

# Triphenylamine–phthalocyanine based sensitizer for sensitization of nanocrystalline TiO<sub>2</sub> films

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## Abstract

We have designed a new triphenylamine–phthalocyanine based sensitizer (Pc-Org-1) having three bulky triphenylamine groups, which acts as donor and two carboxyl groups, which acts as acceptor as well as servers to graft onto nanocrystalline TiO<sub>2</sub>. The new sensitizer was fully characterized by CHN, Mass, UV–Vis, fluorescence spectroscopies and cyclic voltammetry. The bulky triphenylamine groups are further reducing the aggregation of phthalocyanine macrocycle. DFT studies indicate that HOMO is delocalized  $\pi$ -electron system of phthalocyanine and LUMO is located on carboxyl groups. The new photosensitizer was tested in dye-sensitized solar cells using a durable redox electrolyte and compared its performance with PCH001.

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## 1. Introduction

Nanocrystalline Dye-Sensitized Solar Cells (DSSC) are currently wide spread interest because of low-cost, easy of fabrication upon flexible substrate, short energy pay-back time (<1 year), low sensitivity to temperature changes and environmentally pleasant than the conventional solid-state *p–n* photovoltaic devices (Ito et al., 2007; Loenzmann and Kroon, 2007; O'Regan and Durrant, 2009). Typical DSSC consists of nanocrystalline semiconductor which adsorbs the sensitizer on its surface, a Pt-doped counter electrode and a redox electrolyte of the type  $I^-/I_3^-$ . In these devices sensitizers is one of the key component in achieving high efficiency and durability of the devices. The extensively used charge-transfer sensitizers employed so far in such cells are

*bis*(tetrabutylammonium)*cis*-di(thiocyanato)-*bis*(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II) (the N719 dye) and trithiocyanato 4,4',4''-tricarboxy-2,2':6',2''-terpyridine ruthenium(II) (the black dye), produced solar-energy-to-electricity conversion efficiencies ( $\eta$ ) of up to 11% under AM 1.5 irradiation and stable operation for millions of turnovers (O'Regan and Gratzel, 1991; Nazeeruddin et al., 2001; Gratzel, 2001). Nevertheless, a substantial amount of research work is still needed to fill the gap between today's benchmark conversion efficiency and the Shockley-Queiser limit of  $\eta$  32% predicted for a single junction cell (Frank et al., 2004). To achieve the efficiency in DSSC, the most important component of the device was the sensitizer. Even though, ruthenium(II) polypyridyl complexes are more dominant in DSSC, they are very expensive due to the rarity of the metal and more over absorption maximum of ruthenium complexes are limited at around 550 nm. For a light-harvesting system, the essential requirements are that the

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sensitizing dye absorbs light over a wide wavelength range, preferably one that encompasses the visible spectrum, bind strongly to the semiconductor surface, have a suitably high redox potential for regeneration following excitation and be stable over many years of exposure to sunlight.

Based on the absorption, chemical, photo and thermal stability; and have appropriate redox properties for sensitization of wideband-gap semiconductors e.g.  $\text{TiO}_2$ , phthalocyanines are rendering them attractive for DSSC applications (Thomas, 1990). A few phthalocyanines were tested for DSSC applications; they all have reported power conversion efficiencies around 1% until recently (Deng et al., 1998; Nazeeruddin et al., 1998, 1999; He et al., 2002; Palomares et al., 2004). The low performance of cells incorporating phthalocyanines appears to be due to aggregation, solubility and lack of directionality in the excited state. Recently, our group has designed a few unsymmetrical and unsymmetrical extended- $\pi$  conjugated phthalocyanines based on 'push-pull' concept for DSSC applications (Reddy et al., 2007; Giribabu et al., 2007, 2008, 2009). These phthalocyanines were having either bulky *-tert*-butyl or alkoxy groups to increase the solubility in common organic solvents, minimize aggregation and acts as electron releasing ('push'). It has also two carboxyl groups which act as electron withdrawing ('pull') as well as to graft onto nanocrystalline  $\text{TiO}_2$ . It has shown an overall conversion efficiency of 3.05%. Torres and co-workers have slightly modified the molecular structure of phthalocyanine and reported an efficiency of 3.5% (Cid et al., 2007). Mori et al. have used phenoxy substituents in place of bulky *-tert*-butyl and alkoxy groups in unsymmetrical phthalocyanines (Mori et al., 2010). The presence of phenoxy substituents were further minimizes the aggregation of phthalocyanine macrocycle, as a result the efficiency of DSSC test cell has risen up to 4.6%. However, the efficiency is not sufficient for commercialization of the technology based on phthalocyanine sensitizers.

In order to further improve the efficiency of phthalocyanine based DSSC devices, one has to reduce the aggregation of phthalocyanine macrocycle and improve the absorption of phthalocyanine in 400–600 nm region, where the molar absorption coefficient of the macrocycle is minimum. For this reason, we have designed and synthesized an unsymmetrical phthalocyanine [Pc-Org-1] having three triphenylamine groups and two carboxyl groups in its molecular structure. The more bulky triphenylamine groups are further reducing the aggregation and also improve the absorption of the sensitizer. In this manuscript, we reported the synthesis, characterization and DSSC test cell devices of Pc-Org-1 and comparison of its performance with PCH001 sensitizer. The molecular structure of Pc-Org-1 and PCH001 is shown in Fig. 1.

## 2. Experimental

Analytical reagent grade solvents and reagents were used for the synthesis, and distilled laboratory grade sol-

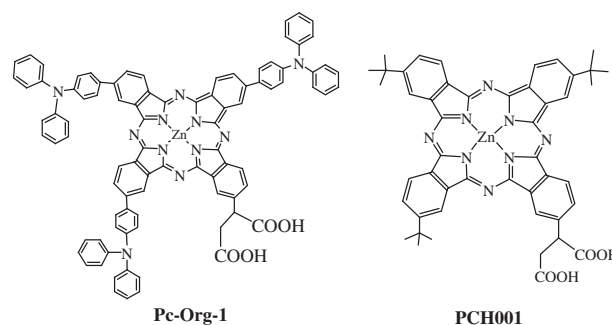


Fig. 1. Molecular structure of Pc-Org-1 & PCH001.

vents were used for chromatography. Milli-Q water was used for synthetic and purification purpose. Absolute ethanol was used for the synthesis. ACME silica gel (100–200 mesh) was used for column chromatography and thin-layer chromatography was performed on Merck-precoated silica gel 60-F<sub>254</sub> plates. Either gravity or flash chromatography was used for compound purification. Where a dual solvent system was used, gradient elution was employed, and the major band was collected. All phthalocyanine reactions were carried out under nitrogen or argon atmosphere using dry degassed solvents, and the apparatus was shielded from ambient light. 4-(1,1,2-Tricarboethoxyethyl) phthalonitrile was synthesized according to the procedure reported in the literature (Sener et al., 2003).

### 2.1. Synthesis

4,4'-Diphenylamino-biphenyl-3,4-dicarbonitrile (**1**): 4-iodo phthalonitrile (254 mg, 1 mmol), N,N'-di-phenylaminophenyl boronic acid (320 mg, 1.1 mmol) and tetrakis (triphenylphosphine) palladium (0) (57 mg, 0.05 mmol) were dissolved in 20 mL of dry toluene-THF mixture. To this aqueous solution of sodium carbonate (53 mg, 0.5 mmol) was added. The resultant reaction mixture was heated at 90 °C under argon atmosphere for 12 h and then the reaction mixture is allowed to cool to room temperature. The reaction mixture was filtered and solvent was evaporated to the solid material. The obtained solid material was subjected to silica gel column chromatography and eluted with hexane-chloroform (1:1) mixture. The solvent front running yellowish color band was collected and solvent was evaporated under reduced pressure to get the desired product in 90% yield. ESI-MS (*m/z*): C<sub>26</sub>H<sub>17</sub>N<sub>3</sub> [371.43]: M<sup>+</sup> 371 (100%). Anal. Calcd. for C<sub>26</sub>H<sub>17</sub>N<sub>3</sub> (371.43): C, 84.07; H, 4.61; N, 11.31. Found C, 84.17; H, 4.70; N, 11.35. IR (KBr): 3058, 2925, 2855, 2226, 1729, 1583, 1487, 1071, 813. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 8.40 (d, 1H, *J* = 4.8 Hz); 8.25 (dd, 2H, *J* = 6.8 Hz); 7.95 (s, 1H); 7.80 (m, 4H); 7.30 (m, 3H); 7.10 (m, 6H).

Triarylaminophenyl monotriester phthalocyanine (**2**): 4-(1,1,2-tricarboethoxyethyl) phthalonitrile (100 mg, 0.269 mmol), **1** (300 mg 0.808 mmol) and catalytic amount of DBU were dissolved in 20 ml of dry 1-Pentanol. The reaction

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