Supporting Information

Viologen cyclophanes: Redox controlled host-guest interactions

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Synthesis

General. Compounds 2c^{2+}(2PF₆⁻), 1 [2e^{2+}(2PF₆⁻), 2 [3a^{2+}](2PF₆⁻), 3 [3b^{2+}](2PF₆⁻), 4 [3c^{2+}](2PF₆⁻) 1 were synthesized by reported methods. Reagents and solvents of reagent-grade were purchased and used without further purification. Anhydrous Na₂SO₄ was used as a drying agent after aqueous workup. Evaporation and concentration in vacuo were carried out at H₂O-aspirator pressure. Column chromatography was performed with silica gel from Merck (Kieselgel 60; 40-63 μm). Mass spectra were performed by le Service de Spectrométrie de Masse de l’Institut de Chimie, Université de Strasbourg. Elemental analyses were performed by le Service d'Analyse Elementaire de l’Institut de Chimie, Université de Strasbourg. ¹H NMR spectra were recorded on Bruker Advance 400 (400 MHz) or 500 (500 MHz) spectrometers. Chemical shifts were determined by taking the solvent as a reference: CD₃CN (1.94 ppm).

Synthesis of [2b²²⁺](2PF₆⁻)

To a refluxing solution of 1,5-dibromopentane (8.7 mL, 64.0 mmol) in MeCN (20 mL), a solution of 4,4’-bipyridine (1.00 g, 6.4 mmol) in MeCN (70 mL) was added dropwise over 1


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The solution was refluxed for a further 72 h under argon. The resulting yellow precipitate was filtered and washed with MeCN. The solid was dissolved in H$_2$O, and a saturated aqueous solution of NH$_4$PF$_6$ was added until no further precipitation was observed. After filtration, the solid was washed with H$_2$O and dried under vacuum to give 2b$^{2+}$2PF$_6^-$ as a white solid (3.03 g, 40.2 mmol, 64%). $^1$H NMR (400 MHz, CD$_3$CN) $\delta$ = 1.54 (tt, $J$ = 7.7 Hz, $J$ = 7.0 Hz, 4H), 1.85 (tt, $J$ = 6.2 Hz, $J$ = 7.7 Hz, 4H) 2.16 (tt, $J$ = 7.7 Hz, $J$ = 7.7 Hz, 4H), 3.40 (t, $J$ = 7.7 Hz, 4H), 4.91 (t, $J$ = 6.2 Hz, 4H), 8.76 (d, $J$ = 6.6 Hz, 4H), 9.39 (d, $J$ = 6.6 Hz, 4H). $^{13}$C NMR (125 MHz, CD$_3$CN) $\delta$ = 25.0, 30.9, 32.5, 34.5, 62.7, 128.1, 146.5, 150.8. ESI HRMS: m/z Calc. [C$_{20}$H$_{28}$Br$_2$N$_2$PF$_6$]$^+$: 601.0236, Found: 601.0204. E.A. (%) calc. for C$_{20}$H$_{28}$N$_4$Br$_2$P$_2$F$_{12}$(744.00): C 32.19, H 3.78, N 3.75, found: C 32.21, H 3.79, N 3.75.

**Synthesis of [2d$^{2+}$](2PF$_6^-$)**

To a refluxing solution of 1,7-dibromoheptane (3.3 mL, 19.4 mmol) in MeCN (7 mL), a solution of 4,4'-bipyridine (0.30 g, 1.9 mmol) in MeCN (25 mL) was added dropwise over 1 h. The solution was refluxed for a further 72 h under argon. The resulting yellow precipitate was filtered and washed with MeCN. The solid was dissolved in H$_2$O and EtOH, and a saturated aqueous solution of KPF$_6$ was added until no further precipitation was observed. After filtration, the solid was washed with H$_2$O and dried under vacuum to give [2d$^{2+}$](2PF$_6^-$) as a white solid (1.18 g, 1.5 mmol, 76%). $^1$H NMR (500 MHz, CD$_3$CN) $\delta$ = 1.40 (m, 12H), 1.84 (tt, $J$ = 6.7 Hz, $J$ = 7.0 Hz, 4H), 2.02 (tt, $J$ = 7.8 Hz, $J$ = 6.9 Hz, 4H), 3.48 (t, $J$ = 6.7 Hz, 4H), 3.49 (t, $J$ = 7.8 Hz, 4H), 8.39 (d, $J$ = 6.2 Hz, 4H), 8.91 (d, $J$ = 6.2 Hz, 4H). $^{13}$C NMR (125 MHz, CD$_3$CN) $\delta$ = 26.2, 28.4, 28.6, 31.7, 33.2, 35.2, 62.9, 128.1, 146.5, 150.8. ESI HRMS: m/z Calc. [C$_{24}$H$_{36}$Br$_2$N$_2$]$:^{2+}$ 256.0608, Found: 252.0597.

**[3d$^{2+}$](2PF$_6^-$)**

1,7-Dibromoheptane (1.1 mL, 6.4 mmol) in MeCN (32 mL) was added dropwise over 1 h to a refluxing solution of 4,4'-bipyridine (2.50 g, 16.0 mmol) in MeCN (24 mL). The solution was refluxed for a further 72 h. The resulting precipitate was filtered and washed with MeCN. The solid was purified by column chromatography (SiO$_2$, MeCN/MeOH/H$_2$O/sat. NH$_4$Cl$_{aq}$ (1/2/1/1)). The fractions containing the product were concentrated then dissolved in H$_2$O. A saturated aqueous solution of NH$_4$PF$_6$ was added until no further precipitation was observed. After filtration, the solid was washed with H$_2$O and dried under vacuum to give [3d$^{2+}$](2PF$_6^-$)
as a white solid (2.63 g, 3.8 mmol, 59%). $^1$H NMR (500 MHz, CD$_3$CN) $\delta = 1.40$ (m, 6H), 1.99 (tt, J = 7.5 Hz, J = 7.3 Hz, 4H), 4.53 (t, J = 7.5 Hz, 4H), 7.78 (d, J = 6.1 Hz, 4H), 8.31 (d, J = 6.9 Hz, 4H), 8.75 (d, J = 6.9 Hz, 4H), 8.84 (d, J = 6.1 Hz, 4H). $^{13}$C NMR (125 MHz, CD$_3$CN) $\delta = 26.2, 28.8, 31.6, 62.3, 122.7, 126.9, 142.1, 145.7, 152.1, 155.0$. ESI HRMS: m/z Calc. $[C_{27}H_{30}N_{4}PF_{6}]^{2+}$: 555.2107, Found: 555.1968.

$[3e^{2+}](2PF_6^-)$

1,8-Dibromo-octane (1.2 mL, 6.4 mmol) in MeCN (32 mL) was added dropwise over 1 h to a refluxing solution of 4,4'-bipyridine (2.50 g, 16.0 mmol) in MeCN (24 mL). The solution was refluxed for a further 72 h. The resulting precipitate was filtered and washed with MeCN. The solid was purified by column chromatography (SiO$_2$, MeCN/MeOH/H$_2$O/sat. NH$_4$Cl$_{aq}$ (1/2/1/1)). The fractions containing the product were concentrated then dissolved in H$_2$O. A saturated aqueous solution of NH$_4$PF$_6$ was added until no further precipitation was observed. After filtration, the solid was washed with H$_2$O and dried under vacuum to give $[3e^{2+}](2PF_6^-)$ as a white solid (2.40 g, 3.5 mmol, 21%). $^1$H NMR (500 MHz, CD$_3$CN) $\delta = 1.37$ (m, 8H), 1.98 (m, 4H), 2.22 (m, 4H), 4.53 (t, J = 7.5 Hz, 4H), 7.83 (d, J = 5.9 Hz, 4H), 8.31 (d, J = 6.6 Hz, 4H), 8.76 (d, J = 6.6 Hz, 4H), 8.86 (d, J = 5.9 Hz, 4H). $^{13}$C NMR (125 MHz, CD$_3$CN) $\delta = 36.1, 39.0, 41.5, 72.1, 132.7, 136.7, 152.5, 155.5, 161.3, 164.5$. ESI HRMS: m/z Calc. $[C_{28}H_{32}N_{4}]^{2+}$: 212.1308, Found: 212.1323.

**Cyclization Route 1**

$[1b^{4+}](4PF_6^-)$

A solution of $[2b^{2+}](2PF_6^-)$ (2.00 g, 2.7 mmol) and 4,4'-bipyridine (0.42 g, 2.7 mmol) in DMF (135 mL) was heated at 80 °C under argon for 10 days. The resulting precipitate was filtered and washed with MeCN. The solid was purified by column chromatography (SiO$_2$, MeCN/MeOH/H$_2$O/sat. NH$_4$Cl$_{aq}$ (2/1/1)). The fractions containing the product were concentrated then dissolved in H$_2$O. A saturated aqueous solution of NH$_4$PF$_6$ was added until no further precipitation was observed. After filtration, the solid was washed with H$_2$O and dried under vacuum to give $[1b^{4+}](4PF_6^-)$ as a white solid (0.19 g, 0.18 mmol, 7%). $^1$H NMR (500 MHz, CD$_3$CN) $\delta = 0.78$ (m, 4H), 1.96 (m, 8H), 4.65 (t, J = 5.9 Hz, 8H), 8.12 (d, J = 7.0 Hz, 8H), 8.70 (d, J = 7.0 Hz, 8H). $^{13}$C NMR (125 MHz, CD$_3$CN) $\delta = 22.2, 30.0, 63.0, 127.9, 146.4, 151.0$. ESI HRMS: m/z Calc. $[C_{30}H_{36}N_{4}PF_{6}]^{3+}$: 199.0855, Found: 199.0997.
Synthesis of $[1d^{4+}](4PF_6^-)$ by route 1

A solution of $[2d^{2+}](2PF_6^-)$ (2.00 g, 2.5 mmol) and 4,4'-bipyridine (0.39 g, 2.5 mmol) in DMF (125 mL) was heated at 80 °C under argon for 10 days. The resulting precipitate was filtered and washed with MeCN. The solid was purified by column chromatography (SiO$_2$, MeCN/MeOH/ H$_2$O/sat. NH$_4$Cl$_{aq}$ (2/1/1/1)). The fractions containing the product were concentrated then dissolved in H$_2$O. A saturated aqueous solution of NH$_4$PF$_6$ was added until no further precipitation was observed. After filtration, the solid was washed with H$_2$O and dried under vacuum to give $[1d^{4+}](4PF_6^-)$ as a white solid (0.29 g, 0.27 mmol, 11%).

$^1$H NMR (500 MHz, CD$_3$CN) $\delta = 0.98$ (m, 8H), 1.27 (tt, $J = 7.0$ Hz, $J = 8.0$ Hz, 4H), 1.91 (br s, 8H), 4.62 (t, $J = 6.2$ Hz, 8H), 8.32 (d, $J = 6.8$ Hz, 8H), 8.78 (d, $J = 6.8$ Hz, 8H). $^{13}$C NMR (125 MHz, CD$_3$CN) $\delta = 25.6, 29.4, 31.2, 63.1, 127.9, 146.2, 150.5$. ESI HRMS: m/z Calc. [C$_{34}$H$_{44}$N$_4$P$_2$F$_{12}$]$_{2^+}$ = 399.1419, Found [M$_{4^+}$2PF$_6$] = 399.1472 and m/z Calc. [C$_{34}$H$_{44}$N$_4$PF$_6$]$_{3^+}$ = 217.7730, Found [M$_{4^+}$PF$_6$] = 217.7754. E.A. (%) calc. for C$_{34}$H$_{44}$N$_4$P$_4$F$_{24}$ (1088.21): C 37.51, H 4.07, N 5.15, found: C 37.21, H 4.21, N 4.89.

Cyclization route 2

Synthesis of $[1b^{4+}](4PF_6^-)$ by route 2

A solution of $[3b^{2+}](2PF_6^-)$ (1.80 g, 2.7 mmol) and 1,5-dibromopentane (0.62 g, 2.7 mmol) in DMF (135 mL) was heated at 80 °C under argon for 10 days. The resulting precipitate was filtered and washed with MeCN. The solid was purified by column chromatography (SiO$_2$, MeCN/MeOH/H$_2$O/sat. NH$_4$Cl$_{aq}$ (2/1/1/1)). The fractions containing the product were concentrated then dissolved in H$_2$O. A saturated aqueous solution of NH$_4$PF$_6$ was added until no further precipitation was observed. After filtration, the solid was washed with H$_2$O and dried under vacuum to give $[1b^{4+}](4PF_6^-)$ as a white solid (0.11 g, 0.11 mmol, 4%). Recorded NMR spectra were consistent with those obtained by route 1.

Synthesis of $[1d^{4+}](4PF_6^-)$ by route 2

A solution of $[3d^{2+}](2PF_6^-)$ (1.88 g, 2.7 mmol) and 1,7-dibromoheptane (0.69 g, 2.7 mmol) in DMF (135 mL) was heated at 80 °C under argon for 10 days. The resulting precipitate was filtered and washed with MeCN. The solid was purified by column chromatography (SiO$_2$, MeCN/MeOH/H$_2$O/sat. NH$_4$Cl$_{aq}$ (2/1/1/1)). The fractions containing the product were concentrated then dissolved in H$_2$O. A saturated aqueous solution of NH$_4$PF$_6$ was added until no further precipitation was observed. After filtration, the solid was washed with H$_2$O and dried under vacuum to give $[1d^{4+}](4PF_6^-)$ as a white solid (0.13 g, 0.11 mmol, 5%). Recorded NMR spectra were consistent with those obtained by route 1.
Chemical reduction of compounds for crystallization

The cyclophanes $1b^4+$ and $1d^4+$ were reduced to their diradical dications by vigorously stirring a degassed solution of the cyclophane in CH$_3$CN (1 mg/mL) with zinc dust for 1 h under argon. For the inclusion complexes, a 1:1 ration of cyclophane and MV$^{2+}$ or TTF was reduced with zinc dust for 1 h under argon. The dark blue mixture was then filtered through a 0.45 µm filter and transferred by cannula to a degassed crystallization tube. Depending on the density of the co-solvent used for crystallization, the degassed co-solvent was transferred via cannula to the tube either before or after transferring reduced species ($1b^{2(+●)}$ or $1d^{2(+●)}$ or MV$^{+●}$. The tube was sealed and crystals were grown by slow diffusion.

X-ray crystallography

The crystals were placed in oil, and a single crystal was selected, mounted on a glass fiber and placed in a low-temperature N$_2$ stream. X-Ray diffraction data collection was carried out on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N$_2$ device, using Mo-Kα radiation ($\lambda = 0.71073$ Å). The crystal-detector distance was 38 mm. The cell parameters were determined (APEX2 software)$^5$ from reflections taken from three sets of 12 frames, each at 10 s exposure. The structure was solved by direct methods using the program SHELXS-2013.$^6$ The refinement and all further calculations were carried out using SHELXL-2013.$^7$ The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F$^2$. A semi-empirical absorption correction was applied using SADABS in APEX2;$^5$ transmission factors: T$_{\text{mm}}$/T$_{\text{max}} = 0.6690/0.7456; 0.6790/0.7456; 0.5892/0.7458; 0.6714/0.7460; 0.6575/0.7458; 0.6915/0.7456 and 0.6432/0.7456 for compounds $1b^4+$, $1d^4+$, $1d^{2(+●)}$, [(1d)(MV)$_2$]$^{3(+●)(2+)}, 1b^{2(+●)}$, $1b^{2(+●)}$ toluene, and $1d^{4+}$ TTF, respectively. For compound $1d^{4+}$, the SQUEEZE instruction in PLATON$^8$ was applied. The residual electron density was assigned to half a molecule of nitromethane.

Solid state characterization of 1d$^{4+}$ as PF$_6$ salt

Packing:

View of the molecular structure:
Solid state characterization of $1b^{4+}$ (left) and $1d^{4+}$ (right) as PF$_6$ salts

$C_4-C_4' = 1.48 \text{ Å}$

Front view

$5.87 \text{ Å}$

$4.86 \text{ Å}$

$48^\circ = \theta = 42^\circ$

N

\[ = \]

\[ = \]

$C_4-C_4' = 1.49 \text{ Å}$

Top view

$19^\circ$

Front view

$7.96 \text{ Å}$

$4.33 \text{ Å}$
Solid state characterization of $1b^{2(+)}$ (top) and $1d^{2(+)}$ (bottom) as PF$_6$ salts

C4-C4' = 1.43 Å

Side view

Front view

Top view
Solid state characterization of [MV$^{2+}$MV$^{*+}$] PF$_6$ salt