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Synthesis and structural characterization of two bis-imidazolium-linked cyclophanes: precursors toward 'carbeneporphyrinoid' ligands

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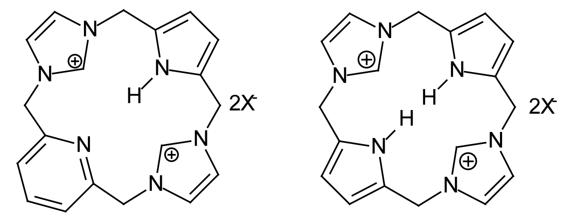
Abstract—The synthesis and spectroscopic characterization of the imidazolium-linked cyclophanes [**1**]$[PF_6]_2$ and [**2**]$[PF_6]_2$ are described. Cyclophane [**1**]$[PF_6]_2$ contains two imidazolium rings bridged by a 2,6-bis(methyl)-pyridine unit and a 2,5-bis(methyl)-pyrrole unit. Cyclophane [**2**]$[PF_6]_2$ contains two imidazolium rings bridged by two 2,5-bis(methyl)-pyrrole units. Cyclophanes [**1**]$[PF_6]_2$ and [**2**]$[PF_6]_2$ have been structurally characterized by X-ray crystallography. © 2002 Elsevier Science Ltd. All rights reserved.

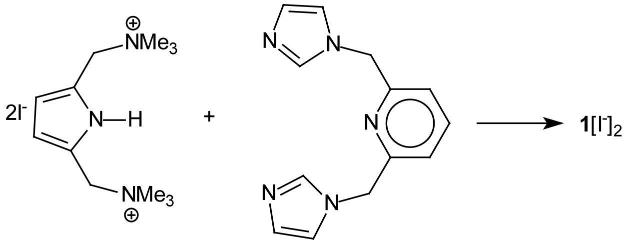
The chemistry of cyclophanes has been of interest for decades.[1] Recently, our group[2] and others[3] have reported the synthesis and characterization of imidazolium-linked cyclophanes. *N*-Confused porphyrins[4] and porphyrinogens[5] have attracted much attention in recent years. Largely, this is due to their ability to coordinate to transition metals in unusual geometries and/or oxidation states. *N*-Heterocyclic carbenes complex to elements from virtually the entire periodic table in a fashion similar to phosphines, however, in many instances, more strongly.[6] A 'porphyrinoid-type' ligand that incorporates *N*-heterocyclic carbenes should be an excellent ligand as it would display the metal complexation chemistry of *N*-confused porphyrins, porphyrinogens and *N*-heterocyclic carbenes. They should bind *very strongly* to transition metals in unusual geometries and/or oxidation states. We have envisioned that imidazolium-linked cyclophanes that contain pyrrole units would be excellent precursors toward bis-*N*-heterocyclic carbene 'porphyrinoid-type' ligands. There have been reports[2,3b] of silver and palladium complexes of *N*-heterocyclic carbene-linked cyclophanes and in the case of the silver complexation chemistry, unique bonding interactions have been observed. For example, we reported the first silver complex that has a *N*-heterocyclic carbene ligand involved in a π-bonding interaction. This novel situation facilitates the stabilization of a $[Ag_4]^{4+}$ cluster with four non-coordinating PF_6 anions. 'Free' *N*-heterocyclic carbene-linked cyclophanes have only been observed in the gas phase.[3f] As a continuation of our efforts in the area of imidazolium-linked cyclophanes, we report herein the synthesis and structural characterization of the dicationic imidazolium-linked cyclophanes **1** and **2** (Fig. 1).

The synthesis of cyclophane **1** is outlined in Eq. (1). The 3+1 condensation reaction of 2,6-bis-(imidazolmethyl)pyridine[7] and 2,5-bis-(trimethylaminomethyl)-pyrrole diiodide **3**[8] in nitromethane affords **1**$[I]_2$ as an off-white solid in 68% yield.[9] Treatment of an aqueous solution of **1**$[I]_2$ with ammonium hexafluorophosphate affords **1** as the hexafluorophosphate salt.



1 **2**

Figure 1.



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Cyclophane **2** was prepared using similar synthetic strategies. 2,5-Bis-(imidazolmethyl)pyrrole **4** was prepared by the reaction of 2 equiv. of imidazole, 2 equiv. of KOH and 1 equiv. of 2,5-bis-(trimethylaminomethyl)pyrrole diiodide **3** in CH_2Cl_2 (Scheme 1).[10] The 3+1 condensation reaction of **4** and **3** in CH_2Cl_2 affords **2**[I]$_2$ as an off-white solid in 55% yield. Treatment of an aqueous solution of **2**[I]$_2$ with ammonium hexafluorophosphate affords **2** as the hexafluorophosphate salt.[11]

The FAB-MS spectra obtained from [**1**][PF_6]$_2$ and [**2**][PF_6]$_2$ in nitrobenzyl alcohol matrices showed [**1**][PF_6]$^+$ ($C_{19}H_{20}N_6PF_6$) at *m*/*z* 474 and [**2**][PF_6]$^+$ ($C_{20}H_{20}N_6PF_6$) at *m*/*z* 465, respectively. The ^{1}H and ^{13}C NMR spectra (DMSO-d_6) for [**1**][PF_6]$_2$ and [**2**][PF_6]$_2$ are consistent with the proposed structures of **1** and **2**. The most notable features of the ^{1}H NMR spectra are the resonances for the imidazolium C–H$^+$ protons at 8.64 and 8.58 ppm for **1** and **2**, respectively.

Crystals of [**1**][PF_6]$_2$ and **2**[PF_6]$_2$ suitable for X-ray crystallography were obtained from concentrated acetonitrile solutions.[12,13] The structure of the dicationic portion of **1** and **2** are illustrated in Figs. 2 and 3, respectively. Cyclophane **1** adopts a distorted asymmetric 'staggered chair' conformation. Cyclophane [**1**][PF_6]$_2$ has an inner cavity that adopts the shape of a box with dimensions 5.1 Å (N1–N4) and 5.6 Å (distance between the centroids of imidazolium rings). In contrast, [**2**][PF_6]$_2$ adopts a 'staggered chair' conformation that is symmetrical about an inversion center. The planes formed by the imidazolium rings are parallel as are the planes formed by the pyrrole rings. Cyclophane [**2**][PF_6]$_2$ has an inner cavity that adopts the shape of a box with dimensions 4.9 Å (N1–N1A) and 6.2 Å (distance between the centroids of imidazolium rings).

In conclusion, two imidazolium-linked pyrrole containing cyclophanes have been synthesized and structurally characterized. We expect these to be excellent precursors toward bis-*N*-heterocyclic carbene 'porphyrinoid type' ligands, that we have termed carbeneporphyrinoids. These ligands should bind *very strongly* to transition metals in unusual geometries and/or oxidation states. The metal complexation chemistry of **1** and **2** is currently underway.

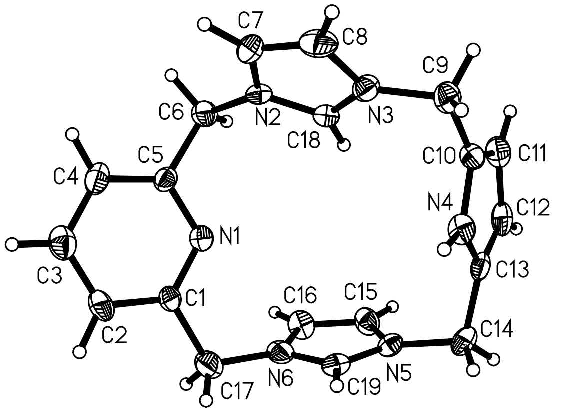


Figure 2. Molecular structure of the dicationic portion of [**1**][PF_6]$_4$ with thermal ellipsoids drawn at a 50% probability.

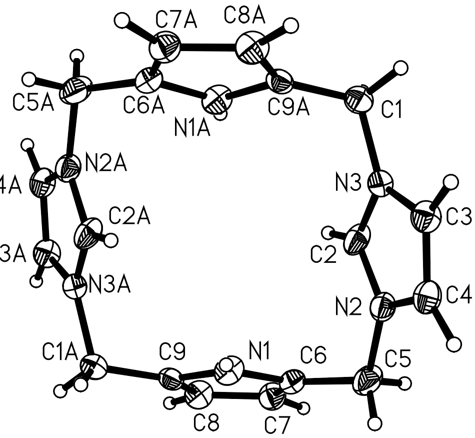
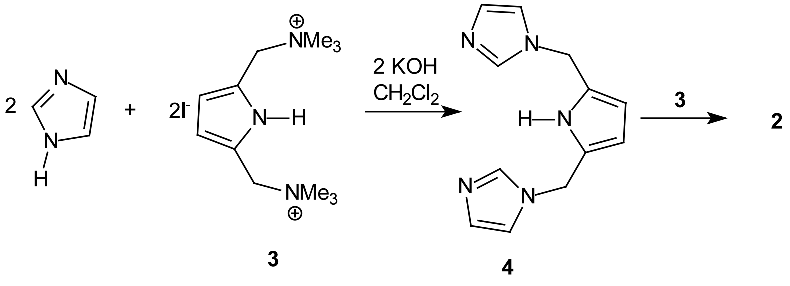


Figure 3. Molecular structure of the dicationic portion of [**2**][PF_6]$_4$ with thermal ellipsoids drawn at a 50% probability.

Supplemental material. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplemental publications number CCDC 177872 and 177873. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(0)-1223-336033 or email: deposit@ccdc.cam.ac.uk).



Scheme 1.

Acknowledgements

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9. Synthesis of [**1**][PF_6]$_2$. 2,6-Bis(imidazolmethyl)pyridine (2.39 g, 10.0 mmol) and 2,5-bis(trimethylaminomethyl)-pyrrole diiodide (4.65 g, 10.0 mmol) were stirred in 100 mL of nitromethane and heated to 55°C for 16 h. The precipitate was filtered and dissolved in 100 mL of water. Ammonium hexafluorophosphate (3.2 g, 20.0 mmol) was added to the solution and the precipitate was collected by filtration. Yield: 4.2 g, 6.8 mmol, 68%. Mp 220°C (dec.). Anal. calcd for $C_{19}H_{20}N_6P_2F_{12}$: C, 36.67; H, 3.24; N, 13.50. Found: C, 36.90; H, 3.33; N, 13.77%. ^1H NMR (300 MHz, DMSO-d_6): δ 5.36 (s, 4H, CH_2), 5.45 (s, 4H, CH_2), 6.25 (s, 2H, C-H(pyrrole)), 7.68 (d, 2H, $J=7.8$ Hz, N-C(H)-CH), 7.78 (d, 7.8 Hz, 2H, N-C(H)-CH), 7.79 (d, 2H, $J=7.8$ Hz, *m*-pyr), 7.97 (t, 1H, $J=7.8$ Hz, *p*-pyr), 8.64 (s, 2H, N-C(H)-N), 11.2 (s, 1H, pyrrole N-H). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6): δ 46.2 (CH_2), 53.4 (CH_2), 110.4 (CH-pyrrole), 123.0, 123.2, 124.2 (aromatic), 126.8 (C-pyrrole), 135.7 (N-C-N), 139.4 (*p*-pyr), 153.9 (C-pyr). FAB-MS: *m*/*z* 474 (M^+ of $C_{19}H_{20}N_6PF_6$).
10. Synthesis of **4**. Imidazole (5.44 g, 80.0 mmol), KOH (4.5 g, 80.0 mmol) and 2,5-bis(trimethylaminomethyl)pyrrole diiodide (9.2 g, 20.0 mmol) were stirred at room temperature in 160 mL of CH_2Cl_2 for 16 h. The solution was filtered and the solvent was removed under reduced pressure to yield a light red solid. Recrystallization of the solid from water yielded **4** as an off-white solid. Yield: 4.1 g, 18.1 mmol, 90%. Mp 124–125°C. Anal. calcd for $C_{12}H_{13}N_5$: C, 63.42; H, 5.77; N, 30.82. Found: C, 63.20; H, 5.44; N, 30.82%. ^1H NMR (300 MHz, DMSO-d_6): δ 5.03 (s, 4H, CH_2), 5.96 (s, 2H, NCH), 6.84 (s, 2H, NCH), 7.09 (s, 2H, C=CH), 7.60 (s, 2H, N-C(H)-N), 11.10 (s, 1H, pyrrole N-H). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6): δ 42.9 (CH_2), 108.7, 119.4, 128.0, 128.5, 137.1.
11. Synthesis of [**2**][PF_6]$_2$. 2,5-Bis(imidazolymethyl)pyrrole (2.3 g, 10.0 mmol) and 2,5-bis(trimethylaminomethyl)-pyrrole diiodide (4.65 g, 10.0 mmol) were stirred in 100 mL of nitromethane and heated to 55°C for 16 h. The precipitate was filtered and dissolved in 100 mL of water. Ammonium hexafluorophosphate (3.2 g, 20.0 mmol) was added to the filtrate and the precipitate was collected by filtration. Yield: 3.4 g, 5.5 mmol, 55%. Mp 200°C (dec.). Anal. calcd for $C_{18}H_{20}N_6P_2F_{12}$: C, 35.42; H, 3.30; N, 13.77. Found: C, 35.20; H, 3.21; N, 13.22%.
   Spectroscopic data for [**2**][PF_6]$_2$. ^1H NMR (300 MHz, DMSO-d_6): δ 5.34 (s, 8H, CH_2), 6.25 (s, 4H, C-H(pyrrole)), 7.85 (s, 4H, N-C(H)-CH), 8.58 (s, 2H, N-C(H)-N), 11.2 (s, 2H, pyrrole N-H). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6): δ 46.4 (CH_2), 110.7, 123.3, 126.8, 135.5. FAB-MS: *m*/*z* 465 (M^+ of $C_{20}H_{20}N_6PF_6$).
12. Crystal data for $C_{19}H_{20}F_{12}N_6P_2$ [**1**][PF_6]$_2$: $M_W=622.34$, monoclinic, space group $P2_1$, $a=9.237(3)$, $b=13.319(5)$, $c=10.031(3)$ Å, $\beta=97.36(3)$°, $V=1224.0(7)$ Å^3, $Z=2$, $D_{calcd}=1.689$ Mg/m^3, $\mu=0.292$ mm^{-1}, $T=130$ K, refinement for data with $I>2\sigma(I)$ (1952 reflections) gave $R_1(F)=0.0435$ and $wR_2(F^2)=0.1063$ for all data.
13. Crystal data for $C_{18}H_{20}F_{12}N_6P_2$ [**2**][PF_6]$_2$: $M_W=610.34$, triclinic, space group $P\bar{1}$, $a=8.675(7)$, $b=8.695(6)$, $c=9.383(6)$ Å, $\alpha=66.47(5)$, $\beta=89.93(6)$, $\gamma=63.80(5)$°, $V=568.9(7)$ Å^3, $Z=1$, $D_{calcd}=1.782$ Mg/m^3, $\mu=0.312$ mm^{-1}, $T=121$ K, refinement for data with $I>2\sigma(I)$ (1023 reflections) gave $R_1(F)=0.0650$ and $wR_2(F^2)=0.1974$ for all data.