

SUPPORTING INFORMATION

Synthesis of Complexes 1 and 3:

L₁ was synthesized following a known procedure (G.R. Deviprasad, B. Keshavan, F. D'Souza, *J. Chem. Soc. Perkin Trans I.* **1998**, 3133) with some modification. Demethylation of respective dimethoxy derivatives is achieved by reaction with molten pyrridinium hydrochloride salt at 170°C and is further purified with column chromatography. Methodology adopted for purification is similar to that described by D'souza et.al. New porphyrin derivative, **L**₃ was obtained by reaction of dipyrromethane (prepared *in-situ* by reaction of 2 equivalent of pyrrole and one equivalent of benzaldehyde and was purified by flash chromatography) with equivalent amount of 3,4-dimethoxy benzaldehyde. Purification and demethylation reaction procedures are same as for **L**₁. Zn-metallated form, **L**₂ and **L**₄, were achieved by reacting **L**₁/**L**₃ with excess zinc acetate, using dmf as solvent. Corresponding ruthenium dioxolene complexes were synthesized by reaction of Ru(bpy)₂Cl₂ with **L**₁-**L**₄ in presence of appropriate mole equivalent of KOH in refluxing ethanol under N₂-atmosphere. To achieve complete conversion to semiquinone-species final reaction mixture was treated with equivalent amount (with respect to catechol functionality in **L**₁-**L**₄) of ferrocenium hexafluorophosphate solution at room temperature for 30 mins. Final product was purified by gravity column chromatography (SiO₂ as stationary phase, CH₃CN-aq. NH₄PF₆ solution (98:2, v/v); yield of the respective semiquinone complexes are ~55-63%. Elemental analysis (C, H, N); found (calculated): **1**: 64.0, 3.5, 9.2 (63.8, 3.6, 9.3); **2**: 60.5, 3.4, 8.9 (60.69, 3.34, 8.85); **3**: 56.5, 3.2, 9.2 (56.17, 3.27, 9.38); **4**: 55.0, 3.1, 9.0 (54.44, 2.99, 9.06). Electron spray mass spectral results: **1** 1202 (M⁺, <1%), 1065 (M⁺-PF₆, ~5%); **2** 1266 (M⁺, ~2%), 1120 (M⁺-PF₆, ~8%); **3** 1790 (M⁺, ~5%), 1645 (M⁺-PF₆, <10%); **4** 1710 (M⁺, <1%).

Calculated results for model systems **X1** and **X2**:

Reports on the calculations of porphyrin and its related isomers suggest that UHF method seem to be a better choice over RHF for porphyrin systems. (C. H. Reynolds, *J. Org. Chem.* **1988**, *53*, 6061) Therefore, all geometries have been completely optimized without any symmetry constraints by using UPM3 Hamiltonian. Unrestricted hartree-fock (UHF) PM3 semi-empirical calculations were employed to optimize the geometries of two isomeric model compounds **X1** and **X2**. The possibility of the biradical, being present as singlet- or triplet-form has been considered. Calculated results suggest that the triplet bi-radical **X1** is more stable than **X2** by 18.7 kcal/mol. The relative instability of **X2** form can be attributed to the severe steric interactions caused by the ortho hydrogen atom of quinone ring with the α -hydrogen atom of the pyrrole ring, deviating porphyrin and quinone rings from planarity (Figure 1; Supporting information). Calculation also reveals that the singlet biradical **X2** is less stable than the triplet form by 1.9 kcal/mole.

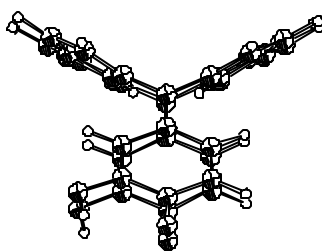


Figure 1 (Supporting information): UPM3 optimized structure of model system **X2**.

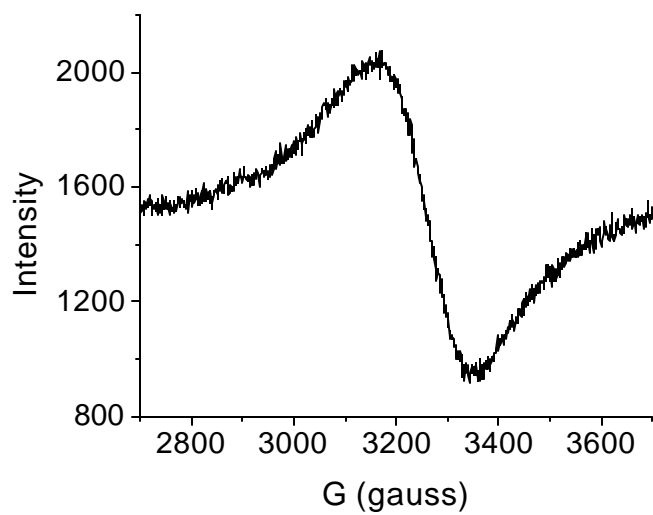


Figure 2 (Supporting information): EPR spectra recorded for complex **3** in powder form at room temperature.

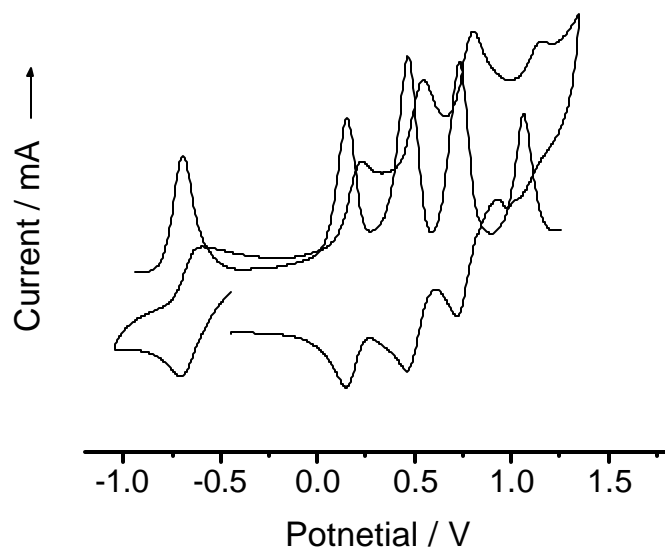


Figure 3 (Supporting information): Cyclic voltammogram and DPV of complex **2** in CH₃CN; Scan rate 200mVs⁻¹, Potential values are express vs. Fc/Fc⁺ couple, used as internal standard as reference.