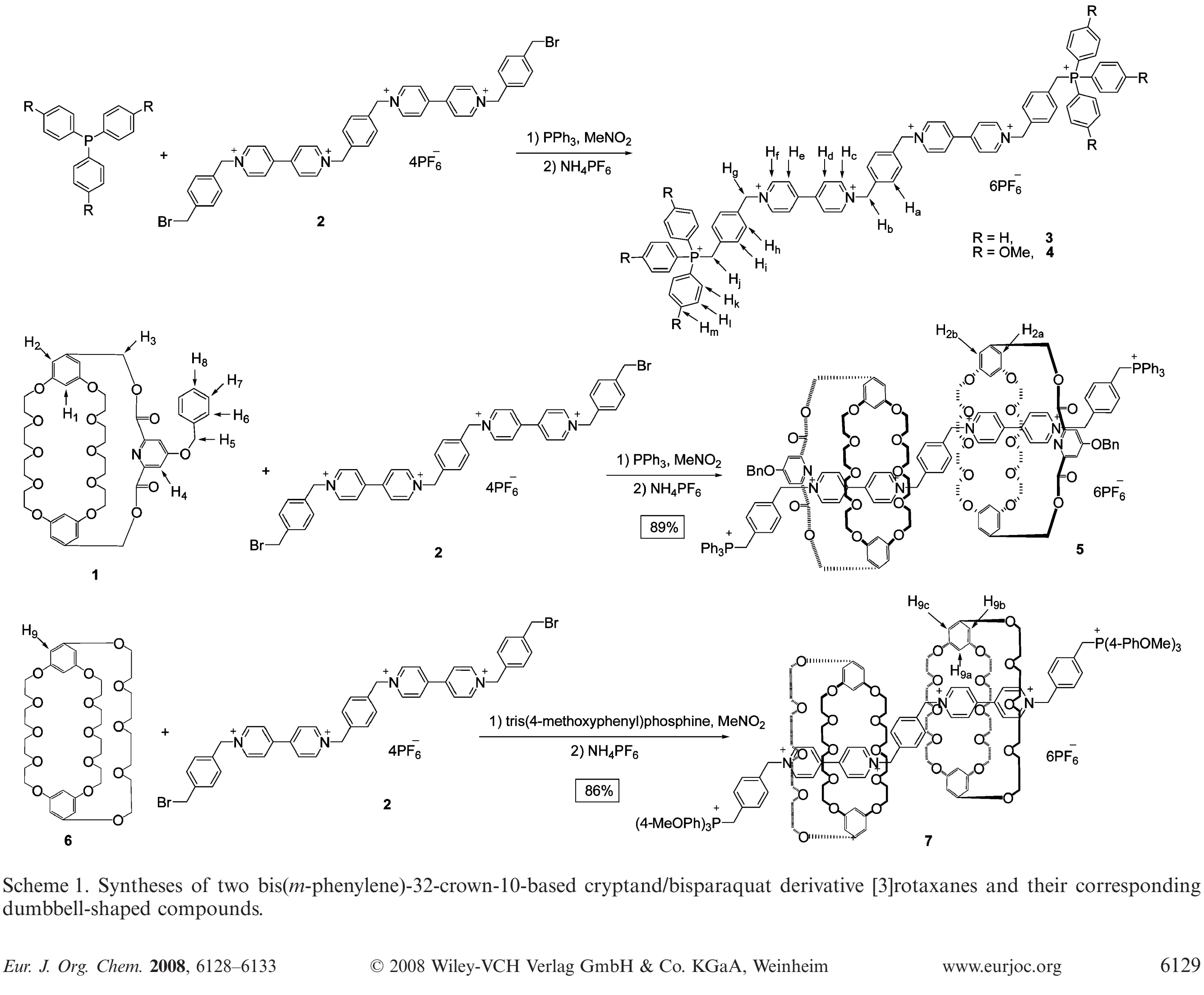
Results and Discussion

Here the threading-followed-by-stoppering strategy[10,12] was applied to synthesize two [3]rotaxanes (Scheme 1). Previously, it was proved that the triphenylphosphane groups are big enough to act as stoppers for cryptand **1**, but for cryptand **6**, tris(4-methoxyphenyl)phosphane groups are needed to serve as stoppers to form rotaxanes.[10] Therefore, the triphenylphosphane groups were used to synthesize [3]rotaxane **5** from cryptand **1**, whereas tris(4-methoxyphenyl)phosphane groups were applied as stoppers to synthesize [3]rotaxane **7** from cryptand **6**.

The synthesis of [3]rotaxane **5** was carried out in $MeNO_2$ by simply adding triphenylphosphane to a dilute solution of cryptand **1** and bisparaquat derivative dibromide **2**[13] (Scheme 1). After counterion exchange, [3]rotaxane **5** was isolated in 89% yield. As a result of strong association and cooperative complexation between the cryptand and the bisparaquat derivative, no [2]rotaxane was found.

Partial ^1H NMR spectra of cryptand **1**, rotaxane **5**, and dumbbell-shaped component **3** in CD_3SOCD_3 are shown in Figure 1. Because one [3]rotaxane **5** molecule contains two cryptand hosts, the aromatic protons H_2 of cryptand **1** are divided into two different types, H_{2a} and H_{2b}, representing the "*exo*-" and "*endo*-" phenylene protons, respectively, and correspondingly two signals were observed for them after the formation of [3]rotaxane **5** (Figure 1, spectra a and b). Furthermore, after the formation of [3]rotaxane **5**, dramatic upfield shifts were observed for the signals of aromatic protons H_1 and H_2 and methylene protons H_3 of cryptand **1**, whereas pyridine protons H_4 and benzyl protons H_5 moved downfield (Figure 1, spectra a and b). Synchronously, the signals of α-pyridinium protons H_c and H_f of **3** moved upfield obviously. The signals of *N*-methylene protons H_b and H_g moved slightly upfield, whereas phenylene protons H_a, H_h, and H_i moved downfield (Figure 1, spectra b and c).

The structure of [3]rotaxane **5** was further deduced from 2D NMR spectra, including H-H COESY, C–H COESY, and NOESY. As shown in Figure 2, except for the through-space correlations between the protons of the host, the through-space correlations between the methylene protons (H_b and H_g) on the dumbbell-shaped component and the ether protons H_{ether} on host cryptand **1** were found in the NOESY spectrum of rotaxane **5**, indicating the existence of interactions between the host and the dumbbell-shaped component.



Scheme 1. Syntheses of two bis(*m*-phenylene)-32-crown-10-based cryptand/bisparaquat derivative [3]rotaxanes and their corresponding dumbbell-shaped compounds.

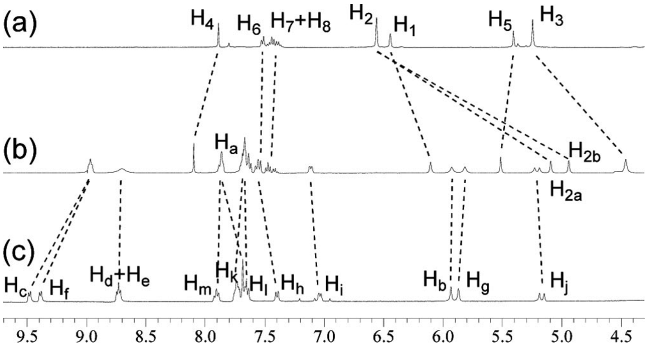


Figure 1. Partial ^1H NMR spectra (400 MHz, CD_3SOCD_3, 22 °C) of (a) cryptand **1**, (b) rotaxane **5**, and (c) dumbbell-shaped compound **3**.

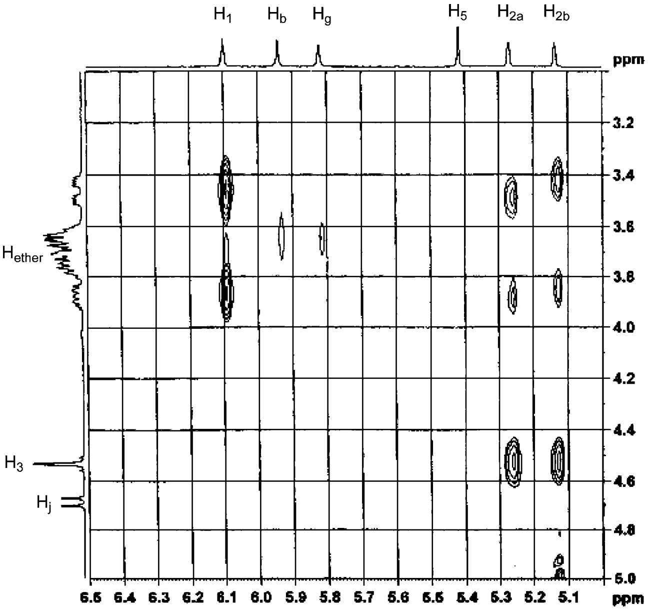


Figure 2. Partial NOESY spectrum (500 MHz, CD_3CN, 22 °C) of [3]rotaxane **5**. H_{ether} stands for the ether protons of host **1**.

The formation of mechanically interlocked [3]rotaxane **5** was further confirmed by its low- and high-resolution electrospray ionization (ESI) mass spectra. Five relevant peaks were observed in its low-resolution mass spectrum and one relevant peak was found in its high-resolution mass spectrum (see Experimental Section).

[3]Rotaxane **7** was synthesized from cryptand **6** also with the threading-followed-by-stoppering method. Tris(4-methoxyphenyl)phosphane was added to a dilute solution of cryptand **6** and bisparaquat derivative dibromide **2** in $MeNO_2$. After counterion exchange, [3]rotaxane **7** was isolated in 86% yield and [2]rotaxane was not detected during the preparation. Partial ^1H NMR spectra of cryptand **6**, rotaxane **7**, and dumbbell-shaped component **4** in CD_3SOCD_3 are shown in Figure 3. After the formation of [3]rotaxane **7** and as a result of the decreased symmetry and the differences in the "*exo*-" and "*endo*-" faces, the aromatic protons (H_9) of cryptand **6** were divided into three different types (H_{9a}, H_{9b}, and H_{9c}), and they dramatically moved upfield (Figure 2, spectra a and b). Significant upfield shifts were also observed for the signals of the α-pyridinium protons (H_c and H_f) and the β-pyridinium protons (H_d and H_e) of **4**, whereas the phenylene protons (H_a, H_h, and H_i) and the methylene protons (H_b, H_g, and H_j) moved downfield (Figure 2, spectra b and c).

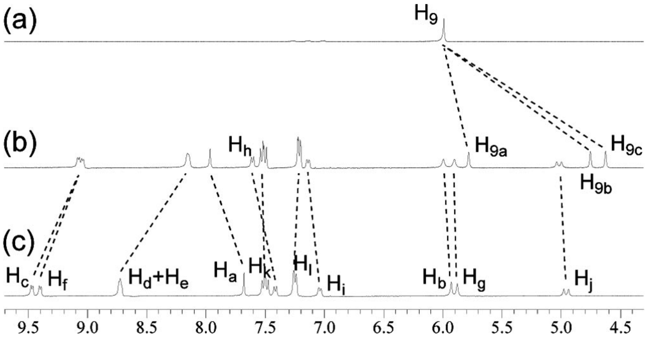


Figure 3. Partial ^1H NMR spectra (400 MHz, CD_3SOCD_3, 22 °C) of (a) cryptand **6**, (b) rotaxane **7**, and (c) dumbbell-shaped compound **4**.

The formation of mechanically interlocked [2]rotaxane **7** was further confirmed by its low- and high-resolution MS (ESI). Five relevant peaks were observed in its low-resolution mass spectrum and one relevant peak was found in its high-resolution mass spectrum (see Experimental Section).

Conclusions

We successfully synthesized two bis(*m*-phenylene)-32-crown-10-based cryptand/bisparaquat [3]rotaxanes by using a threading-followed-by-stoppering method. As a result of the strong association and cooperative complexation between the two cryptands and the bisparaquat derivative, high yields were obtained, even in dilute solutions and no [2]rotaxanes were found during the preparation of these [3]rotaxanes. Future work will be focused on the preparation of more intricate mechanically interlocked molecules and interlocked polymers based on the bis(*m*-phenylene)-32-crown-10-based cryptand/bisparaquat derivative recognition motif.

Experimental Section

General: All reagents were purchased from commercial suppliers and used as received. Bisaraquat derivative dibromide **2**[13] and cryptands **1**[9c] and **6**[9a] were prepared according to the published literature procedures. NMR spectra were recorded with a Bruker Advance DMX 500 spectrophotometer or a Bruker Advance DMX 400 spectrophotometer by using the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Low-resolution electrospray ionization mass spectra were recorded with a Bruker Esruire 3000 Plus spectrometer. High-resolution mass spectrometry experiments were performed with a Bruker Daltonics Apex III spectrometer.

[3]Rotaxane 5: Ph_3P (19.7 mg, 0.0750 mmol) was added to a solution of cryptand **1** (62.6 mg, 0.0750 mmol) and paraquat derivative **2** (34.1 mg, 0.0250 mmol) in $MeNO_2$ (2.5 mL). The reaction mixture was left to stir overnight at room temperature. Et_2O was then added to the reaction mixture, and the resulting precipitate was filtered and washed with Et_2O. The air-dried precipitate was dissolved in H_2O and a saturated aqueous solution of NH_4PF_6 was added until no further precipitation was observed. The resulting solid was filtered, washed with H_2O, and dried. The crude compound was purified by preparative thin-layer chromatography [SiO_2; MeOH/NH_4Cl (2 M)/$MeNO_2$, 17:2:1] to give [3]rotaxane **5** (82.0 mg, 89%) as a yellow solid. M.p. 216–218 °C. ^1H NMR (500 MHz, CD_3CN, 22 °C): δ = 8.80 (br., 8 H), 8.51 (br., 8 H), 8.07 (s, 4 H), 7.86–7.82 (m, 10 H), 7.66–7.62 (m, 12 H), 7.58–7.52 (m, 20 H), 7.48 (t, *J* = 7.5 Hz, 4 H), 7.44–7.41 (m, 2 H), 7.10 (dd, *J* = 8.2 Hz, *J* = 2.2 Hz, 4 H), 6.08 (s, 4 H), 5.92 (s, 4 H), 5.80 (s, 4 H), 5.40 (s, 4 H), 5.25 (s, 4 H), 5.11 (s, 4 H), 4.67 (d, *J* = 15.5 Hz, 4 H), 4.50 (dd, *J* = 14.8 Hz, *J* = 11.2 Hz, 8 H), 3.90–3.82 (m, 8 H), 3.78–3.58 (m, 48 H), 3.49–3.46 (m, 4 H), 3.42–3.39 (m, 4 H) ppm. ^{13}C NMR (125 MHz, CD_3CN, 22 °C): δ = 167.9, 165.8, 160.2, 151.0, 146.4, 146.3, 146.2, 146.1, 137.3, 136.5, 136.4, 136.1, 135.0 ($J_{P,C}$ = 11.2 Hz), 132.8 ($J_{P,C}$ = 5.9 Hz), 131.5, 131.2 ($J_{P,C}$ = 12.6 Hz), 130.1 ($J_{P,C}$ = 8.5 Hz), 129.8, 129.6, 128.9, 126.9, 118.5, 117.8, 117.0, 109.7 ($J_{P,C}$ = 6.8 Hz), 100.6, 71.8, 71.2, 71.1, 70.9, 70.4, 69.2, 68.6, 68.5, 64.7, 64.6, 30.4 ($J_{P,C}$ = 47.8 Hz) ppm. MS (ESI): *m*/*z* (%) = 1697.6 (32) [**5** – $2PF_6]^{2+}$, 1108.5 (100) [**5** – $2PF_6$ – $PhCH_2$ + Na$]^{3+}$, 1001.5 (33) [**5** – $3PF_6$ – 2Ph – $PhCH_2]^{3+}$, 888.5 (30) [**5** – $4HPF_6$ – $2PF_6$ – Ph – $PhCH_2$ + Na$]^{3+}$, 834.4 (28) [**5** – $2PF_6$ – Ph + H + $H_3O]^{4+}$. HRMS (ESI): calcd. for $C_{168}H_{172}F_6N_6O_{30}P_3$ [**5** – $5PF_6]^{5+}$ 592.0241; found 592.0267, error 4.4 ppm.

[3]Rotaxane 7: Tris(4-methoxyphenyl)phosphane (13.2 mg, 0.0375 mmol) was added to a solution of cryptand **6** (27.3 mg, 0.0375 mmol) and paraquat derivative **2** (17.1 mg, 0.0125 mmol) in $MeNO_2$ (1.2 mL). The reaction mixture was left to stir overnight at room temperature. Et_2O was then added to the reaction mixture, and the resulting precipitate was filtered and washed with Et_2O. The air-dried precipitate was dissolved in H_2O and a saturated aqueous solution of NH_4PF_6 was added until no further precipitate was observed. The resulting solid was filtered, washed with H_2O, and dried. The crude compound was purified by preparative thin-layer chromatography [SiO_2; MeOH/NH_4Cl (2 M)/$MeNO_2$, 17:2:1] to give [3]rotaxane **7** (39.2 mg, 86%) as a yellow solid. M.p. 155–157 °C. ^1H NMR (500 MHz, CD_3CN, 22 °C): δ = 8.95–8.93 (m, 8 H), 8.06–8.05 (m, 8 H), 7.97 (s, 4 H), 7.62 (d, *J* = 8.5 Hz, 4 H), 7.44–7.40 (m, 12 H), 7.14–7.11 (m, 16 H), 5.97 (s, 4 H), 5.84 (s, 4 H), 5.75 (s, 4 H), 4.83 (s, 4 H), 4.63 (s, 4 H), 4.52 (d, *J* = 15.0 Hz, 4 H), 3.88–3.82 (m, 26 H), 3.75–3.58 (m, 64 H), 3.53–3.47 (m, 16 H), 3.27–3.21 (m, 8 H) ppm. ^{13}C NMR (125 MHz, CD_3CN, 22 °C): δ = 165.9, 161.1, 161.0, 160.9, 147.5, 147.3, 146.6, 136.9 ($J_{P,C}$ = 11.2 Hz), 136.3, 134.5, 133.0 ($J_{P,C}$ = 5.0 Hz), 132.2, 131.4, 131.1 ($J_{P,C}$ = 7.6 Hz), 126.3, 126.2, 116.7 ($J_{P,C}$ = 13.6 Hz), 109.0 ($J_{P,C}$ = 94.5 Hz), 94.5, 93.9, 93.4, 71.3, 71.2, 71.1, 71.0, 70.9, 70.8, 70.6, 70.5, 69.8, 68.6, 68.5, 68.0, 64.8, 64.7, 56.7, 31.3 ($J_{P,C}$ = 50.2 Hz) ppm. MS (ESI): *m*/*z* (%) = 1747.7 (22) [**7** – PF_6 – $2CH_3$ + $H_3O]^{2+}$, 1689.2 (16) [**7** – $2PF_6$ + $H_2O]^{2+}$, 1680.7 (10) [**7** – $2PF_6]^{2+}$, 1629.7 (100) [**7** – $PhOCH_3$ – CH_3 – $2HPF_6$ + Na$]^{2+}$, 1616.2 (12) [**7** – HPF_6 – $2PF_6$ + $H_2O]^{2+}$. HRMS (ESI): calcd. for $C_{158}H_{190}F_{12}N_4O_{36}P_4$ [**7** – $4PF_6]^{4+}$ 767.7980; found 767.7946, error –4.4 ppm.

Dumbbell-Shaped Compound 3: Triphenylphosphane (19.7 mg, 0.0750 mmol) was added to a solution of paraquat derivative **2** (34.1 mg, 0.0250 mmol) dissolved in $MeNO_2$ (3 mL). The reaction mixture was left to stir overnight at room temperature. Et_2O (20 mL) was added to precipitate the product. The resulting white precipitate was filtered, washed with CH_2Cl_2, and collected. The air-dried precipitate was dissolved in H_2O and a saturated aqueous solution of NH_4PF_6 was added until no further precipitation was observed. The resulting solid was filtered, washed with H_2O, and dried. The crude compound was purified by preparative thin-layer chromatography [SiO_2; MeOH/NH_4Cl (2 M)/$MeNO_2$, 17:2:1] to give dumbbell-shaped compound **3** (46.5 mg, 92%) as a white solid. M.p. 238–240 °C (decomp.). ^1H NMR (500 MHz, CD_3CN, 22 °C): δ = 8.98 (d, *J* = 6.5 Hz, 4 H), 8.91 (d, *J* = 6.5 Hz, 4 H), 8.41–8.38 (m, 8 H), 7.91–7.87 (m, 6 H), 7.71–7.67 (m, 12 H), 7.60 (s, 4 H), 7.59–7.55 (m, 12 H), 7.31 (d, *J* = 8.0 Hz, 4 H), 7.05 (dd, *J* = 8.0 Hz, *J* = 2.5 Hz, 4 H), 5.86 (s, 4 H), 5.76 (s, 4 H), 4.67 (d, *J* = 15.0 Hz, 4 H) ppm. ^{13}C NMR (125 MHz, CD_3CN, 22 °C): δ = 151.5, 151.4, 146.8, 146.7, 136.5 ($J_{P,C}$ = 3.1 Hz), 135.3, 135.2 ($J_{P,C}$ = 10.1 Hz), 132.9 ($J_{P,C}$ = 6.8 Hz), 131.4, 131.2 ($J_{P,C}$ = 12.6 Hz), 130.9 ($J_{P,C}$ = 2.4 Hz), 130.6 ($J_{P,C}$ = 8.9 Hz), 128.6, 128.5, 119.1, 117.8, 65.0, 30.4 ($J_{P,C}$ = 49.1 Hz) ppm. MS (ESI): *m*/*z* (%) = 411.0 (100) [**3** – Ph – $2HPF_6$ – $3PF_6$ + $H_2O]^{3+}$, 381.0 (76) [**3** – Ph – $3PF_6$ + $NH_4]^{4+}$, 365.0 (26) [**3** – HPF_6 – $3PF_6$ + Na$]^{4+}$, 305.0 (20) [**3** – Ph – $3PF_6$ + H + $NH_4]^{5+}$. HRMS (ESI): calcd. for $C_{74}H_{68}F_6N_5P_3$ [**3** – Ph – HPF_6 – $4PF_6$ + $NH_4]^{3+}$ 411.1531; found 411.1499, error –7.8 ppm. HRMS (ESI): calcd. for $C_{74}H_{64}F_{18}N_4P_5$ [**3** – Ph – HPF_6 – $2PF_6]^{4+}$ 376.3383; found 376.3374, error –2.4 ppm.

Dumbbell-Shaped Compound 4: Tris(4-methoxyphenyl)phosphane (26.4 mg, 0.0750 mmol) was added to a solution of paraquat derivative **2** (34.1 mg, 0.0250 mmol) dissolved in $MeNO_2$ (3 mL). The reaction was left to stir overnight at room temperature. Et_2O (20 mL) was added to precipitate the product. The resulting white precipitate was filtered, washed with CH_2Cl_2, and collected. The air-dried precipitate was dissolved in H_2O and a saturated aqueous solution of NH_4PF_6 was added until no further precipitation was observed. The resulting solid was filtered and washed with H_2O to give a white solid. The crude compound was purified by preparative thin-layer chromatography [SiO_2; MeOH/NH_4Cl (2 M)/$MeNO_2$, 17:2:1] to give dumbbell-shaped compound **4** (52.2 mg, 95%) as a white solid. M.p. 170–172 °C (decomp.). ^1H NMR (500 MHz, CD_3CN, 22 °C): δ = 8.97 (d, *J* = 7.0 Hz, 4 H), 8.92 (d, *J* = 7.0 Hz, 4 H), 8.40–8.38 (m, 8 H), 7.60 (s, 4 H), 7.45–7.40 (m, 12 H), 7.32 (d, *J* = 8.5 Hz, 4 H), 7.18–7.16 (m, 12 H), 7.04 (dd, *J* = 8.5 Hz, *J* = 2.5 Hz, 4 H), 5.86 (s, 4 H), 5.77 (s, 4 H), 4.49 (d, *J* = 14.5 Hz, 4 H), 3.90 (s, 18 H) ppm. ^{13}C NMR (125 MHz, CD_3CN, 22 °C): δ = 166.0, 151.5, 151.4, 146.8, 146.7, 137.0 ($J_{P,C}$ = 11.5 Hz), 135.3, 133.9, 132.9 ($J_{P,C}$ = 5.4 Hz), 131.4, 131.3 ($J_{P,C}$ = 8.5 Hz), 130.7, 128.6, 128.5, 116.8 ($J_{P,C}$ = 13.8 Hz), 109.0 ($J_{P,C}$ = 93.1 Hz), 65.1, 65.0, 56.8, 31.4 ($J_{P,C}$ = 51.9 Hz) ppm. MS (ESI): *m*/*z* (%) = 501.2 (75) [**4** – $4HPF_6$ – PF_6 + $2NH_4]^{3+}$, 306.2 (100) [**4** – $PhOCH_3$ – $4PF_6$ + $H_3O]^{5+}$. HRMS (ESI): calcd. for $C_{86}H_{83}F_6N_4O_8P_3$ [**4** – $3HPF_6$ – $2PF_6$ + $2H_2O]^{3+}$ 502.1776; found 502.1776, error 0 ppm.

Supporting Information (see footnote on the first page of this article): Characterization data of [3]rotaxanes **5** and **7** and dumbbell-shaped compounds **3** and **4**.

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