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Electrochemically Triggered Open and Closed Pacman Bis-metalloporphyrins

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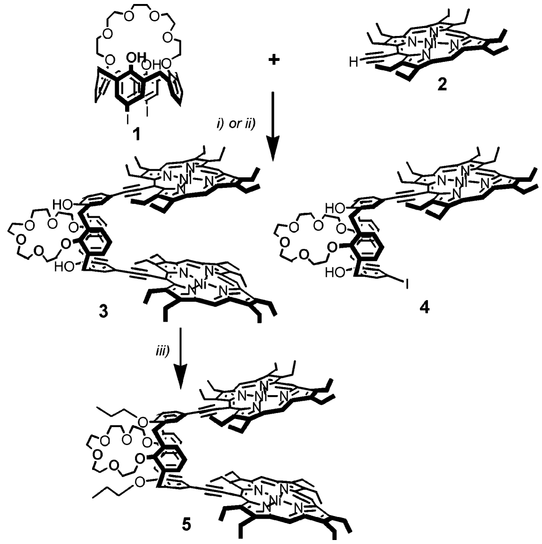
Interest in cofacial bis-porphyrin architectures was originally based on their involvement in photosynthetic events[1] but has taken a new turn toward potential applications in recognition and activation of small substrates,[2,3] sensing,[4] or information storage.[5] In connection with the latter and bistable species, we have recently developed a versatile approach leading to cofacial porphyrins of the Pacman-type in which two tetrapyrrolic macrocycles are maintained in a face-to-face arrangement by a calixarene platform acting as a hinge.[6] After connecting the two macrocycles by coordination of a dabco (diazabicyclooctane) bidentate ligand, bistable Pacman structures were obtained in which a chewing motion could be induced by electrochemistry.[7] Unfortunately, the bistable behavior of the dabco complexes was strongly dependent on their association constants.

We now wish to report the combination of more "stackable" octaethylporphyrins (OEPs) in a cofacial arrangement on the upper rim of a (cone) crown calix[4]arene spacer. In this new generation of Pacman species, the distance separating the calixarene rim and the porphyrin itself has been drastically shortened. Thus, the two macrocycles develop, without the help of a guest, strong through-space interactions that can be detected by cyclic voltammetry. Due to the flexible nature of the calixarene, electrochemically induced molecular motions that are of interest for the development of bistable devices are observed.[8]

The synthetic approach leading to the Pacman bis-porphyrin is depicted in Scheme 1. Established calixarene chemistry[9] led to the diodide intermediate **1**, which was isolated exclusively in cone conformation. The ethynyl derivative of Ni(OEP) **2** was obtained as described by Arnold.[10,11] Sonogashira coupling of **1** with **2** was performed (see Scheme 1 for details), and after removal of the homocoupling butadiyne bis-porphyrin byproduct on SiO_2 chromatography column, the major red−brown band was collected and crystallized from chloroform and methanol to afford fine purple needles of the bis-NiOEP adduct **3** in 25% yield. Monoporphyrin adduct **4** was also obtained in 40% yield. Standard Negishi coupling conditions for the same reaction increased the yield of **3** to 55%. This approach also eliminates the homocoupled diyne species and generates cleaner crude mixtures. It should be noted that, like the diodo starting material, both **3** and **4** display a cone conformation in solution, as observed by ^{1}H NMR. Further alkylation of **3** took place at a rather slow rate to yield the conformationally frozen cone derivative **5** in 55% yield. Both Pacman bis-porphyrins **3** and **5** show a broad Soret band at 418 nm that confirms the cofacial proximity of the chromophores. The blue shift expected for excitonic coupling in these types of architectures is compensated by the forced coplanarity of the calixarene aromatic rings and the porphyrins, extending conjugation through the ethynyl linker for a bathochromic displacement of the absorption maximum (Supporting Information).

Scheme 1 [a]



[a] Conditions: (i) $Pd(PPh_3)_2Cl_2$, (5 mol %), CuI (5 mol %), toluene/NEt_3 (1/1), 60 °C; 3 days, **3** (25%), **4** (40%); (ii) $Pd(PPh_3)_4$ (5 mol %), $ZnBr_2$, 2.4 equiv, THF, NEt_3 (200 equiv), room temperature, 3 days, **3** (55%), **4** (15%); (iii) $BrCH_2CH_2CH_3$ (10 equiv), NaH (10 equiv), THF, reflux, 8 days, **5** (65%).

The two views of the crystal structure of **5** (Figure 1a and 1b) confirm the close packing of the two porphyrins at van der Waals distance, with the shortest interatomic distance of 3.27(2) Å measured between Ni2 and C40.[12] Both porphyrin rings adopt a similar concave shape that results from packing interactions in the cell (Supporting Information). The inter-porphyrin distance is in the range of 3.30−3.40 Å, which is among the shortest reported to date. The stacking of the porphyrin surfaces forces the distortion of the cone calixarene platform that displays pinched aryl groups (dihedral angle 21.5°). The Pacman structure is slightly opened at the porphyrin *meso* positions that bear the ethynyl linkers. The *meso*−*meso* distance (4.04(7) Å) is still significantly short. The latter distance has been frequently used to analyze inter-chromophore interactions in rigidly held Pacman bis-porphyrins.[13] Reported literature values vary from 3.80 Å for a bis-free base etioporphyrin with a biphenylene spacer[14] to 6.33 Å for a dibenzothiophene spacer.[13] The distance of 4.04 Å in **5** is slightly smaller than that observed with a dimethylxanthene spacer for a free base.[15]

In the case of rigid spacers, little variation is expected between the inter-porphyrin distance observed in the solid state and in solution. In our case, due to the flexible nature of the spacer in **5**, attractive or repulsive interactions between the chromophores are expected to cause significant physical changes.

Cyclic voltammetry was used to demonstrate the communication between the two redox-active nickel(II) porphyrins. As shown in Figure 2, 2 one-electron oxidations are observed for NiOEP, used as a reference. The first oxidation generates a $NiOEP^{\bullet+}$ radical

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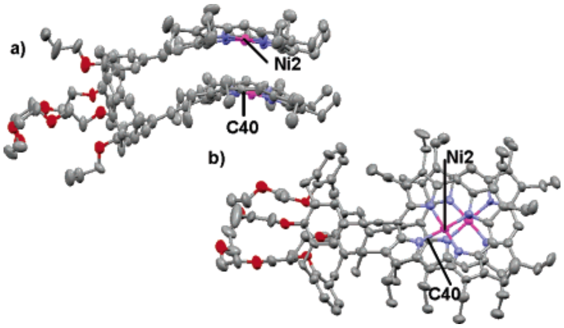

Figure 1. Two side views (a and b 90° rotation of a) of the crystal structure. Solvent molecules (cyclohexane) are omitted for clarity. Distortion of the porphyrin planes is due to packing interactions in the cell (see Supporting Information).

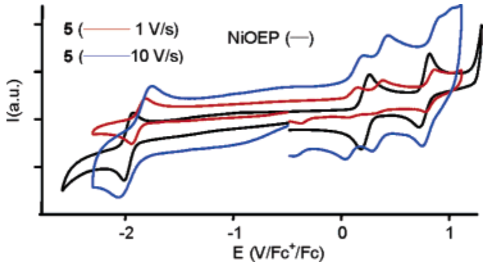

Figure 2. Cyclic voltammograms (1 V·s^{-1}) of **5**, and reference NiOEP at [1.9] and [3.7] × 10^{-4} M, respectively, in CH_2Cl_2 (0.1 M $TBAPF_6$). WE, CE, and RE are glassy carbon disk, Pt wire, and Ag/AgCl, respectively.

cation at +0.280 V/Fc$^+$/Fc that can be further oxidized to the NiOEP^{2+} dication at +0.860 V/Fc$^+$/Fc.

Upon incorporation of the NiOEP moiety in the Pacman structure, the electrochemical formation of the $\mathbf{5}^{2(\bullet+)}$ species is observed as a stepwise process. At 0.140 V/Fc$^+$/Fc, one NiOEP is reversibly oxidized to generate $\mathbf{5}^{(\bullet+)}$ at a potential lower than that in the reference NiOEP, owing to the increased global electronic density in the Pacman scaffold. Due to the presence of strong intermacrocycle interactions and to the proximity of the first NiOEP$^{\bullet+}$, the second NiOEP is then reversibly oxidized at a significantly higher potential (0.380 V/Fc$^+$/Fc) to produce $\mathbf{5}^{2(\bullet+)}$. In this bis(radical cation) state, electrostatic repulsion induces changes in the geometry of the calixarene hinge and forces an increase of the porphyrin−porphyrin distance in the Pacman structure. When sufficiently far apart, the two positive charges do not interact, and the two NiOEP$^{\bullet+}$ moieties behave independently.

Thus, the second oxidation of both porphyrin radical cations to generate $\mathbf{5}^{(4+)}$ is observed as a reversible two-electron process at 0.850 V/Fc$^+$/Fc. At slow scan rates (1 V/s) in CH_2Cl_2, partial deposition of $\mathbf{5}^{2(\bullet+)}$ at the electrode occurs, resulting in a cathodic dissolution signal at ca. −0.3 V/Fc$^+$/Fc. This signal diminishes at fast scan rates and is not observed when only the monocationic $\mathbf{5}^{(\bullet+)}$ is generated or in acetonitrile (Supporting Information). At fast scan rates (10 V/s), all processes become more reversible and the two-electron oxidation at 0.850 V/Fc$^+$/Fc begins to split, suggesting that the rate of the Pacman opening is on a slow (0.5−0.05 s) time scale, probably because of the coupling of the porphyrin motion with the calixarene. This overall oxidation process demonstrates the electrostatic communication between the two macrocycles in **5** and provides a means of switching, in a clapping motion, from a closed to an open Pacman structure under electrochemical stimulus. Partial explanation of the significant splitting of the first oxidation peak may reside in the affinity of NiOEP $^+$ for NiOEP, illustrated by the reported crystal structure of a chemically generated NiOEP/NiOEP $^+$ dimer.[16] In this structure, a mean plane separation of 3.36 Å was found between the two independent tetrapyrrolic macrocycles assembled to form a mixed valence bis-nickel derivative. The two macrocycles are almost eclipsed instead of laterally shifted as in the crystal structure of **5**. It is anticipated that, in **5**, the favorable NiOEP$^{\bullet+}$/NiOEP interactions in the solid state are emphasized in the presence of the calixarene spacer. The Pacman structure renders these interactions persistent in solution, resulting in the significant split of the first oxidation potential. Investigation of the potential use of these Pacman structures for mechanical molecular switches is under progress.

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Supporting Information Available: Experimental details for the coupling reactions, full characterization of **5**, voltammetric studies from 1−10 V·s^{-1}, and cell view of the crystallographic structure of **5**, UV−vis (Soret band) comparison of NiOEP and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) A red−brown platelet of **5** = $C_{120}H_{138}Ni_2N_8O_8 \times 2(C_6H_{12})$, $M_r = 2106.12$, $Z = 4$, with dimensions 0.05 × 0.17 × 0.3 mm has been measured on a Stoe IPDS2 at 130(1) K. At a crystal-to-IP distance of 153 mm, 180 images were exposed for 30 min each. Cell constants are $a = 15.2420(10)$ Å, $b = 12.5285(8)$ Å, $c = 60.386(6)$ Å, $\beta = 96.158(7)°$, and the space group is $P2_1/c$. Numerical absorption correction based on habitus ({001}, {201}, (010), $(1\bar{3}\bar{3})$) yielded transmission factors [0.9086, 0.9798]. Structure solved with the help of SHELXS96 and refined with SHELXL97. Convergence without restraints was to $R_1 = 0.098$ (← geometry within accepted brackets, but data somehow weak, $R_\sigma = 0.1453$ and considerable overlap owing to huge *c* constant). Crystal data and experimental details (excluding structure factors) for **5** have been deposited with the Cambridge Crystallographic Data Center under No. CCDC-285582. Copies of the data may be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (FAX: +44-1223/336-033, e-mail: deposit@ccdc.cam.ac.uk.

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