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Towards dipyrrins: oxidation and metalation of acyclic and macrocyclic Schiff-base dipyrromethanes†

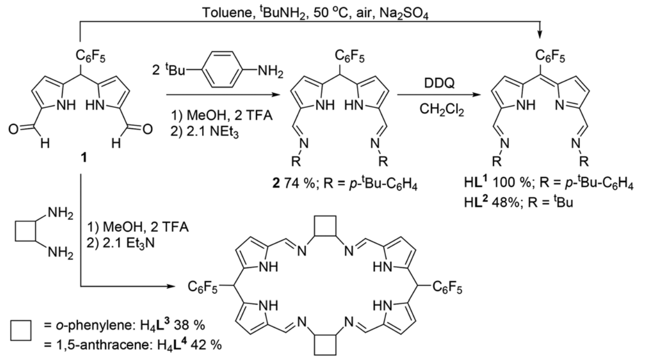
James R. Pankhurst, Thomas Cadenbach, Daniel Betz, Colin Finn and Jason B. Love*

Oxidation of acyclic Schiff-base dipyrromethanes cleanly results in dipyrrins, whereas the macrocyclic 'Pacman' analogues either decompose or form new dinuclear copper(II) complexes that are inert to ligand oxidation; the unhindered hydrogen substituent at the *meso*-carbon allows new structural motifs to form.

Bimetallic complexes with a well-defined molecular structure and controlled internuclear separation are of significant interest in small molecule activation chemistry.[1] In this context, several polypyrrolic Schiff-base macrocycles reported by us and others act as ligands for s-, d- and f-block metals.[2–5] These complexes have a tendency to fold into cofacial or 'Pacman' structures that provide a reactive cleft between the two metals suited to cooperative catalytic reduction chemistry,[6,7] with the macrocycles disubstituted at each dipyrromethane *meso*-carbon position providing two dianionic coordination compartments.

A large number of dipyrromethanes that are mono-substituted at the *meso*-position are readily oxidised to their dipyrrin congeners, most notably by 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ).[8] Significantly, transition metal dipyrrin complexes have interesting photochemical and redox properties,[9] carry out unusual chemical transformations, including C–H bond activation,[10] and flexible N_4-dipyrrin macrocycles have been prepared, although little exploited due to their difficult preparations.[11] As such, we are interested in exploring analogous oxidation procedures to form a new set of dipyrrin Pacman macrocycles with two mono-anionic coordination pockets to stabilise metals in lower oxidation states and hence favour small molecule reduction chemistry.

The preparation of acyclic and macrocyclic dipyrromethanes was achieved by exploiting the mono-*meso*-substituted dialdehyde **1**[12] to form diiminodipyrromethane **2** in 74% yield using standard Schiff-base condensation methods (Scheme 1). The solid-state structure of **1** was determined by X-ray crystallography and is shown in the ESI.† The ^1H NMR spectrum of **2** revealed the appearance of an imine proton resonance at 8.18 ppm accompanied by the loss of the aldehyde resonance of **1** at 9.24 ppm. The absorption band at 1623 cm^{-1} in the IR spectrum of **2** is assigned to the imine functional group.



Scheme 1 Syntheses of acyclic and macrocyclic dipyrromethane (**2**, H_4**L**^{3}, H_4**L**^{4}) and dipyrrin compounds (H**L**^{1}, H**L**^{2}).

Oxidation of **2** was achieved using stoichiometric amounts of DDQ to afford the dipyrrin H**L**^{1} in quantitative yield,[13] and is supported by the loss of the *meso*-proton resonance at 5.69 ppm in the ^1H NMR spectrum. Dipyrrin H**L**^{2} was synthesised by heating a toluene solution of **1** and $^tBuNH_2$ to 50 °C with Na_2SO_4, forming directly in air without a separate oxidation step. The ^1H NMR spectrum of H**L**^{2} includes an imine proton resonance at 7.71 ppm and does not feature a *meso*-proton resonance. The IR absorption band at 1582 cm^{-1} is assigned to the imine functional group. The solid-state structure of H**L**^{2} was determined by X-ray crystallography (ESI†) and displays the expected planar *meso*-carbon geometry. A C_2-symmetric solution-state structure was observed for H**L**^{2} by NMR spectroscopy, but in the solid-state, one imine group is rotated away from the N_4-pocket, lowering the symmetry to

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EaStCHEM School of Chemistry, University of Edinburgh, Joseph Black Building, David Brewster Road, Edinburgh, EH9 3FJ, UK. E-mail: jason.love@ed.ac.uk

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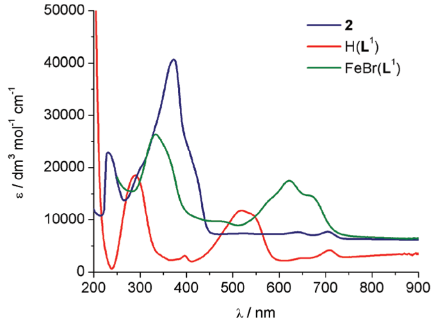

Fig. 1 Electronic absorption spectra for **2**, HL^1 and $FeBr(L^1)$. Spectra for **2** and HL^1 were recorded as CH_2Cl_2 solutions, $FeBr(L^1)$ was recorded as a THF solution.

C_1. HL^2 crystallises as co-planar, π-stacked dimers, arranged head-to-tail.

Reaction between HL^1 and $LiN(SiMe_3)_2$ cleanly generates the lithium dipyrrolide LiL^1 which was then used to form the iron(II) complex $FeBr(L^1)$ by salt metathesis in THF. While not characterised by X-ray crystallography and NMR silent, ESI-MS of microcrystalline $FeBr(L^1)$ supports its formulation. The exclusion of air from these synthetic procedures avoids undesired ligand oxidation reactions which have been shown to occur on oxidation of Group 10 complexes of similar iminodipyrromethane ligands.[13]

Electronic absorption spectra were recorded for **2**, HL^1 and the iron(II) complex $FeBr(L^1)$ (Fig. 1), and the spectra for **2** and HL^1 were accurately reproduced by TD-DFT calculations using the B3LYP functional and 6-311G(d,p) basis set (ESI†). The dominant absorption band for **2** appears at 373 nm and is assigned as a mixture of HOMO (H) to LUMO (L)+1 (59%) and (H−1)–L (32%) transitions, with the H–L transition appearing as a shoulder at 413 nm. Upon oxidation to HL^1, both the (H−1)–L and H–L transitions are red-shifted to 520 and 540 nm, respectively, while the H–(L+1) transition remains in the UV-region at 290 nm. This change in electronic structure is typical for dipyrromethene compounds[14] and reflects a 1.6 eV stabilisation of the LUMO upon oxidation. Although the extinction coefficients of 20 000 M^{-1} cm^{-1} for HL^1 and $FeBr(L^1)$ are small compared to BODIPY compounds (80 000 M^{-1} cm^{-1}) they are similar to pyridomethene-BF_2 complexes.[15]

A small number of crystals were grown from THF–hexane solutions of $FeBr(L^1)$, and were found to be the oxidised iron(III) oxo dipyrrin $\{FeBr(L^1)\}_2(\mu\text{-}O)$ (Fig. 2) in which the Fe centres are five-coordinate and adopt a distorted trigonal bipyramidal geometry with pyrrole N1, Br1, and O1 equatorial and pyrrole N3 and imine N2 axial. As with HL^2, one imine nitrogen N4 is rotated out of the pocket and is not coordinated. The overall dinuclear structure is reminiscent of a Pacman arrangement, with perfluoroaryl groups and ^{t}Bu-aryl substituents adjacent. The XFe(μ-O)FeX core (X = halide) is common in Fe chemistry, albeit usually as part of a wholly inorganic anion.

The *ortho*-phenylene bridged macrocycle H_4L^3 and the 1,8-anthracene bridged macrocycle H_4L^4 were both prepared by acid-promoted condensation of **1** with the appropriate diamine. Upon neutralisation with NEt_3, the free-base precipitates cleanly from the methanol solution as a dull-yellow solid and is isolated by filtration. For both compounds, characteristic imine proton resonances were observed in the ^{1}H NMR spectra at 8.09 ppm (H_4L^3) and 8.38 ppm (H_4L^4) and imine IR absorption bands at 1620 cm^{-1} (H_4L^3) and 1614 cm^{-1} (H_4L^4) were also recorded. No higher-order cyclisation products were observed by ESI-MS with only the expected molecular ions observed at 937 *m/z* for H_4L^3 and 1080 *m/z* for H_4L^4.

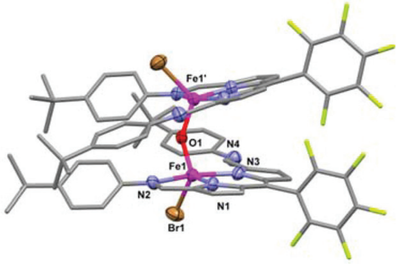

Fig. 2 Solid-state structure of $\{FeBr(L^1)\}_2(\mu\text{-}O)$. For clarity, all protons and solvent of crystallisation are omitted (displacement ellipsoids drawn at 50% probability).

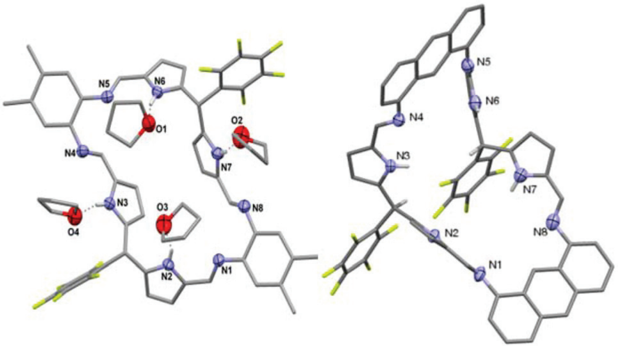

Fig. 3 Solid-state structures of H_4L^3 and H_4L^4. For clarity, all protons except those on the pyrrole N atoms and most solvent molecules are omitted (displacement ellipsoids drawn at 50% probability).

The solid-state structures for both H_4L^3 and H_4L^4 were determined by X-ray crystallography (Fig. 3). Surprisingly, and unlike previous examples, H_4L^3 crystallises excluding any protic solvent molecules that are usually hydrogen-bonded in the cleft.[4,16] Instead, THF solvent molecules are hydrogen-bonded to each pyrrole group with each imino-pyrrole unit twisted with respect to its neighbouring units in a non-folded configuration that minimises ring-strain. Macrocycle H_4L^4 crystallises in a bowl geometry in which the anthracene groups are held further apart than they are commonly found in metal complexes; in this case, protic solvent molecules are present within the cleft.

The [2 + 2] cyclisation between **1** and the diamine could result in either *syn*- or *anti*-isomers in which the relative positions of the *meso*-substituents dictate the identity of the isomer. Importantly, both $H_4\mathbf{L}^3$ and $H_4\mathbf{L}^4$ crystallise as the *syn*-isomer only and, furthermore, there is no evidence to support a mixture of isomers by NMR spectroscopy, which clearly shows a single set of resonances for ^{1}H, ^{13}C and ^{19}F nuclei. Considering the isolated yields of the macrocycles (*ca*. 40%), it is likely that some preferential precipitation of the *syn*-isomer has occurred, with the *anti*-isomer remaining in solution; we have, as yet, been unable to isolate or characterise material consistent with this latter isomer.

In contrast to the acyclic analogues, attempts to oxidise macrocycles $H_4\mathbf{L}^3$ and $H_4\mathbf{L}^4$ to the dipyrrins using DDQ resulted in decomposition to a myriad of unidentifiable products. Similar decomposition was observed on reaction of $H_4\mathbf{L}^3$ and $H_4\mathbf{L}^4$ with chloranil, Ag_2O, I_2 and $Ce(NH_4)_2(NO_3)_6$. Despite previous reports of dipyrromethane macrocycles being successfully oxidised by MnO_2 or by $KMnO_4$,[17] no discernible products have yet been isolated using these oxidants.

To investigate this further, the redox behaviour of $H\mathbf{L}^2$, $H_4\mathbf{L}^3$ and $H_4\mathbf{L}^4$ was investigated by cyclic voltammetry. The CV for $H\mathbf{L}^2$ includes a reversible reduction to the radical anion at $E_{1/2}$ −1.46 V *vs.* Fc^+/Fc and a second, irreversible reduction at E_p^a −2.28 V. This second process is assigned tentatively to the two-electron, proton-coupled reduction to the dipyrromethane, $H_2\mathbf{L}^2$. The CVs for macrocycles $H_4\mathbf{L}^3$ and $H_4\mathbf{L}^4$ do not feature any oxidation processes, only an irreversible reduction at E_p^a −1.41 V *vs.* Fc^+/Fc for $H_4\mathbf{L}^3$ and E_p^a −1.78 V for $H_4\mathbf{L}^4$ (ESI†).

As an alternative route to dipyrrins, attempts were made to oxidise $H_4\mathbf{L}^3$ and $H_4\mathbf{L}^4$ in air in the presence of a metal cation.[18] As such, bimetallic copper(II) complexes were prepared by stirring THF solutions of $H_4\mathbf{L}^3$ or $H_4\mathbf{L}^4$ with $Cu(OAc)_2 \cdot H_2O$ in the presence of NEt_3 in air. The resulting dipyrromethane complexes $Cu_2(\mathbf{L}^3)$ and $Cu_2(\mathbf{L}^4)$ were found to be stable on alumina and were thus purified by column chromatography, eluting the pure products as orange CH_2Cl_2 fractions in high yields; 'accordion' macrocycles that have dipyrromethane head groups but flexible compartmental spacers display similar inertness to oxidation on metalation.[11] The syntheses of these compounds are supported by ESI-MS, with molecular ion peaks at 1058 *m*/*z* for $Cu_2(\mathbf{L}^3)$ and 1203 *m*/*z* for $Cu_2(\mathbf{L}^4)$ with the expected isotope pattern for bimetallic complexes, albeit with seemingly oxidised macrocycles. The vibrational frequencies for the imine groups at 1552 cm^{-1} for $Cu_2(\mathbf{L}^3)$ and 1574 cm^{-1} for $Cu_2(\mathbf{L}^4)$ are lower compared to the free ligands and are indicative of metalation. Both compounds are NMR-silent. The copper(II) complex $Cu_2(\mathbf{L}^5)$ that is similar to $Cu_2(\mathbf{L}^4)$, but differs in that the macrocycle is diethyl-substituted at the *meso*-position, was also made for comparison (ESI†).

The solid-state structures for $Cu_2(\mathbf{L}^3)$, $Cu_2(\mathbf{L}^4)$, and $Cu_2(\mathbf{L}^5)$ were determined by X-ray crystallography (Fig. 4 and 5, and ESI,† respectively) and in all cases show non-oxidised dipyrromethane macrocycles, evident from the tetrahedral bond angles around each *meso*-carbon atom (mean a = 110.2° for $Cu_2(\mathbf{L}^3)$ and 111.0° for $Cu_2(\mathbf{L}^4)$). This is in disagreement with the mass spectrometry data of these complexes and suggests that the macrocycles may oxidise under MS conditions.

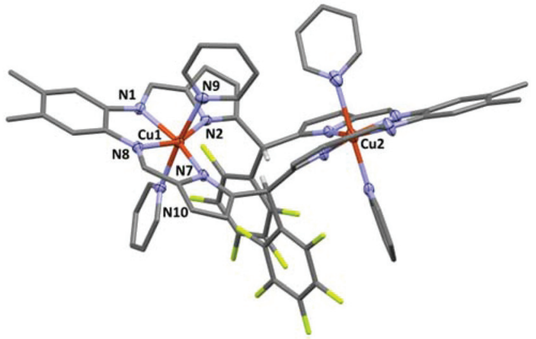

Fig. 4 Solid state structure of $Cu_2(\mathbf{L}^3) \cdot 4Py$. For clarity, most H atoms and three pyridine solvent molecules are omitted (displacement ellipsoids drawn at 50% probability). Cu⋯Cu, 6.493(6) Å; sum of planar angles, 359.8° around Cu1 and 359.0° around Cu2; bite angle, 152°.

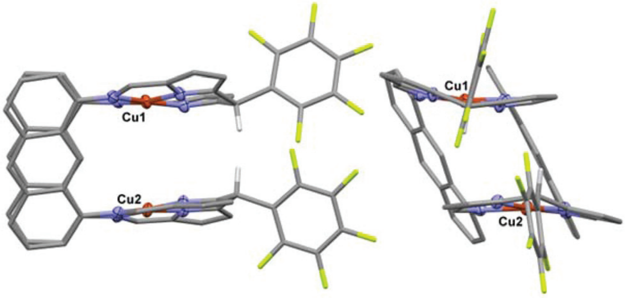

Fig. 5 Solid-state structure of $Cu_2(\mathbf{L}^4)$. For clarity, most protons and one symmetry-generated THF solvent molecule are omitted (displacement ellipsoids drawn at 50% probability). Cu⋯Cu, 4.818(3) Å; sum of planar angles 360.0° around Cu1 and 360.2° around Cu2; twisting angle 30°; bite angle −8.03°.

Unexpectedly, the *o*-phenylene-bridged macrocycle in $Cu_2(\mathbf{L}^3)$ adopts a 'bowl' conformation on metalation,[19] bonding to the metal through two adjacent pyrrolide-imine groups and folding at the *meso*-carbon atoms, resulting in a wide bite angle of 152° between the two N_4-donor compartments and a torsional twist of 24.8(2)°; this results in a long Cu⋯Cu separation of 6.493(6) Å. These data contrast to those of copper(II) complexes of the *meso*-disubstituted macrocyclic analogues, which adopt 'classical' Pacman structures on metalation through hinging at the arene rings, and suggests that the macrocyclic topology is controlled through the choice (or absence) of *meso*-substituent; these latter Pacman complexes exhibit much smaller bite angles (52–62°) and shorter Cu⋯Cu separations of 3.47–4.05 Å.[5,16] A structurally similar U(III) complex was recently reported to adopt a similar coordination geometry to $Cu_2(\mathbf{L}^3)$,[20] but in bowl-shaped complexes of other metals, the pyrrole groups remain protonated and the two metal centres are bridged by anions, such as hydroxides.[2,16] Importantly, $Cu_2(\mathbf{L}^3)$ crystallises as the *syn*-isomer only.

Due to the separation between the imine nitrogen donors in the anthracene-pillared macrocycle $\mathbf{L}^5$, a bowl configuration is not possible; as such, both $Cu_2(\mathbf{L}^4)$ and $Cu_2(\mathbf{L}^5)$ crystallise as Pacman complexes with 30° twist angles between the anthracene groups and the diiminodipyrromethane coordination pockets (Fig. 5). Again, the internuclear separation is controlled through choice of the *meso*-substituent, as $\mathrm{Cu_2}(\mathbf{L}^4)$ has a significantly shorter Cu⋯Cu separation of 4.818(3) Å compared to 5.345(1) Å in $\mathrm{Cu_2}(\mathbf{L}^5)$.

The internuclear distance in $\mathrm{Cu_2}(\mathbf{L}^4)$ is also short compared to related complexes of Co(II), Pd(II) and U(VI) complexes of $\mathbf{L}^5$ (5.377–5.834 Å)[4,7,21] and is more similar to that observed for dinuclear Zn(II) complexes of $\mathbf{L}^5$ that are bridged by anions (3.871–5.532 Å).[22] The small *meso*-proton substituent also has the effect of closing the cleft, so that $\mathrm{Cu_2}(\mathbf{L}^4)$ has a negative bite angle of −8.03° between the two $\mathrm{N_4}$-donor planes, compared to the positive bite angle of 14.83° for $\mathrm{Cu_2}(\mathbf{L}^5)$. As with $\mathrm{Cu_2}(\mathbf{L}^3)$, $\mathrm{Cu_2}(\mathbf{L}^4)$ crystallises as the *syn*, *exo*-isomer only, with no evidence for *syn*, *endo*- or *anti*-isomers.

The redox chemistry of $\mathrm{Cu_2}(\mathbf{L}^3)$, $\mathrm{Cu_2}(\mathbf{L}^4)$ and $\mathrm{Cu_2}(\mathbf{L}^5)$ was investigated by cyclic voltammetry. The CVs of $\mathrm{Cu_2}(\mathbf{L}^4)$ and $\mathrm{Cu_2}(\mathbf{L}^5)$ showed no oxidation features, with only irreversible reductions for both at E_p^a −1.51 V *vs.* $\mathrm{Fc^+/Fc}$ for $\mathrm{Cu_2}(\mathbf{L}^4)$ and E_p^a −1.70 V and −2.30 V for $\mathrm{Cu_2}(\mathbf{L}^5)$ (ESI†). In contrast, the CV of $\mathrm{Cu_2}(\mathbf{L}^3)$ shows one quasi-reversible, two-electron oxidation at E_p^a −0.10 V and two quasi-reversible, one-electron reductions at E_p^c −1.47 V and −1.76 V (Fig. 6). These redox events are assigned tentatively to the formation of $\mathrm{Cu_2}(\mathbf{L}^3)^{2+}$, $\mathrm{Cu_2}(\mathbf{L}^3)^{-}$, and $\mathrm{Cu_2}(\mathbf{L}^3)^{2-}$, respectively, *i.e.* oxidation to Cu(III) and sequential reduction to Cu(I). The reversibility of these processes suggest they are metal-based; electrochemical oxidation of the macrocycle to the dipyrrin is anticipated to be irreversible due to the loss of hydrogen atoms and the required change in geometry that would follow.

We have synthesised two new acyclic dipyrrin compounds and two new Schiff-base macrocycles. These macrocycles are not readily oxidised to their dipyrrin congeners, even when metalated, yet due to the sterically unhindered *meso*-carbon we have been able to prepare two new copper(II) macrocyclic complexes that adopt unexpected structures with very dissimilar Cu⋯Cu separations; we are currently investigating the electronic structures and redox behaviours of these complexes by EPR spectroscopy and electrochemistry, as well as their reactivity towards $\mathrm{CO_2}$ and other reducible substrates.

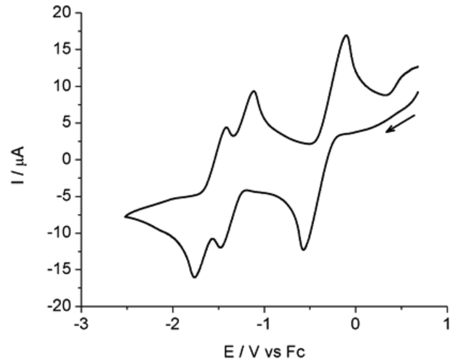

Fig. 6 Cyclic voltammogram of $\mathrm{Cu_2}(\mathbf{L}^3)$, measured as a 3 mM solution in THF. Electrolyte: 0.2 M $[^n\mathrm{Bu_4N}][\mathrm{BF_4}]$. Pt disc working-electrode, Pt gauze counter-electrode, Ag wire pseudo-reference electrode.

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