Models for photosynthetic reaction center: Synthesis, structure and electrochemical properties of a cofacial di-palladium bisporphyrin

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A novel cofacial dipalladium(II) bisporphyrin (Pd₂DEP) of Pacman-type is reported herein. Structural characterization suggests very strong π-π interactions between two planar porphyrins that closely mimic the spatial orientation observed in the so called ‘special pair’. The electrochemical response reveals four consecutive ring-centered oxidations in CH₂Cl₂, indicative of strong through-space electronic communication between two redox-active Pd-porphyrins. At 0.66V, one Pd-porphyrin unit is oxidized to generate a radical cation at a potential much lower than that of monomeric unit (PdOEP), owing to the increased electron density in the bisporphyrin scaffold. However, due to the presence of strong inter-macrocyclic interactions, the second Pd-porphyrin is then oxidized at a significantly higher potential (0.97 V) to produce radical cation species. In the bis(radical cation) state, electrostatic repulsion induces change in the geometry due to flexible spacer which eventually forces an increase in the porphyrin-porphyrin distance. As a result, the second oxidation of both the porphyrin radical cations is observed at 1.42 V as a single reversible two-electron process. The overall oxidation process thus demonstrates strong electrostatic communication between the two macrocycles in Pd₂DEP and also provides a means of switching, in a clapping motion, from a closed to an open Pacman structure under electrochemical stimulus.

Keywords: Porphyrins, Palladium, Porphyrin dimers, Pi-pi interactions, Molecular motions, Electrochemical properties

Photosynthesis is one of the most fundamental processes in nature, since it efficiently converts light energy into chemical energy. The heart of the photosynthetic reaction centre is a pair of chlorophyll molecules, often referred to as the ‘special pair’, which is in face-to-face orientations.¹-² High-resolution X-ray crystallographic studies have revealed the mean plane separations of ~3.5 Å between two chlorophyll molecules in a special pair of the bacteriochlorophylls.² This particular arrangement provides a unique way to place two porphyrin chromophores at a given distance, inducing a through-space energy transfer as the shortest pathway for inter-macrocyclic interactions. Extensive efforts have been devoted towards mimicking the special pair structure and the properties therein in order to understand the importance of its role in the photosynthetic reaction center.³-⁸

The cofacial bisporphyrin architectures also have various potential applications in recognition and activation of small substrates, sensing, information storage and so on.³-⁰ The cooperative interaction between two porphyrin unit plays a crucial role in exerting these functions. The model systems presented here have been designed to closely mimic the spatial orientation observed in the so-called ‘special pair’. Two octaethylporphyrins units have been covalently linked by flexible diethyl pyrrole moiety leading to the formation of cofacial bisporphyrin of Pacman-type, the Pd-complex of which shows strong through-space interactions between porphyrin chromophores. Because of flexible nature of the linker, electrochemically triggered molecular motions that are of interest for the development of bistable devices are also observed.

Materials and Methods

The free base diethlypyrrole bridged bisporphyrin (H₂DEP) has been prepared using a reported procedure.¹¹ Reagents and solvents are purchased from commercial sources and purified by standard procedures before use.

The steady state fluorescence spectra were recorded using Perkin-Elmer LS-55 fluorescence spectrometer. UV-vis spectra were recorded on a Perkin-Elmer UV/vis spectrometer. Elemental (C, H, and N) analyses were performed on CE-440 elemental analyzer. ¹H NMR spectra were recorded on a Jeol 500 MHz instrument. The residual ¹H resonances of the solvents were used as a secondary reference.
Cyclic voltammetric studies were performed on a BAS Epsilon electrochemical workstation in dichloromethane with 0.1 M tetrabutylammonium hexa-fluorophosphate (TBAG) as supporting electrolyte, Ag/AgCl as the reference electrode while the auxiliary electrode was a Pt wire. The concentration of the compounds was in the order of $10^{-3}$ M. The ferrocene/ferrocenium couple occurs at $E_{1/2} = +0.45$ (65) V versus Ag/AgCl under the same experimental conditions.

**Preparation of Pd$_2$DEP**

A saturated solution of palladium acetate (47 mg, 0.21 mmol) in 20 mL methanol was added to 50 mL of CHCl$_3$/NEt$_3$ (20:1) solution of H$_4$DEP (100 mg, 0.083 mmol) in presence of N$_2$ atmosphere and refluxed for 1 h. The progress of the reaction was monitored by TLC as well as UV-vis spectra until no trace of free base bisporphyrin was detected. The resulting solution was evaporated to complete dryness under vacuum and the crude solid was then purified by column chromatography on silica gel using CHCl$_3$ as elutant. Yield: 93 mg (80 %). Anal. (%): Calcd (Found): C, 69.11 (68.92); H, 7.15 (7. 24); N, 8.85 (8.73). UV-vis (dichloromethane) $\lambda_{\text{max}},$ nm ($\varepsilon,$ M$^{-1}$ cm$^{-1}$): 395 (2.2 x 10$^5$), 521 (2.6 x 10$^3$), 555 (3.8 x 10$^4$).

$^1$H NMR (CDCl$_3$, 295 K): 9.72 ($s$, 2H, 10-meso-H); 8.32 ($s$, 4H, 5, 15-meso-H); 6.21 ($s$, 1H, br, NH-pyrrole); 5.64 ($s$, 4H, 37-C$_2$H$_2$); 4.2-2.8 ($m$, 32H, -CH$_2$); 2.65 ($q$, 4H, 40-C$_3$H$_2$); 1.83 ($t$, 12H, -CH$_2$); 1.77 ($t$, 12H, -CH$_3$); 1.45 ($t$, 12H, -CH$_3$); 1.33 ($t$, 12H, -CH$_3$); 1.16 ($t$, 6H, 41-CH$_3$) ppm.

**X-ray structure solution and refinement**

Crystals were coated with light hydrocarbon oil and mounted in the 100 K dinitrogen stream of Bruker Smart Apex CCD diffractometer equipped with a Cryo Industries low-temperature apparatus. Intensity data were collected using graphite-monochromated Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å). The data integration and reduction were processed with SAINT software.$^{12}$ An absorption correction was applied.$^{13}$ Structures were solved by the direct method using SHELXS-97 and were refined on $F^2$ by full-matrix least-squares technique using the SHELXL-97 program package.$^{14}$ Non-hydrogen atoms were refined anisotropically. In the refinement, hydrogens were treated as riding atoms using SHELXL default parameters. No disorder was observed in the X-ray structure of the molecule.

**Results and Discussion**

The free base diethylpyrrole bridged bisporphyrin (H$_4$DEP) has been synthesized using the reported procedure.$^{11}$ To a mixture of CHCl$_3$ and NEt$_3$ (20:1), H$_4$DEP was added with excess of Pd(OAc)$_2$ in methanol and refluxed for an hour under N$_2$ atmosphere, which upon chromatographic purification gave a dark reddish brown solid in excellent yield that has been spectroscopically characterized as Pd$_2$DEP (Scheme 1). UV-vis spectrum has an intense Soret band at 395 nm and two Q bands at 521 and 555 nm in CH$_2$Cl$_2$. X-ray structure of the complex has been reported here while detailed synthetic procedure along with spectral characterizations are given in the Materials and Methods Section (vide supra).

**Crystallographic characterization of Pd$_2$DEP**

The single crystals of the molecule were obtained via slow diffusion of acetonitrile into the chloroform solution of the complex; two perspective views are shown in Fig. 1, while the selected bond distance and angles are given in Table 1. The crystallographic data are collected in Table 2. There is no disorder observed
in the X-ray structure of the molecule. Trends in bond lengths and angles of macrocyclic core structures and side chains agree well with those observed in related bisporphyrins. The complex has two Pd centers, each in a four-coordinate square-planar geometry in which the metal ions are almost in the least-squares plane of C₂₀N₄ porphyrinato core. The average Pd-Np distance is found to be 2.015(5) Å which is a typical distance observed in the X-ray structure of Pd-porphyrins known in the literature. The porphyrin rings are nearly planar with average deviations of 0.12 Å (core-I) and 0.09 Å (core-II), while the interplanar angle of 5.1° is observed between two cores. The bridging meso carbons, namely, C20 and C120, are considerably out of the mean porphyrin plane with C\text{meso}/C\text{meso} nonbonding distance of 5.06 Å; this is presumably to minimize the nonbonded contact between the two rings. Two porphyrin macrocycles are not perfectly cofacial but slipped, intramolecular mean plane separations of 3.80 Å and the lateral shift of 3.00 Å have been observed which suggest strong intramolecular interactions between two cofacial porphyrins. Figure 2 shows the packing diagram of the complex showing π-π interactions between the dimers.

In the special pair of photosynthetic reaction center (PRC) proteins isolated from *Rhodobacter*
spheroides, an interplanar separation of ~3.8 Å was observed along with the interplanar angle of 9.4°. Also, in the case of special pair isolated from Rhodopseudomonas viridis, the interplanar separation and interplanar angle were found to be ~3.3 Å and 11.1° respectively.² Pd₂DEP, however, has a good match with the special pair since it also displays interplanar separations of 3.80 Å and interplanar angle of 5.1°. Thus, π-π interactions between two rings demonstrate a tendency to pull the macrocycles into a degree of overlap, similar to what has been observed in the special pair.

Table 3 compares the geometrical features of all the structurally characterized cofacial di-palladium bisporphyrins reported in the literature along with the Pd₂DEP complex reported here. However, in both Pd₂DPX and Pd₂DPD, the two porphyrin rings are anchored by rigid xanthene (in Pd₂DPX) and dibenzofuran (in Pd₂DPD) pillars, while in Pd₂DEP, it is bridged by a flexible diethyl pyrrole spacer. As a result, the slip angle (38.9°) and the lateral shift (3.00Å) are highest in the present complex (Pd₂DEP), which eventually increases Pd⋯Pd and Cₘ⋯Cₘ non-bonding distances also.

¹H NMR spectral studies

¹H NMR spectrum of the complex was recorded at 298 K in CDCl₃. Figure 3 shows the well-resolved ¹H NMR spectrum of poly-crystalline sample of the complex along with the assignments of each peak, which suggest that the solid state structure retains its identity in solution phase also. The presence of two meso signals in 1:2 intensity ratios suggests that the two porphyrin units are structurally equivalent in solution.

Cyclic voltammetric studies

Electrochemical studies using cyclic voltammetry and differential pulse voltammetry (DPV) have been performed for the complex at 25 °C under nitrogen in CH₂Cl₂ using 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as supporting electrolyte. Two one-electron oxidative responses are observed.

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Table 3—Selected geometrical parameters

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<th>Complex</th>
<th>Pd-Nₚ</th>
<th>Δₑ</th>
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<th>MPS</th>
<th>C₁⋯C₄</th>
<th>Cₘ⋯Cₘ</th>
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<td>0.09</td>
<td>3.97</td>
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<tr>
<td>Pd₂DPD</td>
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<td>5.57</td>
<td>11.9</td>
<td>5.5</td>
<td>0.65</td>
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</table>

ᵃAverage value.ᵇAverage displacement of atoms from the least-square plane of C₂₀N₄ porphyrinato core.ᶜNon-bonding distance between two Pd in a molecule.ᵈAverage distance of two least-squares plane of C₂₀N₄ porphyrinato core.ᵉNon-bonding distance between two macrocyclic center (Cₘ) in a molecule, the macrocyclic center (Cₘ) was calculated as the center of the C₂₀N₄ porphyrinato core for each macrocycle.ᶠNon-bonding distance between two meso carbons that are covalently connected.ᵍAngle between two least-squares planes of C₂₀N₄ porphyrinato core.ʰSlip angle α, calculated as the average angle between the vector joining the two macrocyclic centers and the unit vectors normal to the two macrocyclic the C₂₀N₄ porphyrinato core.ᵢLateral shift, defined as [sin(α) x (Cₘ⋯Cₘ distance)].
observed for PdOEP alone (Fig. 4A); the first oxidation generates a radical cation (PdOEP$^{•+}$) at +0.81 V which is further oxidized to dication (PdOEP$^{2+}$) at +1.55 V. However, when two PdOEP moieties are covalently connected through the diethylpyrrole in Pd$_2$DEP, the electrochemical response reveals four consecutive ring-centered oxidations (Fig. 4B), which are indicative of strong through-space electronic communication between the two cofacial Pd-porphyrins. At 0.66 V, one PdOEP unit is oxidized to generate PdOEP$^{•+}$ at a potential much lower than that of monomeric PdOEP, owing to the increased electron density in the bisporphyrin scaffold. Similar lowering of the first oxidation potential of the special pair of photosynthetic reaction center has also been observed as compared to the monomeric counterpart.  

However, due to the presence of strong intermacrocyclic interactions and also due to close proximity of the first PdOEP$^{•+}$, the second PdOEP is then oxidized at a significantly higher potential (0.97 V) to produce Pd$_2$DEP$^{2•+}$. This overall oxidation process demonstrates the strong electrostatic communication between the two porphyrin macrocycles in Pd$_2$DEP. Partial explanation of the significant splitting of the first oxidation peak resides in the affinity of PdOEP$^{•+}$ for a neutral PdOEP, as illustrated in the crystal structures of mixed valence π-cation radicals such as NiOEP/NiOEP$^{•+}$ and CuOEP/CuOEP$^{•+}$ dimers reported previously.

In the bis(radical cation) state, electrostatic repulsion induces change in the geometry of the highly-flexible diethylpyrrole bridged dipalladium(II) bisporphyrin, Pd$_2$DEP, and eventually forces for increase in the porphyrin-porphyrin distance in the Pacman structure. When the two rings move sufficiently far apart, the two positive charges do not interact with each other, and thus, the two PdOEP moieties in Pd$_2$DEP behave as independent units. As a result, the second oxidation of both porphyrin radical cations to generate Pd$_2$DEP$^{4+}$ is observed as a reversible two-electron process at 1.42 V. This demonstrates the electrochemically triggered open and closed Pacman bisporphyrin as reported here.

Fig. 4—Cyclic voltammogram (CV) and differential pulse voltammograms (DPV) (at 298 K) for (a) PdOEP and (b) Pd$_2$DEP in CH$_2$Cl$_2$ (scan rate 100 mV/s) with 0.1 M tetra(n-butyl) ammonium hexafluorophosphate as supporting electrolyte and Ag/AgCl as reference electrode.

Fig. 5—Comparison of normalized emission spectra (in dichloromethane) of H$_4$DEP (curve 1) and Pd$_2$DEP (curve 2) excited at 546 nm.
In the case of rigid spacers, however, little variation is expected between the inter-porphyrin distance observed in the solid state and in solution. In the case of Pd2DEP, due to the flexible nature of the diethylpyrrole spacer, attractive or repulsive interactions between the chromophores are expected to cause significant physical changes. The overall oxidation process demonstrates the electrostatic communication between two macrocycles in Pd2DEP and provides a means of switching, in a clapping motion, from a closed to an open Pacman structure under electrochemical stimulus.

Photophysical properties
We have also investigated the photophysical properties of dipalladium(II) bisporphyrin through the steady-state fluorescence measurement. Steady state fluorescence spectra of free base bisporphyrin (H2DEP) and dipalladium(II) bisporphyrin (Pd2DEP) are compared in Fig. 5. The quenching of bisporphyrin fluorescence takes place upon metallation of Pd because of heavy metal effect. Pd-porphyrin possesses a very efficient intersystem crossing due to heavy metal effect and therefore the lowest excited state is a long lived triplet state.

Conclusions
A novel cofacial dipalladium(II) bisporphyrin (Pd2DEP) of Pacman-type is reported here which closely mimics the spatial orientation observed in the so-called ‘special pair’. In the X-ray structure of the molecule, two porphyrin macrocycles are slipped with an intramolecular mean plane separation of 3.80 Å and lateral shift of 3.00 Å which suggest very strong π–π interactions between the two planar porphyrins. The cofacial nature in the solid state also retained its identity in solution. The electrochemical response in CH2Cl2 reveals four consecutive ring-centered oxidations, indicative of strong through-space electronic communication between the two redox-active Pd-porphyrins. At 0.66 V, one PdOEP unit is oxidized to generate PdOEP+ at a potential much lower than that of monomeric PdOEP, owing to the increased electron density in the bisporphyrin scaffold. However, due to the presence of strong inter-macrocyclic interactions, the second PdOEP is then oxidized at a significantly higher potential (0.97 V) to produce Pd2DEP2+⁷. In the bis(radical cation) state, electrostatic repulsion induces change in the geometry of Pd2DEP which eventually forces an increase in the porphyrin-porphyrin distance. When two rings move sufficiently far apart, the two PdOEP moieties in Pd2DEP behave as independent moieties and as a result, the second oxidation of both porphyrin radical cations is observed at 1.42 V as a single reversible two-electron process. The overall oxidation process demonstrates strong electrostatic communication between two macrocycles in Pd2DEP and also provides a means of switching, in a clapping motion, from a closed to an open Pacman structure under electrochemical stimulus.

Supplementary Data
CCDC 824651 contains the supplementary crystallographic data of Pd2DEP. These data can be obtained free of charge from the Director, CCDC, 12 Union road, Cambridge, CB2 1EZ, UK or via www.ccdc.cam.ac.uk; Fax.: +44 1223 336 033, Email: deposit@ccdc.cam.ac.uk.

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References
12 SAIN T+ ver. 6.02, (Bruker AXS, Madison, USA) 1999.