SUMMARY OF THE FINDINGS of UGC MRP

New Sapphyrin Derivatives for Anion Discrimination"

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The synthesis of a highly electron-rich β-decamethoxysapphyrin and its 27-N-benzyl analogue is reported for the first time. The effects of β-methoxy and 27-N-benzyl substitution on structure, anion binding, absorption, and electrochemical properties were explored in detail. Upon 27-N-benzyl substitution, counter anion-induced structural deformation arises in the diprotonated state, which could be clearly noticed both in solution ^{1}H NMR study and solid-state structural analysis. This type of anion-induced structural deformation is noted for the first time in β-substituted sapphyrins. The anion-binding study of diprotonated salts (2HCl, 2HBr and 2HF) of decamethoxysapphyrin was carried out in methanol by a UV–vis spectroscopic method. The binding studies were carried out with tetrabutylammonium (TBA) salts of fluoride, chloride and bromide ions. The binding constant was measured by the Connor equation, which could nicely fit with 1:1 binding stoichiometry, which was further confirmed by Job's plot analysis. Owing to the increased basicity, protonated decamethoxysapphyrin binds selectively with fluoride ion only, although with reduced affinity (Ka 1.03 × 105 M^{-1}), compared to protonated decaalkylated sapphyrin (Ka 2.8 × 105 M^{-1}). Both β-decamethoxysapphyrin (Φ_Δ, 0.44) and its 27-N-benzyl analogue ((Φ_Δ, 0.42) generate singlet oxygen with moderate yield and, hence, may find application as good photosensitizers. Electrochemical studies of β-decamethoxysapphyrin and its 27-N-benzyl analogue and their perchlorate salts provide important information about electronic properties of both free-base and protonated sapphyrins. We observed three reversible and/or quasi-reversible oxidation potentials and one detectable irreversible reduction potential for free-base sapphyrins, β-decamethoxysapphyrin and its 27-N-benzyl analogue. We could notice only one reduction potential at −1.16 and −1.30 V for β-decamethoxysapphyrin and its 27-N-benzyl analogue, respectively, whereas the oxidation potentials of free-base sapphyrins may be attributed to the formation of π-cation radical, dicationic species, and tricationic species. Most interestingly, protonation leads to the disappearance of first two oxidation potentials of free base sapphyrins and then the appearance of two more reversible reduction potentials. In addition, the third oxidation potential of free base and the oxidation potential of the diprotonated salts are very similar, indicating that probably they originated from the same electrochemical oxidation states. Most interestingly, both ^{1}H NMR studies and solid-state characterization of diprotonated 27-N-benzyl analogue reveal anion induced out-of-plane deformation of the N-benzylpyrrole unit for the first time. This unravels a new way to control the anion binding event in sapphyrins and with appropriate substituents may lead to exciting results. This work has been published as: **Anup Rana, B. Sathish Kumar and Pradeepta K. Panda* *Org. Lett.* 2015, *17*, 3030-3333.**

In addition, two novel stable β-tetraethylporphycenes (TEPos), namely, *trans*-TEP and its unsymmetrical isomer *cis*-TEPo, were synthesized. Both isomers showed interesting photophysical properties. Their corresponding dibromo derivatives were found to form an unprecedented 2:1 supramolecular sandwich complex through π–π stacking interactions, and in addition, only strong C–H···Br–C interactions among the oppositely oriented *cis* isomers led to the formation of 2D arrays in the solid state. As many porphycene derivatives are in clinical trials, their solid state properties based on weak interactions will be of great interest, in particular during the formulation stage. Our dibromoporphycenes are well matched with the porphycenes under clinical study in terms of their photophysical properties. This work has been published as: **Narendra Nath Pati, B Sathish Kumar, Brijesh Chandra, Pradeepta K. Panda* *Eur. J. Org. Chem.* 2017, 741-745.**

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