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Macrocyclic diiminodipyrromethane complexes: structural analogues of Pac-Man porphyrins†

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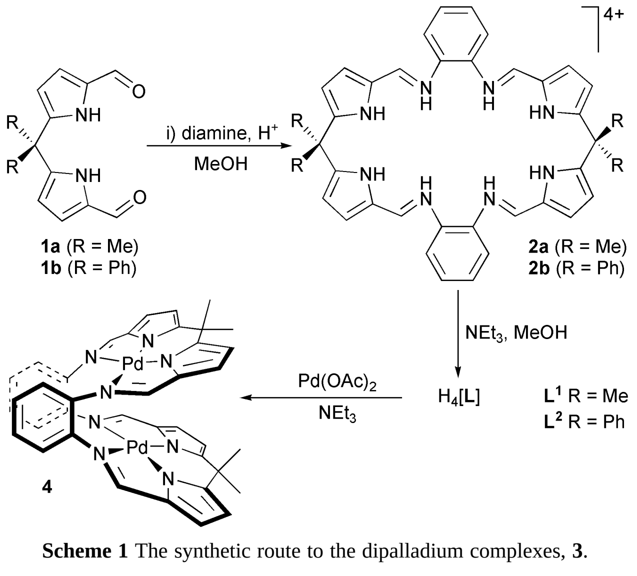
The complexation of palladium(II) by a unique family of [2+2] diiminodipyrromethane macrocycles yields compounds that adopt structures reminiscent of Pac-Man porphyrins.

Polypyrrolic macrocycles exhibit a rich and diverse chemistry. For example, the flexible frameworks of calixpyrroles can accommodate a variety of transition metals and f-block elements in a range of oxidation states, from which elegant transformations of the macrocycle itself or the activation of small molecules such as N_2 can ensue.[1] Calixpyrroles are also extremely efficient and sometimes selective anion binding agents.[2] Furthermore, Schiff-base polypyrrolic lanthanide complexes such as motexafin lutetium are receiving considerable attention as photodynamic therapy agents,[3] and similar iminopolypyrroles can complex actinide cations such as uranyl and late first-row transition metals.[4] Also, the larger "accordion" porphyrins, iminopolypyrrolic macrocycles that contain two distinct donor compartments, have been shown to functionally model binuclear metalloenzymes.[5]

Following our successful syntheses of acyclic, N-donor elaborated dipyrromethanes,[6] we were interested in using the diformyldipyrromethane synthon **1** in the preparation of polypyrrolic macrocycles. We report herein the acid-template synthesis of the new, compartmentalised diiminodipyrromethane macrocycles H_4[**L**] and their complexation of Pd(II).

The addition of *p*-toluenesulfonic acid to a stirred mixture of dialdehydes **1a** or **1b** and 1,2-diaminobenzene in methanol cleanly generates the [2+2] Schiff-base condensation products **2a** or **2b**, respectively, in high yield as orange, microcrystalline solids (Scheme 1).† Electrospray mass spectrometry of the reaction mixture showed that no higher order cyclisation products are present. The X-ray crystal structure of the salt **2a** was determined and confirms that [2+2] cyclisation has occurred (Fig. 1). The tetraprotonated macrocycle adopts a bowl-like conformation with one TsO^- group (S1) hydrogen bonded through O2 and O3 to opposing pairs of iminopyrrole units. Two further TsO^- groups (S2 and S4) interact with the remaining iminopyrrole units through O5 and O11, respectively. This conformation suggests a possible mode of complexation for transition metals as two N_4 compartments are defined by the resultant wedge at the dipyrromethane *meso*-carbons.



Scheme 1 The synthetic route to the dipalladium complexes, **3**.

The macrocyclic salts can be neutralised by the addition of NEt_3, which quantitatively forms the free ligands H_4[**L**] as poorly soluble, amorphous, yellow powders, although addition of a protic solvent such as d_4-methanol to a slurry of H_4[**L**] in $CDCl_3$ results in immediate dissolution. The ^1H NMR spectrum of H_4[**L**^{1}] reveals the retention of the characteristic resonance of the imine proton at 8.10 ppm. The relative simplicity of the synthesis and the high yields afforded mean that multigram quantities can be readily prepared.

Addition of triethylamine to a stirred mixture of $Pd(OAc)_2$ and either macrocycle in CH_2Cl_2 results in the clean generation of the orange dipalladium compounds [Pd_2(**L**^{1})] **3a** and [Pd_2(**L**^{2})] **3b**, respectively. The electrospray mass spectrum of the reaction medium of **3a** showed only one signal at 872 amu with the correct isotopic pattern for [Pd_2(**L**^{1})]$^+$. The X-ray crystal structures of both **3a** and **3b** were determined and were found to be similar (Fig. 2).‡ In **3a**, Pd1 and Pd2 are both coordinated by diiminodipyrrolide donor compartments and adopt similar square planar geometries (Σ angles Pd1 = 360.03, Pd2 = 359.85°) with standard Pd–N bond lengths. The presence of the rigid *o*-aryl spacer between the donor compartments has a profound effect on the overall molecular geometry with face-to-face π-stacking of the *o*-aryl groups enforcing a unique wedge-like arrangement of the two PdN_4 square planes. This is unlike bimetallic accordion porphyrins, in which flexible

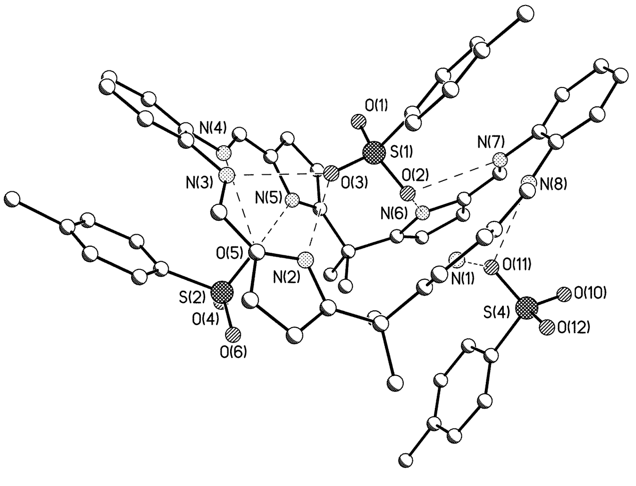


Fig. 1 Structure of the macrocyclic salt **2a**. Omitted for clarity are one TsO^- molecule (S3, half occupancy with MeO^-) not hydrogen bonding to the macrocycle, MeOH solvate molecules and all H atoms.

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† Electronic supplementary information (ESI) available: experimental and crystallographic details. See http://www.rsc.org/suppdata/cc/b3/b308443d/

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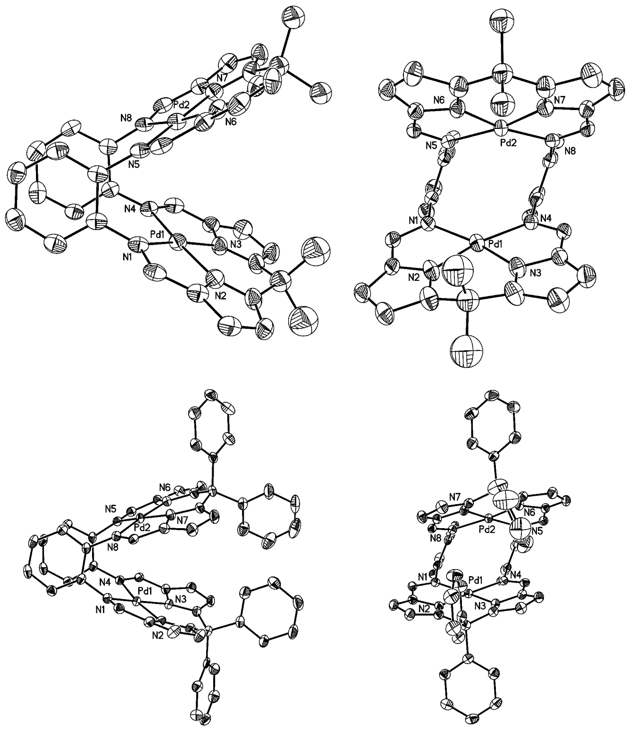

Fig. 2 Solid state structures of the dipalladium compounds **3a** and **3b** (50 % ellipsoids). H-atoms are omitted for clarity.

alkyl chain linkers between the two donor compartments lead to greater conformational flexibility but is more reminiscent of single-pillared, or 'Pac-Man' porphyrins (Fig. 3).[7,8] It is significant that while ligands H_4[**L**] appear highly flexible, the dipalladium complexes **3a** and **3b** are highly rigid and synthetically more available than their Pac-Man analogues. Although the presence of the sp^3-CMe_2 group in the dipyrrolide backbone precludes full conjugation of the N_4-donor set, the planarity observed and structural similarity to single-pillared porphyrins warrants comparison. In **3a**, the Pd···Pd distance of 3.76 Å is similar to that seen in the cofacial, single-pillared diporphyrin complex Pd_2(DPX) (dibenzoxanthene pillar) (Pd···Pd = 3.97 Å).[9] However, the 'bite angle,' θ, between the PdN_4 planes of 56.5° in **3a** is much greater than that observed in Pd_2(DPX), where the porphyrin rings are effectively co-planar (θ = 3.9°);§ the use of single dibenzofuran pillars results in larger bite angles (θ = 20–25°) and can accommodate metal–metal distances from 3.5 to 7.8 Å.[10] A torsional twist is evident in **3a** (Φ = 19°) and **3b** (Φ = 22°) (Fig. 2). These values lie between those of the torsionally rigid Pac-Man porphyrins (Φ = 2–7°) and the more flexible cofacial, amide-linked diporphyrins (*e.g.* dicopper hexyldiporphyrin-7, Φ = 43.2°, Fig. 3).[11] This relatively large twist in **3a** and **3b** is presumably a consequence of destabilising, steric interactions between the *meso*-groups of the dipyrrolide unit, and the need to maximise face-to-face π-stacking in the *o*-aryl backbone. The solid state structure of **3a** (and by inference, **3b**) appears to be retained in solution. The ^1H NMR spectrum of **3a** reveals the presence of two distinct methyl groups at 1.61 and 1.50 ppm, assigned to the *meso*-substituents that lie *syn* and *anti* to the cleft, respectively. A dynamic process that would render these environments equivalent in solution is precluded as Pd–N(imino) bond cleavage is a prerequisite in order to progress through a symmetrical, flattened macrocyclic conformation.

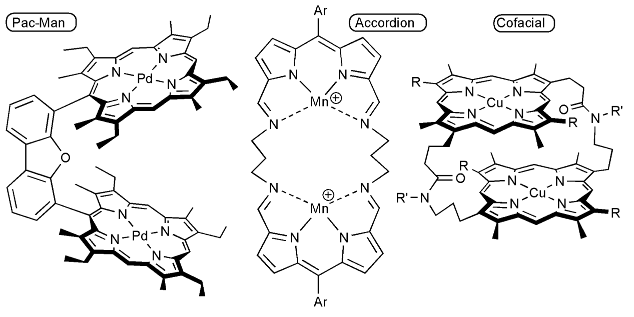

Fig. 3 Examples of Pac-Man, accordion and cofacial porphyrins.

We are at present investigating the luminescent properties of **3a** and **3b**, and the syntheses of transition metal complexes incorporating **L**. Preliminary results suggest that, as with bimetallic cofacial diporphyrins,[8] dicobalt(II) complexes of **L** react spontaneously with O_2; thus, reaction between $Co(OAc)_2$ and H_4[$\mathbf{L^1}$]/NEt_3 in air forms the oxo-complex [Co_2O($\mathbf{L^1}$)] as the sole product (by ESMS, 735 amu).

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Notes and references

† Electronic supplementary information (ESI) available: experimental and crystallographic details. See http://www.rsc.org/suppdata/cc/b3/b308443d/

‡ Satisfactory combustion analyses were obtained for all reported compounds. *Crystal data*: **2a**: $C_{64.5}H_{72}N_8O_{12.5}S_{3.5}$, triclinic, a = 12.9007(10), b = 16.2779(13), c = 18.0091(14) Å, α = 75.638(1), β = 75.199(1), γ = 85.938(1) °, U = 3542.0(5) Å^3, T = 150(2) K, space group $P\bar{1}$, Z = 2, μ(Mo-K$_\alpha$) = 0.181 mm^{-1}, 32396 reflections measured, 16861 unique (R_{int} = 0.005) which were used in all calculations. The final $wR(F^2)$ was 0.2704 (all data). **3a**: $C_{38.25}H_{33}N_8O_{0.25}Pd_2$, triclinic, a = 9.4559(8), b = 13.2076(11), c = 14.3084(12) Å, α = 74.331(2), β = 86.576(2), γ = 81.503(2) °, U = 1701.3(4) Å^3, T = 150(2) K, space group $P\bar{1}$, Z = 2, μ(Mo-K$_\alpha$) = 1.099 mm^{-1}, 14533 reflections measured, 7481 unique (R_{int} = 0.032) which were used in all calculations. The final $wR(F^2)$ was 0.0704 (all data). **3b**: $C_{60}H_{45}N_8O_{0.5}Pd_2$, triclinic, a = 10.3192(14), b = 13.238(2), c = 14.403(2) Å, α = 88.446(2), β = 77.151(2), γ = 75.866(2) °, U = 2374.4(9) Å^3, T = 150(2) K, space group $P1$, Z = 2, μ(Mo-K$_\alpha$) = 0.810 mm^{-1}, 20521 reflections measured, 10455 unique (R_{int} = 0.030) which were used in all calculations. The final $wR(F^2)$ was 0.0964 (all data). CCDC 216097–216099. See http://www.rsc.org/suppdata/cc/b3/b308443d/ for crystallographic data in .cif or other electronic format.

§ θ = Pd1–X–Pd2 angle, where X = bisector of normal between aryl ring centroids;Φ = normal − dihedral angle of PdN_4 and aryl C_6 plane.

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