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Sterically demanded unsymmetrical zinc phthalocyanines for dye-sensitized solar cells

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ABSTRACT

Three new sterically demanding unsymmetrical zinc phthalocyanines have been designed and synthesized as sensitizers for dye-sensitized solar cells. All three unsymmetrical phthalocyanines have been completely characterized by elemental analyses, mass spectrometry, FT-IR, ^{1}H NMR, UV–Visible, and fluorescence (steady-state and life-time) spectroscopies as well as electrochemical methods. Photophysical properties (absorption, emission and redox properties) indicate that the LUMO of unsymmetrical phthalocyanines lies above the TiO_2 conduction band and HOMO is below the redox electrolyte. The experimental results are supported by DFT/TD-DFT studies. Electrochemical and *in-situ* spectroelectrochemical studies suggest that the redox reactions belong to the macrocyclic ring-based electron transfer processes. All three unsymmetrical phthalocyanines were tested in DSSC using I^-/I_3^- redox electrolyte system.

1. Introduction

The world is rapidly approaching a precarious environmental state owing to the extensive use of fossil fuels, which may be depleted in the near future. In this regard, solar energy is expected to play a key role in sustainable development [1]. Among the various photovoltaic technologies, dye-sensitized solar cells, (DSSC) have emerged alongside conventional *p*–*n* junction solar cells [2–4]. In a typical DSSC, upon photo excitation, the dye injects an electron into the conduction band of a nanocrystalline film of a wide-band-gap oxide semiconductor, such as titanium dioxide (TiO_2), and is subsequently regenerated back to the ground state by electron donation from a redox couple. Energy conversion efficiencies up to 11.4% have been achieved using Ru(II) polypyridyl complexes as molecular sensitizers [5,6]. However, Ru(II) polypyridyl complexes are expensive to the rarity of the metal in the earth's crust and also they lack strong absorption in the red or near-infrared region (NIR), where the solar flux of photons is still significant, thus limiting the realization of high efficient devices. For this reason, dyes with large π-conjugated systems such as porphyrins and phthalocyanines are receiving considerable attention for sensitization of nanocrystalline TiO_2 in view of their efficient electron transfer process [7–9]. Recently, Grätzel, Diau, and Yeh et al. have reported a DSSC with an incorporated porphyrin dye having a cell performance that achieves with an efficiency of 12.3% [10].

Phthalocyanine (Pc) derivatives are also suitable DSSC sensitizers because of their intense and tunable absorption in the red to NIR, transparency over a large portion of the visible spectrum, and extraordinary thermal as well as photochemical stability [11,12]. However, the efficiencies of DSSC employing phthalocyanines as sensitizers have not been impressive. This is mainly due to the fact that the phthalocyanine molecule has strong tendency to aggregate on the TiO_2 surface and also a lack of directionality of the electron transfer in the excited state. Nazeeruddin and co-workers reported

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an unsymmetrical amphiphilic zinc phthalocyanine (PCH001, *see* Fig. 1) having three bulky *tert*-butyl groups, which minimizes the aggregation and two carboxylic acids in its molecular structure showing an overall conversion efficiency of up to 3.05% [13,14]. Moreover, Mori et al. recently confirmed that the presence of bulky substituents at peripheral positions of phthalocyanine macrocyle, completely suppress aggregation and, therefore achieved high energy conversion efficiency of 4.6% [15]. The carboxyl-functionalized zinc phthalocyanine substituted at the periphery with six 2,6-diphenylphenoxy groups achieved up to a 4.6% conversion efficiency. Recently, Torres and co-workers have extended this concept and introduced more rigid π-conjugated bridges (either $C{=}C$ or $C{\equiv}C$ bond) between the anchoring carboxyl groups and the phthalocyanine macrocycle with an overall conversion of up to 6.13% [16].

In this manuscript, as part of our efforts to investigate further improvement of efficiency of DSSC devices based on phthalocyanine sensitizers, we report the synthesis and photovoltaic characterizations of a series of sterically demanded phthalocyanines (**DMPCH-1**, **DMPCH-2** and **DMPCH-3**) shown in Fig. 1. **DMPCH-1&2** differ in having number of anchoring groups and **DMPCH-3** possesses a different donor moiety. All the sensitizers have been completely characterized by elemental analyses, Mass, ^{1}H NMR, UV–vis and emission spectroscopies (both steady-state and time-resolved), as well as cyclic voltammetry including spectroelectrochemistry. The studied phthalocyanines have also been investigated computationally by means of DFT and TDDFT theories. The introduction of 3,4-dimethoxy phenyl and 2,6-dimethoxy phenyl at the six peripheral positions of the benzene rings of phthalocyanine **DMPCH-1&2** and **DMPCH-3**, respectively, is supposed to cause steric crowding and hence reduce the aggregation, which will afford high power conversion. The structures of three unsymmetrical phthalocyanines are shown in Fig. 1. We have used I^-/I_3^- based redox electrolyte for the fabrication of devices.

2. Experimental

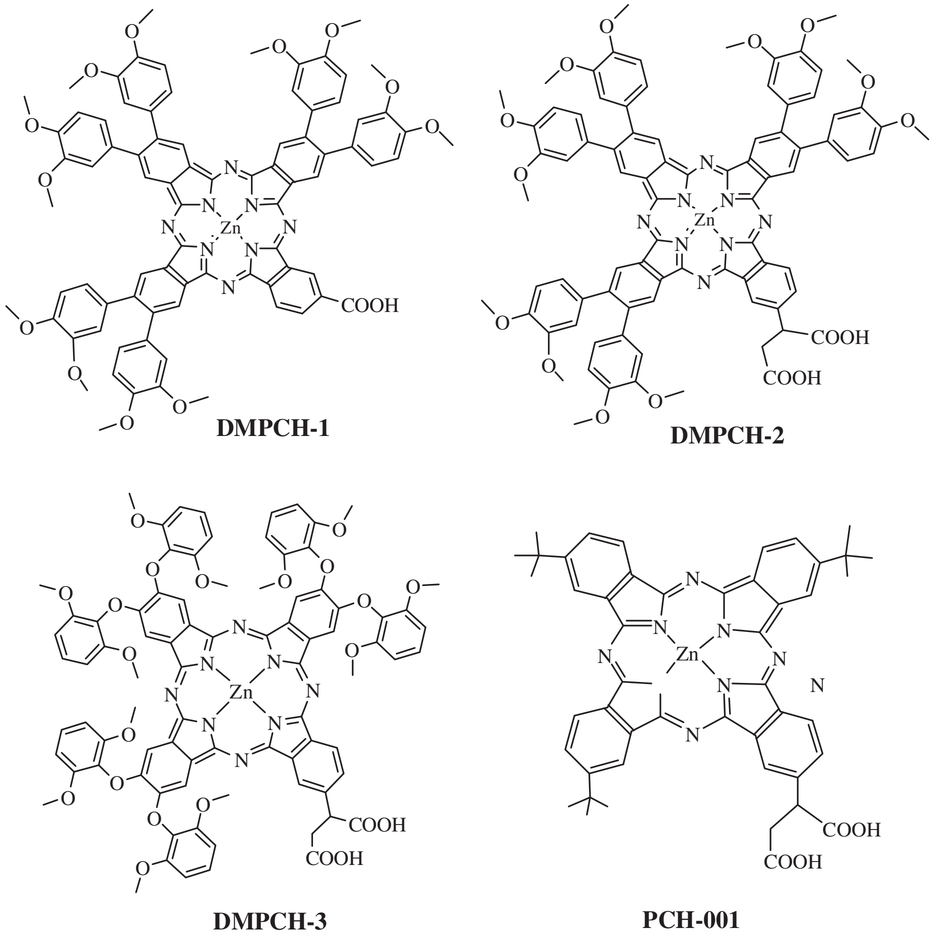
4,5-dichlorophthalnitrile, 3,4-dimethoxy phenyl boronic acid, 2,6-dimethoxy phenol, 1,8-diazabicyclo[5.4.0]undec-7-ene, $Pd(PPh_3)_4$, K_3PO_4, and $Zn(OAc)_2$ are procured from Aldrich and were used as such. The solvents 1,4-dioxane, THF, 1-pentanol, and DMF were obtained from BDH (India) and were purified prior to use [17]. Analytical grade ethanol was also obtained from BDH and was used as such. Column chromatography was performed on Aceme silica gel (60–120).

2.1. Synthesis

3,4-dimethoxy phenyl boronic acid (**1**), 3,4-dicyanobenzoic acid (**3**) and triester phthalonitrile were synthesized as per the literature methods [18,19].

2.1.1. 4,5-Bis(3,4-dimethoxy phenyl) phthalonitrile (2)

Anhydrous 1,4-dioxane (20 mL) was taken in a 100 mL round bottom flask. To this charged with 4,5-dichlorophthalonitrile



DMPCH-1 **DMPCH-2** **DMPCH-3** **PCH-001**

Fig. 1. Molecular structures of unsymmetrical phthalocyanines.