

Supporting Information

Viologen cyclophanes: Redox controlled host-guest interactions

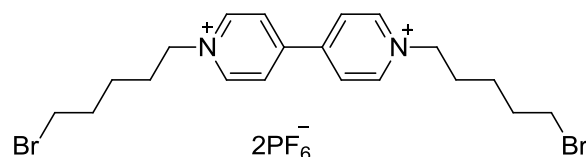
Mathilde Berville, Lydia Karmazin, Jennifer A. Wytko and Jean Weiss

Content:

Synthesis	S1
Reduction and preparation of crystallization tubes	S5
X-ray crystallography methods	S5
Solid state characterization of 1d ⁴⁺ as PF ₆ ⁻ salt	S6
Solid state characterization of 1b ⁴⁺ and 1d ⁴⁺ as PF ₆ ⁻ salts	S7
Solid state characterization of 1b ^{2(+•)} and 1d ^{2(+•)} as PF ₆ ⁻ salts	S8
Solid state characterization of [MV ²⁺ MV ^{•+}] PF ₆ ⁻ salt	S9

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 **[2b**²⁺](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

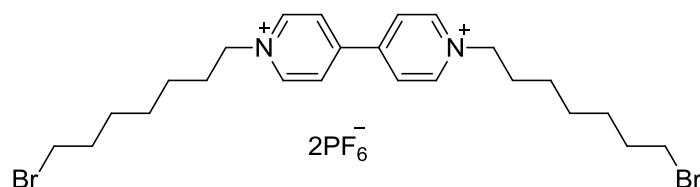
¹ J. B. Wittenberg, P. Y. Zavalij, L. Isaacs, *Angew. Chem. Int. Ed.*, 2013, **52**, 3690–3694.

² D.G. Wu, C.H. Huang, Y. Huang, L. B. Gan, A. C. Yu, L. M. Ying, X. S. Zhao, *J. Phys. Chem. B*, 1999, **103**, 7135–7144.

³ D. Schilter, J. K. Clegg, M. M. Harding, L. M. Rendina, *Dalton Trans.* 2010, **39**, 239-247.

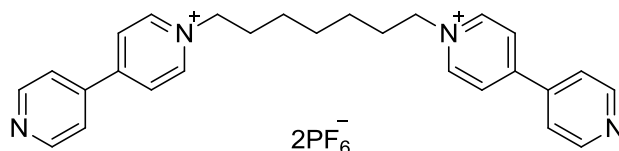
⁴ D. A. Foucher, D. H. Macartney, L.J. Warrack, J. P. Wilson, *Inorg. Chem.*, 1993, **32**, 3425-3432.

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 H₂O, and a saturated aqueous solution of NH₄PF₆ was added until no further precipitation was observed. After filtration, the solid was washed with H₂O and dried under vacuum to give **2b**²⁺ **2PF**₆⁻ as a white solid (3.03 g, 40.2 mmol, 64%). ¹H NMR (400 MHz, CD₃CN) δ = 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). ¹³C NMR (125 MHz, CD₃CN) δ = 25.0, 30.9, 32.5, 34.5, 62.7, 128.1, 146.5, 150.8. ESI HRMS: m/z Calc. [C₂₀H₂₈Br₂N₂PF₆]⁺: 601.0236, Found: 601.0204. E.A. (%) calc. for C₂₀H₂₈N₄Br₂P₂F₁₂ (744.00): C 32.19, H 3.78, N 3.75, found: C 32.21, H 3.79, N 3.75.



Synthesis of [2d²⁺](2PF₆⁻)

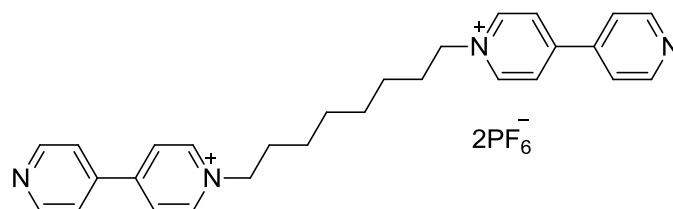
To a refluxing solution of 1,7-dibromoheptane (3.3 mL, 19.4 mmol) in MeCN (7 mL), a solution of 4,4'-bipyridine (0.30 g, 1.9 mmol) in MeCN (25 mL) was added dropwise over 1 h. The solution was refluxed for a further 72 h under argon. The resulting yellow precipitate was filtered and washed with MeCN. The solid was dissolved in H₂O and EtOH, and a saturated aqueous solution of KPF₆ was added until no further precipitation was observed. After filtration, the solid was washed with H₂O and dried under vacuum to give [2d²⁺](2PF₆⁻) as a white solid (1.18 g, 1.5 mmol, 76%). ¹H NMR (500 MHz, CD₃CN) δ = 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). ¹³C NMR (125 MHz, CD₃CN) δ = 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. [C₂₄H₃₆Br₂N₂]²⁺: 256.0608, Found: 252.0597.



[3d²⁺](2PF₆⁻)

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 (SiO₂, MeCN/MeOH/H₂O/sat. NH₄Cl_{aq} (1/2/1/1)). The fractions containing the product were concentrated then dissolved in H₂O. A saturated aqueous solution of NH₄PF₆ was added until no further precipitation was observed. After filtration, the solid was washed with H₂O and dried under vacuum to give [3d²⁺](2PF₆⁻)

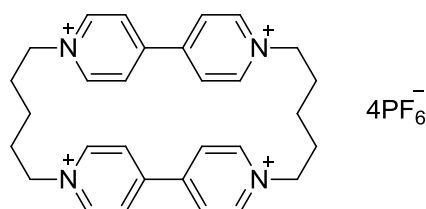
as a white solid (2.63 g, 3.8 mmol, 59%). ^1H NMR (500 MHz, CD_3CN) δ = 1.40 (m, 6H), 1.99 (tt, J = 7.5 Hz, J = 7.3 Hz, 4H), 4.53 (t, J = 7.5 Hz, 4H), 7.78 (d, J = 6.1 Hz, 4H), 8.31 (d, J = 6.9 Hz, 4H), 8.75 (d, J = 6.9 Hz, 4H), 8.84 (d, J = 6.1 Hz, 4H). ^{13}C NMR (125 MHz, CD_3CN) δ = 26.2, 28.8, 31.6, 62.3, 122.7, 126.9, 142.1, 145.7, 152.1, 155.0. ESI HRMS: m/z Calc. $[\text{C}_{27}\text{H}_{30}\text{N}_4\text{PF}_6]^{2+}$: 555.2107, Found: 555.1968.



[3e²⁺](2PF₆⁻)

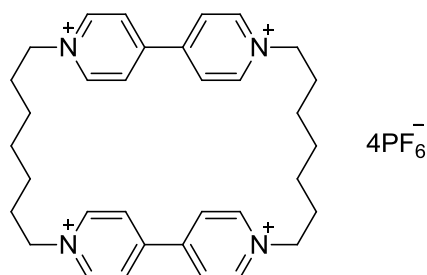
1,8-Dibromooctane (1.2 mL, 6.4 mmol) in MeCN (32 mL) was added dropwise over 1 h to a refluxing solution of 4,4'-bipyridine (2.50 g, 16.0 mmol) in MeCN (24 mL). The solution was refluxed for a further 72 h. The resulting precipitate was filtered and washed with MeCN. The solid was purified by column chromatography (SiO_2 , MeCN/MeOH/ $\text{H}_2\text{O}/\text{sat. NH}_4\text{Cl}_{\text{aq}}$ (1/2/1/1)). The fractions containing the product were concentrated then dissolved in H_2O . A saturated aqueous solution of NH_4PF_6 was added until no further precipitation was observed. After filtration, the solid was washed with H_2O and dried under vacuum to give **[3e²⁺](2PF₆⁻)** as a white solid (2.40 g, 3.5 mmol, 21%). ^1H NMR (500 MHz, CD_3CN) δ = 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_3CN) δ = 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. $[\text{C}_{28}\text{H}_{32}\text{N}_4]^{2+}$ = 212.1308, Found: 212.1323.

Cyclization Route 1



Synthesis of [1b⁴⁺](4PF₆⁻) by route 1

A solution of **[2b²⁺](2PF₆⁻)** (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/ $\text{H}_2\text{O}/\text{sat. NH}_4\text{Cl}_{\text{aq}}$ (2/1/1/1)). The fractions containing the product were concentrated then dissolved in H_2O . A saturated aqueous solution of NH_4PF_6 was added until no further precipitation was observed. After filtration, the solid was washed with H_2O and dried under vacuum to give **[1b⁴⁺](4PF₆⁻)** as a white solid (0.19 g, 0.18 mmol, 7%). ^1H NMR (500 MHz, CD_3CN) δ = 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_3CN) δ = 22.2, 30.0, 63.0, 127.9, 146.4, 151.0. ESI HRMS: m/z Calc. $[\text{C}_{30}\text{H}_{36}\text{N}_4\text{PF}_6]^{3+}$: 199.0855, Found: 199.0997.



Synthesis of [1d⁴⁺](4PF₆⁻) by route 1

A solution of [2d²⁺](2PF₆⁻) (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 (SiO₂, MeCN/MeOH/ H₂O/sat. NH₄Cl_{aq} (2/1/1/1)). The fractions containing the product were concentrated then dissolved in H₂O. A saturated aqueous solution of NH₄PF₆ was added until no further precipitation was observed. After filtration, the solid was washed with H₂O and dried under vacuum to give [1d⁴⁺](4PF₆⁻) as a white solid (0.29 g, 0.27 mmol, 11%). ¹H NMR (500 MHz, CD₃CN) δ = 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). ¹³C NMR (125 MHz, CD₃CN) δ = 25.6, 29.4, 31.2, 63.1, 127.9, 146.2, 150.5. ESI HRMS: m/z Calc. [C₃₄H₄₄N₄P₂F₁₂]²⁺ = 399.1419, Found [M⁴⁺ 2PF₆⁻] = 399.1472 and m/z Calc. [C₃₄H₄₄N₄PF₆]³⁺ = 217.7730, Found [M⁴⁺ PF₆⁻] = 217.7754. E.A. (%) calc. for C₃₄H₄₄N₄P₄F₂₄ (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 [1b⁴⁺](4PF₆⁻) by route 2

A solution of [3b²⁺](2PF₆⁻) (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 (SiO₂, MeCN/MeOH/H₂O/sat. NH₄Cl_{aq} (2/1/1/1)). The fractions containing the product were concentrated then dissolved in H₂O. A saturated aqueous solution of NH₄PF₆ was added until no further precipitation was observed. After filtration, the solid was washed with H₂O and dried under vacuum to give [1b⁴⁺](4PF₆⁻) as a white solid (0.11 g, 0.11 mmol, 4%). Recorded NMR spectra were consistent with those obtained by route 1.

Synthesis of [1d⁴⁺](4PF₆⁻) by route 2

A solution of [3d²⁺](2PF₆⁻) (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 (SiO₂, MeCN/MeOH/H₂O/sat. NH₄Cl_{aq} (2/1/1/1)). The fractions containing the product were concentrated then dissolved in H₂O. A saturated aqueous solution of NH₄PF₆ was added until no further precipitation was observed. After filtration, the solid was washed with H₂O and dried under vacuum to give [1d⁴⁺](4PF₆⁻) 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 CH₃CN (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 N₂ stream. X-Ray diffraction data collection was carried out on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N₂ device, using Mo-Kα radiation (λ = 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 F². A semi-empirical absorption correction was applied using SADABS in APEX2;⁵ transmission factors: T_{min}/T_{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 PLATON⁸ was applied. The residual electron density was assigned to half a molecule of nitromethane.

⁵ "M86-E01078 APEX2 User Manual", Bruker AXS Inc., Madison, USA, 2006.

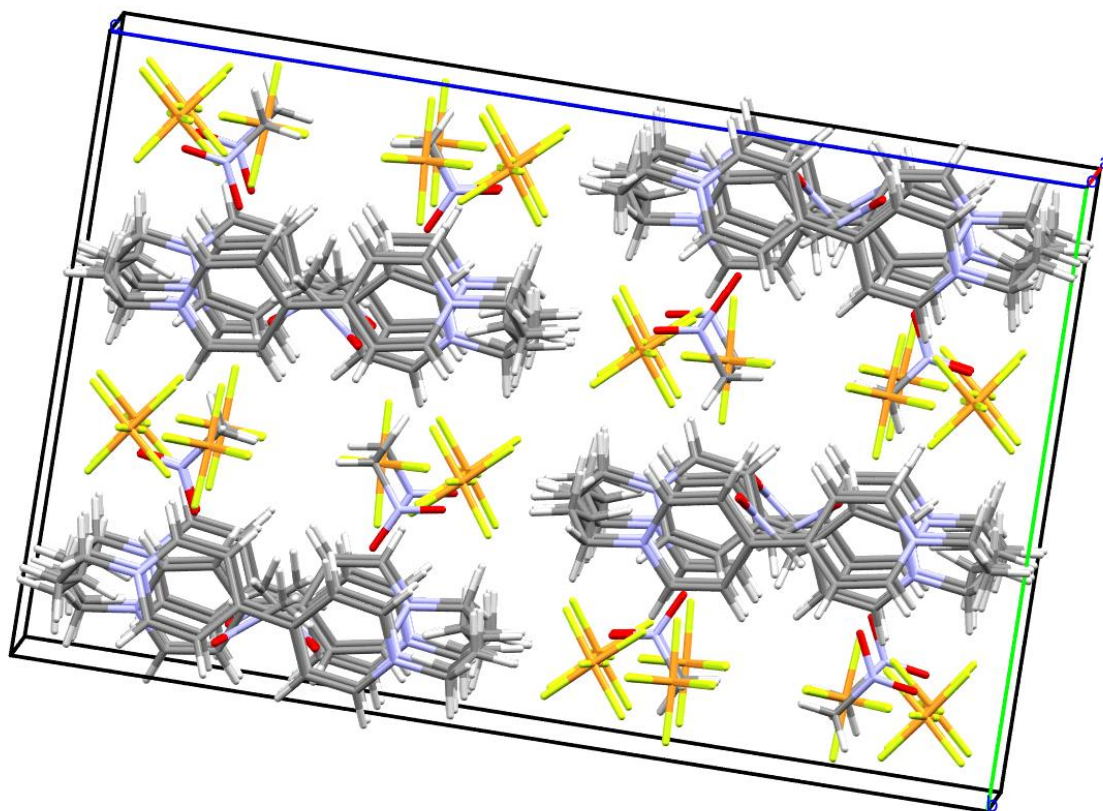
⁶ G. M. Sheldrick, *Acta Cryst.* 1990, **A46**, 467-473.

⁷ G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112-122.

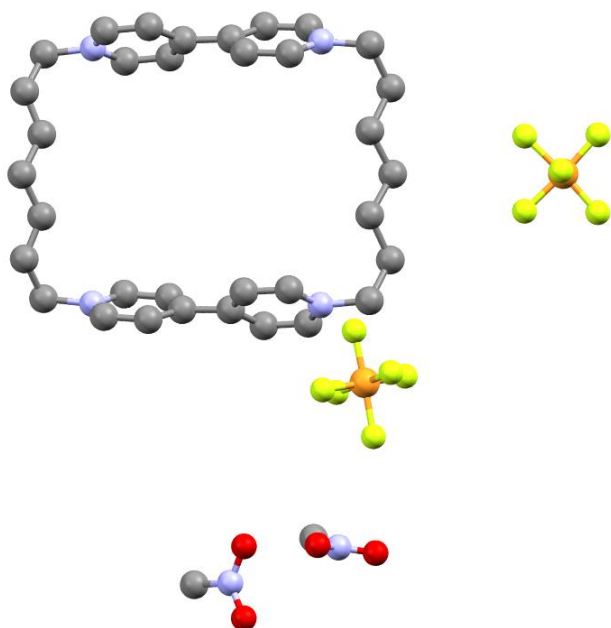
⁸ Spek, A.L., *J.Appl.Cryst.*, 2003, **36**, 7-13.

Solid state characterization of $1d^{4+}$ as PF_6 salt

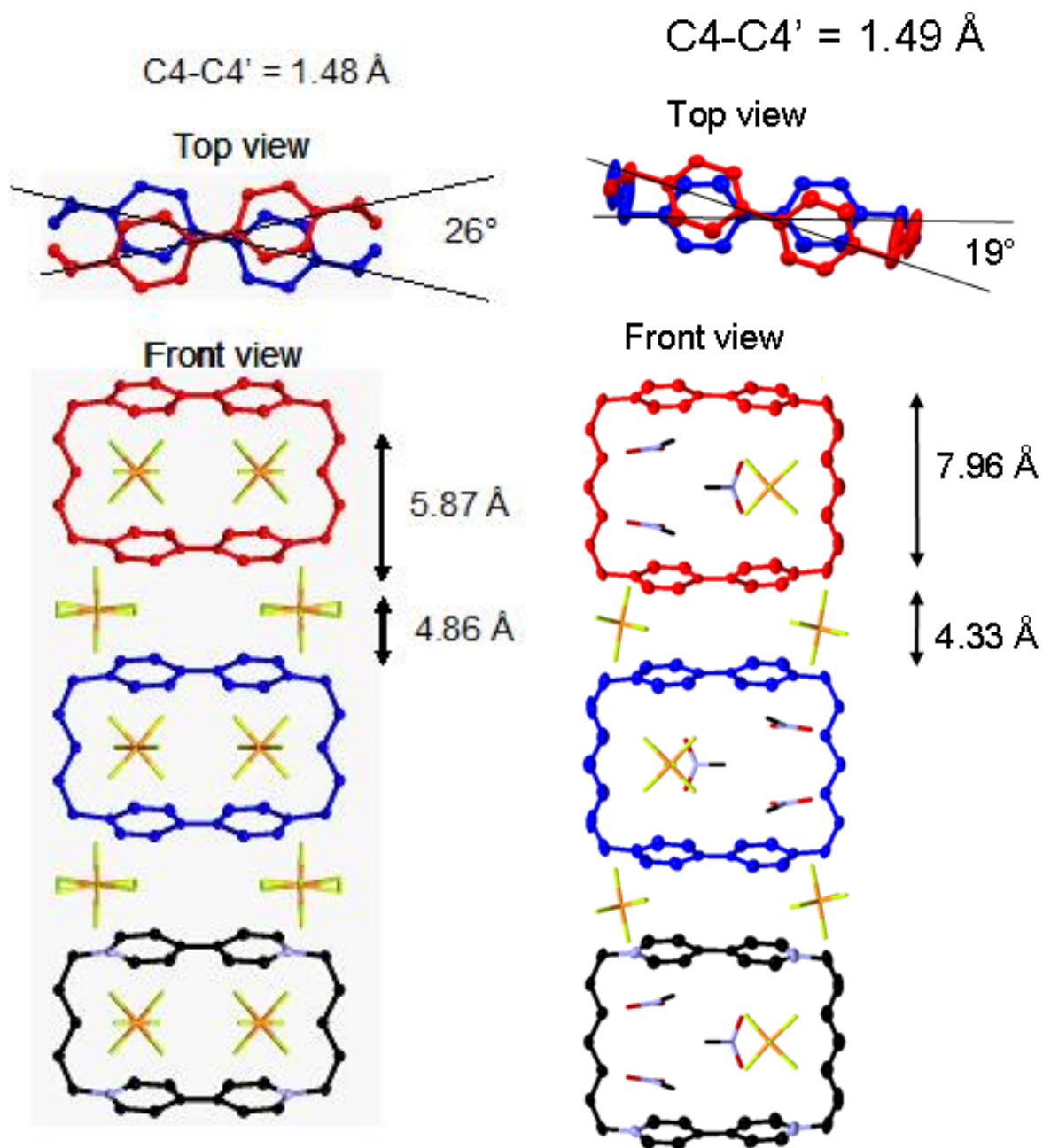
Packing :



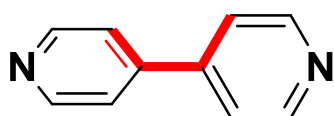
View of the molecular structure:



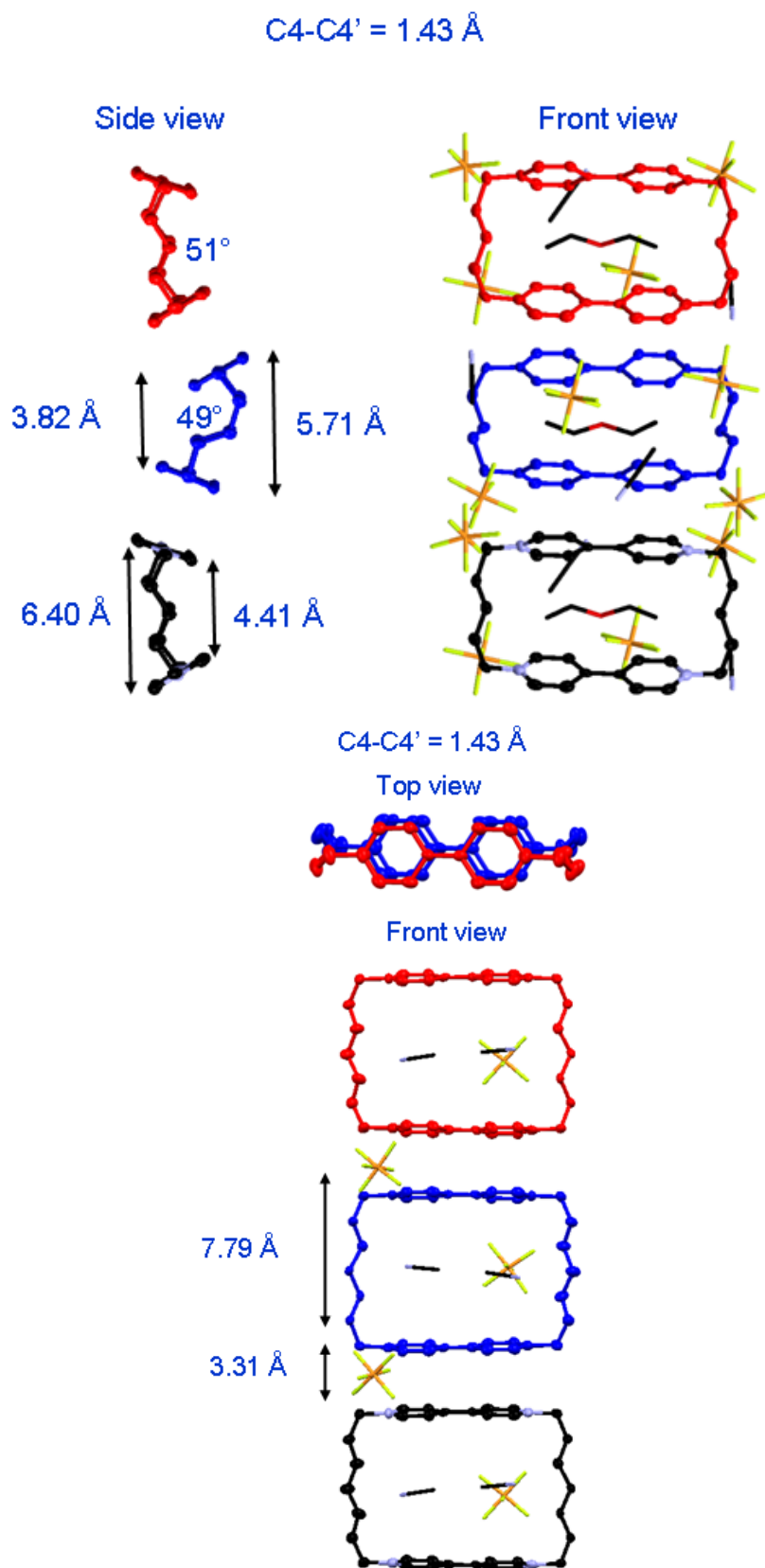
Solid state characterization of $1b^{4+}$ (left) and $1d^{4+}$ (right) as PF_6 salts



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



Solid state characterization of $1b^{2(\bullet)}$ (top) and $1d^{2(\bullet)}$ (bottom) as PF_6 salts



Solid state characterization of $[MV^{2+}MV^{\bullet+}] PF_6$ salt

