High-yield preparation of [2]rotaxanes based on the bis(*m*-phenylene)-32-crown-10-based cryptand/paraquat derivative recognition motif†

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Based on the complexation between bis(*m*-phenylene)-32-crown-10-based cryptands and a paraquat derivative, two [2]rotaxanes were synthesized by using a threading-followed-by-stoppering method. Due to the strong associations between the cryptands and the paraquat derivative, high yields were achieved even in dilute solution.

Introduction

Mechanically interlocked structures, such as rotaxanes and catenanes, have attracted great interest not only because of the fascinating aspect of their topologies but also due to their potential applications in nanotechnology.[1] These interlocked structures are usually prepared by template-directed protocols depending on molecular recognition and self-assembly processes. To synthesize various interlocked compounds with efficiency, strong binding interactions between hosts and guests are necessary. Generally high association constants should result in high yields in the syntheses of mechanically interlocked structures, which was one of the significant reasons to develop more efficient recognition motifs in host–guest chemistry.[2]

Crown ethers and their derivatives have been universally utilized as hosts to form mechanically interlocked structures.[2a–c,3] It has been proved that bis(*m*-phenylene)-32-crown-10-based cryptands, compared with the corresponding simple bis(*m*-phenylene)-32-crown-10 (BMP32C10), are powerful hosts to complex paraquat derivatives (*N*,*N*′-dialkyl-4,4′-bipyridinium salts),[4] diquat,[5] monopyridinium salts,[6] and diazapyrenium salts.[7] The much stronger complexation between cryptands and guests should result in higher efficiency, when these cryptands instead of BMP32C10 are used to prepare mechanically interlocked structures with these guests. Herein, we report for the first time the syntheses of bis(*m*-phenylene)-32-crown-10-based cryptand/paraquat derivative [2]rotaxanes. Due to the strong associations between the cryptands and paraquat derivatives, high yields were achieved even in dilute solutions.

Results and discussion

Here the threading-followed-by-stoppering strategy[2a–d] was applied to synthesize rotaxanes. Firstly triphenyl phosphine groups were investigated as potential stoppers to form [2]rotaxanes from bis(*m*-phenylene)-32-crown-10-based cryptands **1**[4d] and **6**[4a] (Scheme 1). It was found that the triphenyl phosphine groups were big enough to act as stoppers for cryptand **1**, but not big enough for cryptand **6**. As shown in Fig. 1, neither chemical shift changes nor signal doubling occurred upon mixing cryptand **1** and dumbbell-shaped paraquat derivative **3** (Scheme 1) in CD_3CN. This indicated that **3** can not thread through the cavity of cryptand **1** and the triphenyl phosphine groups are big enough to act as stoppers to form rotaxanes from cryptand macrocycle **1**. However, comparison of the ^1H NMR spectra of host **6**, dumbbell-shaped paraquat derivative **3**[2b] and their mixture in CD_3CN indicated that **3** can thread through the cavity of cryptand **6** to form a [2]pseudorotaxane in slow exchange on the ^1H NMR time scale since three sets of peaks, corresponding to uncomplexed **6**, uncomplexed **3** and their complex **6**·**3**, were found in the spectrum of their mixture (Fig. 2)

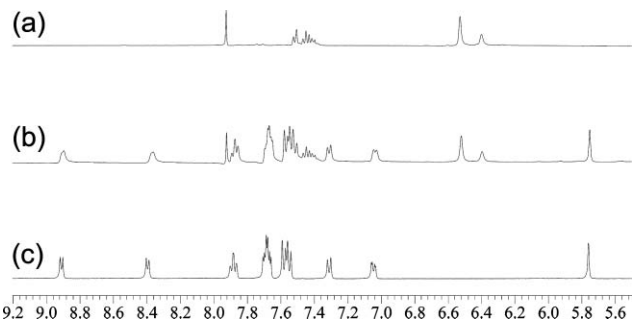

Fig. 1 Partial proton NMR spectra (400 MHz, CD_3CN, 22 °C) of (a) cryptand **1**, (b) mixture of **1** and **3**, and (c) dumbbell-shaped compound **3**.

Then tris(4-methoxyphenyl)phosphine was used to synthesize dumbbell-shaped paraquat derivative **4** (Scheme 1). As shown in

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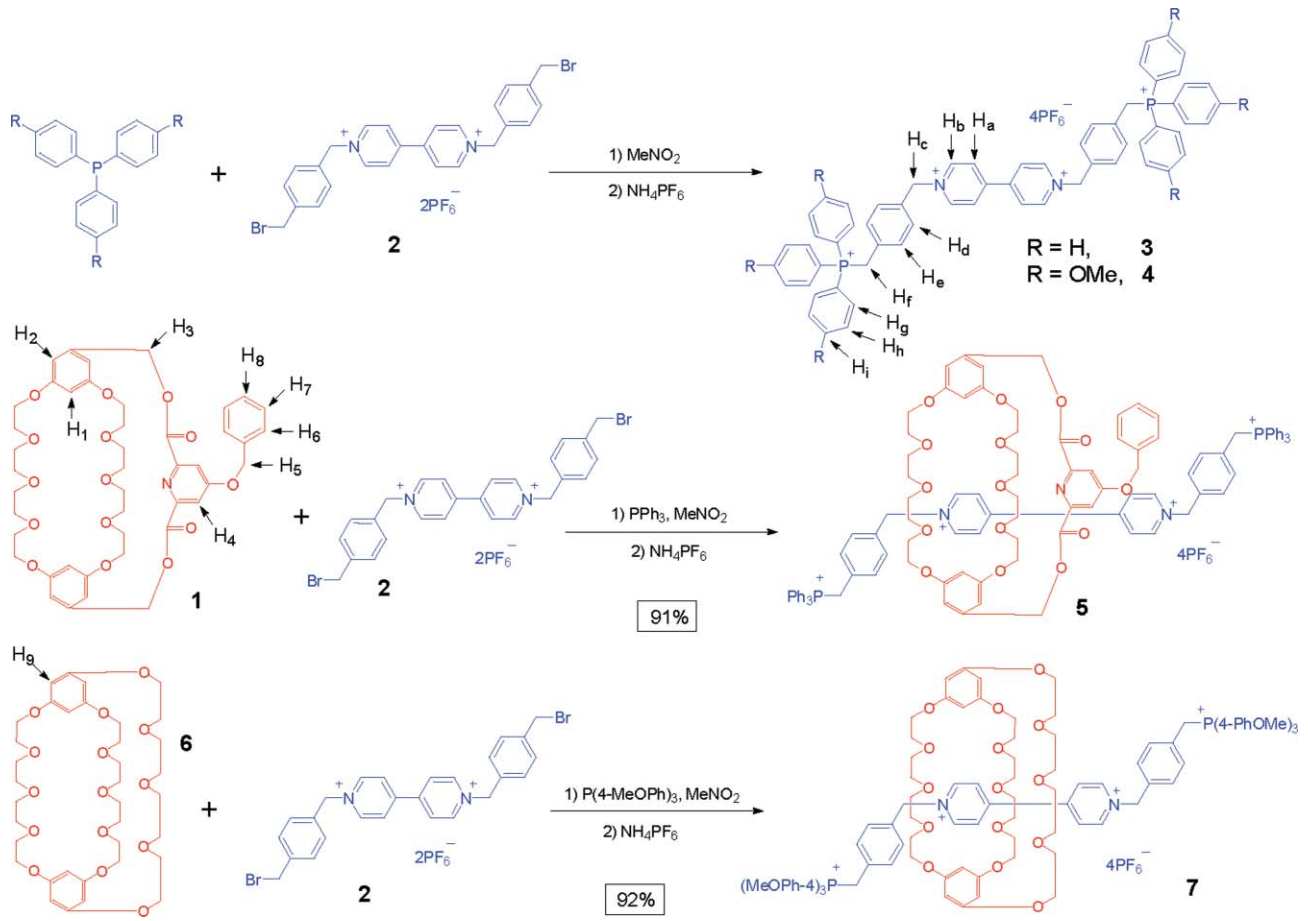
† Electronic supplementary information (ESI) available: NMR spectra, and mass spectra of rotaxanes and dumbbell-shaped compounds. See DOI: 10.1039/b803927e



Scheme 1 Syntheses of two bis(*m*-phenylene)-32-crown-10-based cryptand/paraquat derivative [2]rotaxanes and their corresponding dumbbell-shaped compounds.

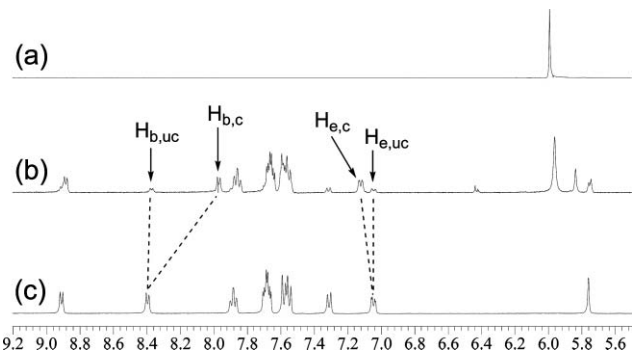


Fig. 2 Partial proton NMR spectra (400 MHz, CD_3CN, 22 °C) of (a) cryptand **6**, (b) mixture of **6** and **3**, and (c) dumbbell-shaped compound **3**. Complexed and uncomplexed species are denoted by 'c' and 'uc' respectively.

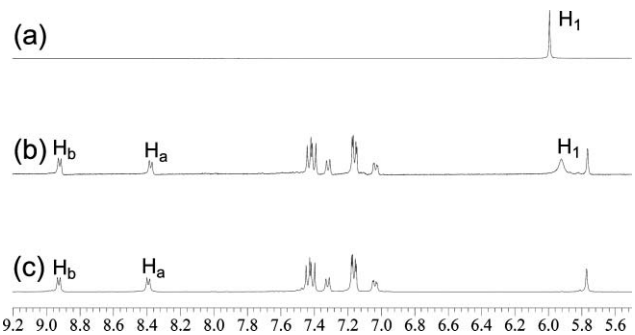


Fig. 3 Partial proton NMR spectra (400 MHz, CD_3CN, 22 °C) of (a) cryptand **6**, (b) mixture of **6** and **4**, and (c) dumbbell-shaped compound **4**.

Fig. 3, neither signal doubling nor chemical shift changes occurred except that the peak due to aromatic protons H_1 shifted a little and was broadened, and the peaks of pyridinium protons H_a and H_b shifted somewhat upon mixing cryptand **6** and dumbbell-shaped paraquat derivative **4** in CD_3CN. The slight changes of the chemical shifts of these aromatic protons are possibly due to the side-on interactions between electron-rich phenyl rings of **6** and electron-poor pyridinium rings of **4** as shown by the light yellow colour observed upon mixing **4** and **6**. These indicated that dumbbell-shaped paraquat derivative **4** can not thread through the cavity of cryptand **6**. That is to say, the tris(4-methoxyphenyl)phosphine groups are big enough to act as stoppers to form rotaxanes from cryptand macrocycle **6**.

The synthesis of [2]rotaxane **5** was carried out in $MeNO_2$ by simply adding triphenyl phosphine to a 5 mM solution of cryptand **1** and paraquat derivative dibromide **2**[8] (Scheme 1). After counterion exchange, [2]rotaxane **5** was isolated in 91% yield. Partial proton NMR spectra of cryptand **1**, rotaxane **5** and dumbbell-shaped component **3** in CD_3SOCD_3 are shown

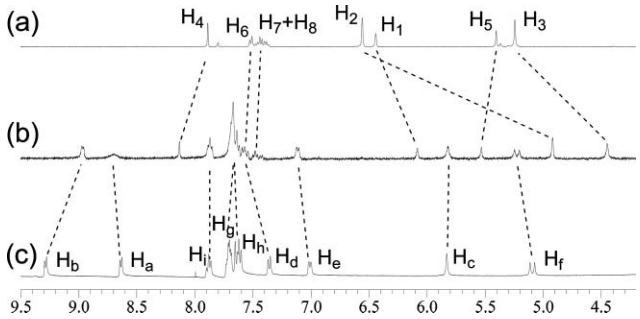


Fig. 4 Partial proton NMR spectra (400 MHz, CD_3SOCD_3, 22 °C) of (a) cryptand **1**, (b) rotaxane **5**, and (c) dumbbell-shaped compound **3**.

in Fig. 4. After the formation of rotaxane **5**, the dramatic upfield shifts were observed for the signals of the aromatic protons H_1 and H_2, and methylene protons H_3 of cryptand **1**, while H_4 and H_5 moved downfield. Synchronously, the signals of α-pyridinium protons H_b and *N*-methylene H_c on **3** moved upfield while β-pyridinium protons H_a, phenyl protons H_d and H_e, and *p*-methylene H_f moved downfield. The formation of mechanically interlocked [2]rotaxane **5** was further confirmed by its low- and high-resolution electrospray ionization mass spectra (ESIMS). Two relevant peaks were observed in its low-resolution ESIMS: the peak at $m/z = 2157.7$ (30%) corresponds to $[\mathbf{5} - PF_6 + H]^+$ and the peak at $m/z = 1006.3$ (100%) corresponds to $[\mathbf{5} - 2PF_6]^{2+}$. Three relevant peaks were found in its high-resolution ESIMS: m/z calcd for $[\mathbf{5} - 2PF_6]^{2+}$ $C_{106}H_{105}F_{12}N_3O_{15}P_4$, 1005.8152, found 1005.8106, error −4.6 ppm; calcd for $[\mathbf{5} - 3PF_6]^{3+}$ $C_{106}H_{105}F_6N_3O_{15}P_3$, 622.2221, found 622.2209, error −1.9 ppm; and calcd for $[\mathbf{5} - 3PF_6 - HPF_6]^{4+}$ $C_{106}H_{104}N_3O_{15}P_2$, 430.1623, found 430.1646, error 5.3 ppm.

[2]Rotaxane **7** was synthesized in a similar way from cryptand **6**. Tris(4-methoxyphenyl)phosphine was added to a 5 mM solution of cryptand **6** and paraquat derivative dibromide **2** in $MeNO_2$. After counterion exchange, [2]rotaxane **7** was isolated in 92% yield. Partial proton NMR spectra of cryptand **6**, rotaxane **7** and dumbbell-shaped component **4** in CD_3SOCD_3 are shown in Fig. 5. After the formation of rotaxane **7**, due to the decrease of the symmetry, the identical aromatic protons (H_9) of cryptand **6** were divided into two different types (H_{9a} and H_{9b}) and dramatically moved upfield. Significant upfield shifts were also observed for the signals of pyridinium protons H_a and H_b on **4**, while H_d, H_e, and H_f were slightly moved downfield. The formation of

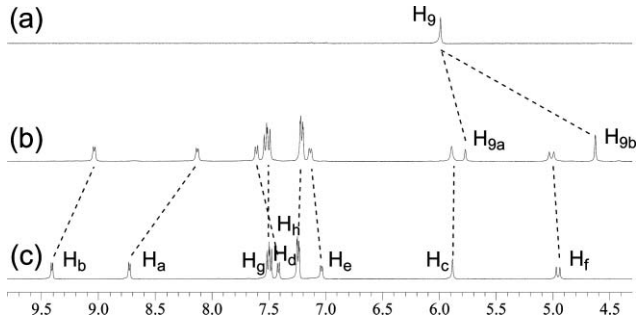


Fig. 5 Partial proton NMR spectra (400 MHz, CD_3SOCD_3, 22 °C) of (a) cryptand **6**, (b) rotaxane **7**, and (c) dumbbell-shaped compound **4**.

mechanically interlocked [2]rotaxane **7** was further confirmed by its low- and high-resolution ESIMS. Three relevant peaks were observed in its low-resolution ESIMS: the peak at $m/z = 646.8$ (11%) corresponds to $[\mathbf{7} - 3PF_6]^{3+}$, the peak at $m/z = 598.2$ (7%) corresponds to $[\mathbf{7} - 3PF_6 - HPF_6]^{3+}$, and the peak at $m/z = 448.8$ (100%) corresponds to $[\mathbf{7} - 4PF_6]^{4+}$. Two relevant peaks were found in its high-resolution ESIMS: m/z calcd for $[\mathbf{7} - 3PF_6]^{3+}$ $C_{104}H_{120}F_6N_2O_{21}P_3$, 646.5833, found 646.5832, error −0.2 ppm, and calcd for $[\mathbf{7} - 4PF_6]^{4+}$ $C_{104}H_{120}N_2O_{21}P_2$, 448.6965, found 448.6962, error −0.7 ppm.

Though here rather dilute solutions (5 mM) were used in the syntheses of [2]rotaxanes **5** and **7**, rather high yields were achieved owing to the high association constants between cryptands and paraquat derivatives (for the complex based on cryptand **1** and paraquat, *N*,*N*′-dimethyl-4,4′-biyridinium, $K_a = 5.0 \times 10^6$ M^{-1} in CD_3COCD_3 and for the complex based on cryptand **6** and paraquat, $K_a = 6.1 \times 10^4$ M^{-1} in CD_3COCD_3).[4a,d]

Conclusion

We have successfully prepared the first two bis(*m*-phenylene)-32-crown-10-based cryptand/paraquat derivative [2]rotaxanes by using a threading-followed-by-stoppering method. Even in dilute solutions, high yields were given due to the high association constants between the cryptands and the paraquat derivative. Different groups were applied to act as stoppers for the syntheses of the two [2]rotaxanes because of the difference in the dimensions of the two cryptand cavities. The triphenyl phosphine groups were big enough to act as stoppers for cryptand **1**, but they were not big enough for cryptand **6** and tris(4-methoxyphenyl)phosphine groups were needed. Further work will include the fabrication of other mechanically interlocked structures based on the bis(*m*-phenylene)-32-crown-10-based cryptand/paraquat derivative recognition motif.

Experimental

All reagents were purchased from commercial suppliers and used as received. Paraquat derivative dibromide **2**[8] and cryptands **1**[4d] and **6**[4a] were prepared according to published literature procedures. NMR spectra were recorded on a Bruker Advance DMX 500 spectrophotometer or a Bruker Advance DMX 400 spectrophotometer 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 on a Bruker Esruire 3000 Plus spectrometer. High-resolution mass spectrometry experiments were performed on a Bruker Daltonics Apex III spectrometer.

Synthesis of [2]rotaxane 5

Ph_3P (9.40 mg, 0.0360 mmol) was added to a solution of cryptand **1** (10.0 mg, 0.0120 mmol) and paraquat derivative **2** (9.80 mg, 0.0120 mmol) in $MeNO_2$ (3 mL). The reaction was left to stir overnight at room temperature. Et_2O was then added to the reaction mixture and the resulting precipitate was filtered off 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 off, 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 [2]rotaxane **5** (25.0 mg, 91%) as a yellow solid. Mp 176–178 °C (decomp.). ^{1}H NMR (500 MHz, CD_3CN, 22 °C): δ 8.76 (4 H, d, J = 4.4 Hz), 8.49 (4 H, br), 8.09 (2 H, s), 7.84–7.81 (6 H, m), 7.64–7.61 (12 H, m), 7.56–7.51 (18 H, m), 7.48–7.45 (2 H, m), 7.43–7.41 (1 H, m), 7.09–7.07 (4 H, m), 6.06 (2 H, s), 5.79 (4 H, s), 5.40 (2 H, s), 5.10 (4 H, d, J = 1.6 Hz), 4.66 (4 H, d, J = 12.4 Hz), 4.56 (4 H, s), 3.84–3.81 (4 H, m), 3.77–3.73 (4 H, m), 3.71–3.59 (20 H, m), and 3.42–3.39 (4 H, m). Low-resolution ESIMS: m/z 2157.7 (30%) $[\mathbf{5} - PF_6 + H]^+$ and 1006.3 (100%) $[\mathbf{5} - 2PF_6]^{2+}$. High-resolution ESIMS: m/z calcd for $[\mathbf{5} - 2PF_6]^{2+}$ $C_{106}H_{105}F_{12}N_3O_{15}P_4$, 1005.8152, found 1005.8106, error −4.6 ppm; calcd for $[\mathbf{5} - 3PF_6]^{3+}$ $C_{106}H_{105}F_6N_3O_{15}P_3$, 622.2221, found 622.2209, error −1.9 ppm; and calcd for $[\mathbf{5} - 3PF_6 - HPF_6]^{4+}$ $C_{106}H_{104}N_3O_{15}P_2$, 430.1623, found 430.1646, error 5.3 ppm.

Synthesis of [2]rotaxane 7

Tris(4-methoxyphenyl)phosphine (14.6 mg, 0.0414 mmol) was added to a solution of cryptand **6** (10.0 mg, 0.0138 mmol) and paraquat derivative **2** (11.2 mg, 0.0138 mmol) in $MeNO_2$ (3 mL). The reaction was left to stir overnight at room temperature. Et_2O was then added to the reaction mixture and the resulting precipitate was filtered off 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 off, 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 [2]rotaxane **7** (30.0 mg, 92%) as a yellow solid. Mp 202–204 °C (decomp.). ^{1}H NMR (400 MHz, CD_3CN, 22 °C): δ 8.92 (4 H, d, J = 7.0 Hz), 8.06 (4 H, d, J = 7.0 Hz), 7.58 (4 H, d, J = 8.0 Hz), 7.47–7.40 (12 H, m), 7.14–7.11 (16 H, m), 5.84 (4 H, s), 5.73 (2 H, s), 4.67 (4 H, d, J = 1.6 Hz), 4.51 (4 H, d, J = 14.8 Hz), 3.85–3.81 (22 H, m), 3.76–3.61 (32 H, m), 3.53–3.51 (4 H, m), 3.48–3.44 (4 H, m), and 3.27 (4 H, br). Low-resolution ESIMS: m/z 646.8 (11%) $[\mathbf{7} - 3PF_6]^{3+}$, 598.2 (7%) $[\mathbf{7} - 3PF_6 - HPF_6]^{3+}$, and 448.8 (100%) $[\mathbf{7} - 4PF_6]^{4+}$. High-resolution ESIMS: m/z calcd for $[\mathbf{7} - 3PF_6]^{3+}$ $C_{104}H_{120}F_6N_2O_{21}P_3$, 646.5833, found 646.5832, error −0.2 ppm, and calcd for $[\mathbf{7} - 4PF_6]^{4+}$ $C_{104}H_{120}N_2O_{21}P_2$, 448.6965, found 448.6962, error −0.7 ppm.

Synthesis of dumbbell-shaped compound 3[2c]

Triphenylphosphine (65.5 mg, 0.250 mmol) was added to a solution of paraquat derivative **2** (81.4 mg, 0.100 mmol) dissolved in $MeNO_2$ (5 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 off, 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 off and washed with H_2O to give a white solid. The crude product was treated with MeCN and Et_2O to remove the residue impurities. Drying gave the dumbbell-shaped compound **3** (126 mg, 86%) as a white solid. Mp 195–197 °C (decomp.). ^{1}H NMR (400 MHz, CD_3CN, 22 °C): δ 8.91 (4 H, d, J = 7.0 Hz), 8.39 (4 H, d, J = 7.0 Hz), 7.86–7.90 (6 H, m), 7.66–7.70 (12 H, m), 7.54–7.59 (12 H, m), 7.32 (4 H, d, J = 7.6 Hz), 7.04 (4 H, d, J = 7.6 Hz), 5.76 (4 H, s), and 4.66 (4 H, d, J = 14.8 Hz).

Synthesis of dumbbell-shaped compound 4

Tris(4-methoxyphenyl)phosphine (88.0 mg, 0.250 mmol) was added to a solution of paraquat derivative **2** (81.4 mg, 0.100 mmol) dissolved in $MeNO_2$ (5 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 off, 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 off and washed with H_2O to give a white solid. The crude product was treated with MeCN and Et_2O to remove the residue impurities. Drying gave the dumbbell-shaped compound **4** (115 mg, 70%) as a white solid. Mp 161–163 °C (decomp.). ^{1}H NMR (400 MHz, CD_3CN, 22 °C): δ 8.92 (4 H, d, J = 6.6 Hz), 8.39 (4 H, d, J = 6.6 Hz), 7.45–7.40 (12 H, m), 7.32 (4 H, d, J = 8.0 Hz), 7.18–7.15 (12 H, m), 7.03 (4 H, d, J = 7.6 Hz), 5.77 (4 H, s), 4.49 (4 H, d, J = 14.8 Hz), and 3.10 (18 H, m). Low-resolution ESIMS: m/z 1502.0 (25%) $[\mathbf{4} - HPF_6]^+$, 1022.7 (43%) $[\mathbf{4} - 2PF_6 - 2HPF_6 - 2OCH_3 + H_2O]^+$, 757.0 (100%) $[\mathbf{4} - 3PF_6 - (4\text{-}MeOPh)_3PCH_2PhCH_2]^+$, 679.1 (28%) $[\mathbf{4} - 2PF_6]^{2+}$, 611.2 (76%) $[\mathbf{4} - 3PF_6 - HPF_6 - (4\text{-}MeOPh)_3PCH_2PhCH_2]^+$, 606.2 (62%) $[\mathbf{4} - HPF_6 - 2PF_6]^{2+}$, 533.4 (9%) $[\mathbf{4} - 2HPF_6 - 2PF_6]^{2+}$. High-resolution ESIMS: m/z calcd for $[\mathbf{4} - PF_6]^+$ $C_{68}H_{66}F_{18}N_2O_6P_5$, 1503.3322, found 1503.3221, error 6.7 ppm; and calcd for $[\mathbf{4} - 2PF_6]^{2+}$ $C_{68}H_{66}F_{12}N_2O_6P_4$, 679.1840, found 679.1825, error 2.2 ppm.

Acknowledgements

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