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In-situ spectroelectrochemistry (EPR, UV–visible) and aggregation behavior of H_2 BDCP and Zn(II)BDCP [BDCP = {5,10,15,20-tetrakis[3,4-(1,4-dioxan)phenyl]porphyrin}$^{2-}$]

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ABSTRACT

In-situ UV–visible and EPR Spectroelectrochemistry of a free base porphyrin, 5,10,15,20-tetrakis[3,4-(1,4-dioxan)phenyl]porphyrin, and its zinc derivative, 5,10,15,20-tetrakis[3,4-(1,4-dioxan)phenyl]porphyrinatozinc(II) were performed. On one-electron oxidation of the free base porphyrin in dichloromethane/0.1 M BuN_4PF_6 using an optically transparent thin layer cell, the initial Soret band retains its intensity and an equally intense new band appears at 453 nm. The initial Q bands disappear, and new bands appear at 516, 555 and 694 nm. At 295 K, it exhibits an isotropic EPR signal with a peak to peak separation of about 6 G and centered at $g = 2.004$. On one-electron oxidation of the zinc-porphyrin in similar conditions, the Soret band loses its intensity, and a new band appears at 466 nm. The in-situ generated one-electron oxidized species exhibits an isotropic EPR signal at 295 K which is centered at $g = 2.0035$. The formations of aggregates/self-assemblies of zinc-porphyrin were monitored by UV–vis spectroscopy, fluorescence imaging by confocal microscope, TEM, SEM and DLS measurements. A tentative mechanism has been also proposed for the generation of different aggregates, with varying size and shape, in water–DMF binary mixtures.

1. Introduction

Porphyrin/metalloporphyrin assemblies are of fundamental importance in various natural systems like photosynthesis due to their critical role in the electron and energy transfer pathways [1,2]. Thus the understanding of the electron and energy transfer pathways of photosynthesis is a major step towards the development of artificial photosynthetic devices [3]. For fabrication of various devices like optical devices, photovoltaic devices, optical switches, and molecular wires, the basic understanding of inter porphyrin/metalloporphyrin electronic coupling is extremely essential [4–10]. The electrochemical and spectroelectrochemical investigation of porphyrin/metalloporphyrin cation/anion radical has also been a long sought area because of their potential role in unraveling many important biological processes [11–14]. All these observations have generated tremendous interest in studying the electronic properties of various porphyrins/metallo-porphyrins [15–18]. Electrochemistry in combination with UV–vis–NIR and EPR spectroelectrochemical measurements are helpful in assigning the electronic properties of porphyrin/metalloporphyrin [19–23]. One important route to prepare the self-assembled metalloporphyrin systems is to exploit the axial coordination of central metal ion with judicious choice of a peripheral substituent that can act as an axial ligand [24–28]. 1,4-Benzodioxan appended peripheral moiety can easily coordinate axially to the central zinc ion of neighboring zinc-porphyrin systems and thus it leads to the formation of various self-assemblies easily. One such *meso-* substituted free base porphyrin and its Zn-derivative were picked up as our test systems for the facile synthesis of self-assemblies. Our work here demonstrates a comparative study between a free base porphyrin and its Zn-derivative and aims at elucidating the electronic structures of the porphyrin/zinc-porphyrin based cation/anion radicals on the basis

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of electrochemical and spectroelectrochemical measurements. The present work describes the synthesis of 5,10,15,20-tetrakis[3,4-(1,4-dioxan)phenyl]porphyrin, **1** and of 5,10,15,20-tetrakis[3,4-(1,4-dioxan)phenyl]porphyrinatozinc(II) complex, **2**, the crystal structure of **1**, and electrochemistry, EPR and UV–vis spectroelectrochemical investigations of **1** and **2**. Structures of the free base porphyrin, **1** and its Zn-derivative, **2** are shown in Fig. 1. The synthesis of free base porphyrin, **1** and its formation of well-ordered colloidal self-assembly have been already reported in the literature [29–31]. However, the crystal structure of **1** has not been reported so far. In addition to the EPR and UV–vis spectroelectrochemical investigations of **1** and **2**, it has been also observed that **2** forms self-assembled systems in DMF-water binary mixture. The absorption spectra, confocal microscope images, TEM, SEM and DLS measurements suggest the formation of *J*-aggregates in case of **2**.

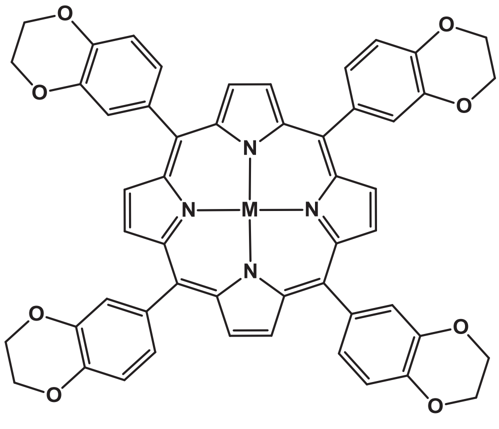
2. Experimental section

2.1. Materials

The precursors pyrrole, 1,4-Benzodioxan-6-carboxaldehyde, DDQ(2,3-Dichloro-5,6-dicyano-1,4-benzoquinone), TBAP (Tetrabutyl ammonium perchlorate) were purchased from Aldrich, USA. Other chemicals were of reagent grade. Hexane and CH_2Cl_2 were distilled from KOH and CaH_2 respectively. For spectroscopy and electrochemical studies HPLC grade solvents were used.

2.2. Physical measurements

UV–vis spectral studies were performed on a Perkin–Elmer LAMBDA-750 spectrophotometer. Emission spectral studies were performed on a Perkin Elmer, LS 55 spectrophotometer using optical cell of 1 cm path length. The fluorescence quantum yields were determined using tetraphenylporphyrin, [TPP] as a reference. Time resolved fluorescence measurements were carried out using a time-correlated single photon counting (TCSPC) spectrometer (Edinburgh, OB 920). The elemental analyses were carried out with a Perkin–Elmer 240C elemental analyzer. GC–EIMS spectra were recorded on a Thermo Scientific ITQ 900 spectrometer. FT–IR spectra were recorded on a Perkin–Elmer spectrophotometer with samples prepared as KBr pellets. The NMR measurements were carried out using a Bruker AVANCE 400 NMR spectrometer. Tetramethylsilane (TMS) was the internal standard. Electrospray mass spectra were recorded on a Bruker Micro TOF– QII mass spectrometer. Cyclic voltammetry measurements were carried out using a CH Instruments model CHI1120A electrochemistry system. A glassy–carbon working electrode, a platinum wire as an auxiliary electrode and a saturated calomel reference electrode (SCE) were used in a three-electrode configuration. Tetrabutyl ammonium perchlorate (TBAP) was the supporting electrolyte (0.1 M) and the concentration of the solution was 10^{-3} M with respect to the complex. The standard reduction potential E^0 was set equal to $0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are anodic and cathodic cyclic voltammetric peak potentials, respectively. The scan rate used was 100 mV s^{-1}. The oxidation processes at the positive side of SCE reference electrode [32] were recorded by using a platinum working electrode; a glassy–carbon working electrode was used for recording the reduction processes. EPR spectra in the X band were recorded with a Bruker System EMX. Simulations of EPR spectra were done using the Simfonia program. UV–vis–NIR absorption spectra were recorded on an Avantes spectrometer system: Ava Light-DH-BAL (light source), AvaSpec-ULS2048 (UV–vis-detector) and AvaSpec-NIR256-2.5TEC (NIR-detector). Spectroelectrochemical measurements were carried out using an optically transparent thin layer electrochemical (OTTLE) cell. The nano-particles were imaged by using a confocal microscope (LSM780, Zeiss, Germany). Transmission electron microscope (TEM) images for size and its distribution were obtained by using a 200 KV Tecnai- 20 G2. TEM images for the samples were obtained by using a bottom mounted MultiScan charge-coupled device (CCD) camera (Model 794, Gatan). The microstructure/morphological features were observed by using a scanning electron microscope (SEM), Hitachi-3400N, Tokyo, Japan.



1 M = 2H

2 M = Zn

Fig. 1. The structures of the free base porphyrin, **1** and Zn-porphyrin, **2**.

2.3. Aggregation preparation methods

The nano-baskets, nano-rings, nano-disk wheels, and nano-rectangles of **2** were synthesized through a solvent mixing method. In a standard protocol, 1–5 mL of water was added in stepwise manner with constant stirring to a 1 mL of DMF solution (2×10^{-6} M) at room temperature (298 K). Then this mixture was shaken vigorously for 5 min. The resulting solution was colloidal in nature. The solution was stable without precipitation for few months. In this study, DMF mole fraction of the DMF and H_2O mixture was varied from ~0.05 to ~0.2. Milli-Q water was used in sample preparation. For TEM measurements, the samples were suspended in a DMF-water binary mixture, and ultrasonic dispersion was performed for 3 min. Subsequently, a drop of the suspension was deposited on a perforated carbon-coated copper grid followed by drying under lamp. For SEM measurements, same dispersed TEM sample was used; it was dried on a glass slide and then thin conduction gold coating was done to reduce the charging effect before inserting into SEM.

2.4. Crystal structure determination

Single crystals of **1** were grown by slow diffusion of a solution of the porphyrin in acetonitrile into benzene, followed by slow evaporation under atmospheric conditions. The crystal data of **1** was collected on a Bruker Kappa APEX II CCD diffractometer at 293 K. Selected data collection parameters and other crystallographic results are summarized in Table 1. All data were corrected for Lorentz polarization and absorption effects. The program package SHELXTL [33] was used for structure solution and full matrix least squares refinement on F^2. Hydrogen atoms were included in the refinement using the riding model. Contributions of H atoms for the water molecules were included but were not fixed. Disordered solvent molecules were taken out using SQUEEZE [34] command in PLATON.