Effect of $\beta-\beta'$ fusion on metal ion complexation of porphycene

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Abstract. Complexation of $\beta-\beta'$ fused π -extended porphycene, namely dinaphthoporphycene was carried out successfully with copper(II) and its solid state structure shows a square-type planar N4-coordination core. The photophysical and electrochemical properties of this complex, along with the nickel(II) complex were also investigated. Further, electronic paramagnetic resonance (EPR) analysis of this complex is also reported.

Keywords. Porphycene; porphyrin isomer; $\beta-\beta'$ fused porphycene; π -extended porphycene; porphycene complexation; square-type-coordination.

1. Introduction

Porphycene is the first constitutional isomer of porphyrin, to be synthesized by Vogel in 1986.¹ It could be realized via rearrangement of the meso-methine groups of the porphyrin macrocycle. For this, Vogel employed McMurry coupling of bipyrrrole dialdehyde, which is the most accessible approach towards this class of macrocycles. Although it was of intellectual curiosity at the initial stage, soon it was noticed that porphycene displays unique abilities, owing to its rectangular N4-binding core. For example, as a result of the reduced symmetry in comparison to porphyrin, porphycene displays a higher absorption cross-section in the red region making it a better candidate as a photosensitizer for the photodynamic therapy (PDT) of cancer cells.² Further, non-bonding interactions between the two inner β -substituents of the bipyrrrolic entities make porphycene very sensitive to the nature of the substituents.³ Consequently, the presence of substituents at these inner β -positions makes this macrocycle slightly non-planar, besides making the N4 coordination core more square-type. On the other hand, the absence of these inner β -substituents makes the porphycene more planar. While this β -tetra-substituted macrocycle displays good fluorescence, and more importantly, high singlet oxygen generation quantum yield (an attribute highly desirable for PDT), the β -octa-substituted porphycenes did not fluoresce. The latter pattern of substitution makes the porphycene derivatives emerge as an excellent ligand for metal complexation,⁴ whereas the former tetra-substituted analogue was found difficult to metallate.^{3c,5}

Porphycenes display strong N–H...N hydrogen bonding, compared to porphyrins and hence their tautomerism is of great fundamental interest to researchers.⁶ Upon complexation, porphycenes again display a structural rearrangement with a rectangular type of core with N1–N4 distance becoming shorter than freebases macrocycle (figure 1), where in general N1–N2 distance was the shortest (owing to strong N–H...N hydrogen bonding). Recently, we found porphycenes whose inner $\beta-\beta'$ positions are fused, display large red-shifted absorption spectra compared to the isoindole-derived analogues, with very interesting nonlinear optical (NLO) properties.⁷ For example, the resultant dinaphthoporphycenes exhibit high third order nonlinear optical absorption cross-section, with laser intensity dependent multi-photon absorption phenomena. While at lower laser intensity, these porphycenes and their Ni(II)-derivatives display two-photon absorption (2PA), at higher laser intensity, these compounds showed effective three-photon absorption (3PA), an observation to our knowledge noticed for the first time in the porphyrinoid chemistry.^{7a,8} Further, we noticed owing to $\beta-\beta'$ fusion, complexation of nickel resulted in an unprecedented square-type N4-coordination core, for this otherwise rectangular macrocyclic ligand.^{7a}

In order to explore the generality of the complexation of β -tetra-*i*-propyldinaphthoporphycenes, we report here the complexation of copper (which eluded us earlier), along with its structural analysis in solid state by single crystal XRD analysis and photophysical studies, including the electronic paramagnetic resonance (EPR) analysis and compared these data with that of the nickel(II) complex reported earlier (scheme 1).

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Scheme 1. Synthesis of Cu(II)-complex of dinaphthoporphyrcene.

2. Experimental

2.1 Materials

β -Tetra-*i*-propyldinaphthoporphyrcene and its Ni(II) complex were synthesized by following our earlier reported procedure.^{7a} HPLC grade solvents were used for all analytical measurements. Electrochemical measurement grade tetrabutylammoniumhexafluorophosphate (TBAPF_6) was purchased from Acros Organics and used as received.

2.2 Instrumentation and methods

Electronic absorption spectra of metalloporphyrines were recorded on Perkin Elmer Lambda 35 spectrophotometer. HRMS (High-resolution Mass Spectrometry) data were recorded with Bruker Maxis spectrometer.

Crystallographic data for Cu(II)-complex was collected on Oxford Gemini A Ultra diffractometer with dual sources. $\text{Mo-K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation was used to collect the X-ray reflections of the crystal. Data reduction was performed using CrysAlis^{Pro} 171.33.55 software.⁹ Structures were solved and refined using Olex2-1.0, with anisotropic displacement parameters for non-H atoms. All C–H atoms were fixed geometrically. Empirical absorption correction was done using spherical harmonics, implemented in SCALE3

ABSPACK scaling algorithm. A check of the final CIF file using PLATON¹⁰ did not show any missed symmetry.

Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) measurements were done using Zahner Zennium Electrochemical Workstation and electrodes were purchased from CH Instruments Inc. All measurements were done in dichloromethane under flow of nitrogen and 0.1 M tetrabutylammoniumhexafluorophosphate (TBAPF_6) used as a supporting electrolyte. Platinum disc as working electrode, platinum wire as counter electrode and Ag/AgCl in 1(M) KCl as reference electrode were used. Ferrocenium/Ferrocene, Fc^+/Fc couple was used as external reference for calibration. The redox potentials were referenced vs. saturated calomel electrode, SCE (0.48 V vs SCE for Fc^+/Fc couple). All cyclic voltammetric data were recorded at 50 mV/s scan rate.

EPR measurements were carried out on Bruker EMX microX spectrometer at room temperature.

2.3 Synthesis of Cu(II)-complex of tetra-*i*-propyldinaphthoporphyrcene **2b**

To a solution of freebase tetra-*i*-propyldinaphthoporphyrcene **1** (20 mg, 0.032 mmol) in chloroform (30 mL), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (160 mg, 0.8 mmol) in methanol (1 mL) was added, followed by triethylamine (1 mL, 7.2 mmol).

Figure 1. Schematic diagram of porphyrine showing the general trend of inner N4 core modification upon metallation.

The reaction mixture was refluxed for 12 h under N_2 atmosphere. Solvent was evaporated under reduced pressure and the residue was washed with methanol to remove the excess metal salt. The resultant product was recrystallized from chloroform–hexane (1:5) mixture, to obtain the desired complex as green solid. Yield: 16 mg (72%).

UV/Vis (Chloroform): $\lambda_{\max}$ in nm (ϵ) 272 (103997), 293 (72563), 383 (97380), 386 (45941), 409 (112990), 502 (21535), 536 (21824), 657 (39954), 723 (70167). HR-MS (ESI): m/z calcd. for $C_{44}H_{41}CuN_4$: 688.2627; found $[M+H]^+$ 688.2627.

3. Results and Discussion

3.1 Synthesis and characterization

Complexation of the dinaphthoporphycene **1** was successfully carried out following the standard literature procedure using copper acetate as the metal carrier. Our efforts to insert Zn(II) onto the porphycene macrocycle, though resulted in change in the absorption spectrum, it could not be successfully isolated owing to its labile nature. Similarly, complexation with other metal ions, viz. Ru(II), Sn(II), Pd(II), etc. was always accompanied with considerable change in their corresponding absorption spectra. However, lack of mass data and failure to obtain diffraction grade crystals in those cases did not permit us to comprehend their structure unequivocally. Fortunately, similar to the Ni(II) complex **2a**, we could obtain clear HRMS (High-resolution Mass Spectrometry) data for the copper(II) complex **2b**. Further, the solid state structure of **2b**, could also be unequivocally derived via single crystal XRD. Both the metallo-porphycenes (i.e., Ni(II) and Cu(II) complexes) displayed 4-banded Q-bands, as seen in case of the freebase porphycene, a pattern not reported so far for this class of macrocycles (figure 2). This may be attributed to the rigid framework of these macrocycles having D_{2h} symmetry, owing to the β – β' bipyrrrole fusion. Unlike Ni(II)-complex **2a** (701 nm), Cu(II)porphycene **2b** showed red-shifted Q-band in the lowest energy band (723 nm) compared to its freebase counterpart **1** (718 nm). Further, Cu(II)-complex **2b** also displays higher extinction coefficient than its Ni(II)-counterpart **2a**, which is comparable with the freebase dinaphthoporphycene **1**.^{7a} The ratio between lowest energy Q-band and Soret band also increases upon metallation, with nickel insertion possessing greater enhancement than copper (~ 0.76 vs. ~ 0.62). Complexation did not exert much effect on the Soret band, with both the complexes displaying a band around 409 nm, which indicates that β – β' bipyrrrole fusion perturbs only the

Figure 2. UV-Vis spectra of Ni(II) **2a** and Cu(II)-complex **2b** of dinaphthoporphycene in $CHCl_3$.

frontier orbitals significantly. The higher energy bands around 300 nm are assigned to the naphthalene moiety fused onto the porphycene periphery.

The crystal structure of Cu(II)-complex **2b** of tetra-*i*-propyldinaphthoporphycene was derived via XRD analysis. Pertinent crystallographic data collection and refinement parameter are shown in table 1. Complex **2b** shows slight deviation from planarity compared to previously reported freebase **1** and Ni(II)-complex **2a**,^{7a} as average deviation of nitrogen atoms from the mean porphycene plane (excluding the isopropyl substituents)

Table 1. Crystallographic parameters of Cu(II)-complex **2b**.

Crystal data	2b
Formula unit	$C_{44}H_{40}N_4Cu$
Formula wt.	688.34
Crystal system	Monoclinic
T [K]	298 (2)
a [Å]	15.4483 (15)
b [Å]	6.4601 (5)
c [Å]	19.949 (3)
α [°]	90
β [°]	124.174 (7)
γ [°]	90
Volume [Å ³]	1647.1 (3)
Space group	P21/c
Z'	0.5
Z	2
D_{calc} [g.cm ^{−3}]	1.388
μ /mm ^{−1}	0.703
Reflections collected	6974
Unique reflections	3784
Observed reflections	1234
R(int)	0.0732
R_1 [$I > 2\sigma(I)$]	0.0763
wR_2	0.2343
GOF	0.857

is ± 0.20 Å, where the Cu(II) ion resides in the plane of the porphycene. Probably, this deviation from planarity induces the red shift observed in the absorption spectrum. Ni(II)-complex **2a** showed a much planar core with Ni sitting in the same plane of the porphycene and the nitrogen atoms are slightly less deviated (± 0.12 Å) from the mean porphycene plane.^{7a} As anticipated, similar to the Ni(II)-complex **2a**, Cu(II) insertion led to similar geometrical changes in the N4-core in case of the Cu(II)-complex **2b**. Here the, N1–N2 distance decreases from 2.95 to 2.75 Å upon metallation, whereas the N1–N2' undergoes a concomitant increase from 2.49 to 2.70 Å, thereby resulting in an almost square-type core. This is unprecedented in porphycene chemistry, because all porphycenes exhibit rectangular core upon metallation, irrespective of the geometry of freebase porphycene (whether square or rectangular-type N4-core).^{3–5} In case of complex **2b**, expansion of porphycene core was observed probably owing to larger covalent radius of copper

in comparison to nickel (for nickel complex **2a** N1–N2 and N1–N2' were found to be 2.64 and 2.67 Å, respectively).^{7a} ORTEP (Oak Ridge Thermal Ellipsoid Plot) of metallo-derivative **2b** indicating the N...N distance is shown in figure 3.

Electrochemical analysis of both the freebase and metallo-derivatives of dinaphthoporphycene was carried out using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) (figure 4). All the porphycenes exhibit two reversible one-electron reduction potentials and two one-electron oxidation potentials, except the Ni(II)-complex, which showed three close oxidation potentials (also confirmed by DPV). The freebase porphycene **1** shows the first oxidation and reduction potentials at 0.99 and -0.59 V, respectively, whereas complexation led to facile oxidation of the macrocycles (Ni: 0.87 and Cu: 0.78 V) and harder reduction (Ni: -0.64 and Cu: -0.66 V). Further, when compared to the Ni(II)-dibenzoporphycene reported by D'Souza *et al.* (1.06 and -0.58 V respectively),

Figure 3. ORTEP of Cu(II)-porphycene **2b**: top–front view, bottom–side view. Thermal ellipsoids are scaled to 35% probability level. For clarity, *i*–Pr group has been omitted from side views.

Figure 4. CV (below) and DPV (above) of **1**, **2a** and **2b** in dichloromethane measured at 298 K.

Figure 5. (a) Solid and (b) solution (toluene) state EPR spectra of **2b** at room temperature.

the Ni(II)-dinaphthoporphycene exhibits relatively facile oxidation and harder reduction (0.87 and -0.64 V, respectively).^{4b} However, the presence of two additional oxidation potentials, not noticed only in case of the Ni(II)-dibenzoporphycene among the several Ni(II)-porphycenes investigated by D'Souza *et al.* possibly indicates that these macrocycles behave differently, owing to the presence of additional benzene rings (in the naphtho-analogue **2a**), which may be stabilizing the resultant cation radical and the dications. By simple comparison of the redox potentials between the freebase **1** and the metallo-derivatives, we suppose the oxidation occurs at 1.01 V probably owing to oxidation of Ni(II) to Ni(III). However, only further detailed study can confirm this assignment. Potential difference between the first oxidation and the first reduction, $\Delta E_{1/2}$, corresponding to the electrochemically determined HOMO–LUMO energy gap, gets reduced upon π -extension as resulted from the fusion of aromatic rings at the porphycene $\beta-\beta'$ position (Ni(II)dibenzoporphycene: 1.64 V vs **2a**: 1.58 V).

EPR spectra of Cu(II)-complex **2b** were recorded in both solid and solution states at 298 K (figure 5). In solid state, no hyperfine splitting was observed probably due to exchange interaction. $g_{||}$ (2.1774) was found to be greater than $g_{\perp}$ (2.0469), which is typical of square planar Cu^{2+} complex. In solution (toluene), the complex exhibits hyperfine/super hyperfine splitting. However, splitting at lower magnetic fields is not resolved due to line broadening.

4. Conclusion

A novel metal complex namely, Cu(II)-complex of tetra-*i*-propyldinaphthoporphycene was synthesized and characterized structurally as well as by other spectroscopic means. In solid state rectangular core of the freebase dinaphthoporphycene was found to be transformed into an almost square-type core upon complexation. Similar behaviour was also observed for the analogous Ni(II)-complex. This indicates that probably $\beta-\beta'$ fusion led to structural rigidification of the bipyrrrole moiety and consequently, controls the coordination geometry of the otherwise rectangular N4-core of porphycene ligand. Dinaphthoporphycenes display a square-type coordination complex, an attribute not observed in any other porphycenes reported till date. This possibly indicates a general route for obtaining square-type metalloporphycene complex via $\beta-\beta'$ fusion of their bipyrrrole constituents. Comparative photophysical properties, electrochemical studies of Cu(II)-complex to that of Ni(II) and freebase dinaphthoporphycene were also presented. Further, we have also reported EPR studies of this complex both in solid and solution phases.

Supplementary Information

Crystallographic data (excluding the structure factor) for structures **2b** in this study have been deposited in

the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1030058 (Number is yet to be received). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44(0) 1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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