

PHthalOCYANINES FOR MOLECULAR PHOTOVOLTAICS

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Introduction

Phthalocyanines (Pcs) have emerged as promising molecular components of organic solar cells due to their strong absorption in the red/near IR regions of the solar spectrum (between 640 - 700 nm), their suitable photophysical properties, and remarkable chemical and thermal stability (1). Consequently, Pcs have emerged as excellent light harvesting antennas for incorporation into donor-acceptor systems, mainly in connection with fullerenes as an acceptor moiety (2,3). On the other hand the performance of Pcs in dye-sensitized solar cells (DSSCs) strongly depends on their aggregation tendency and directionality in the excited state. The combination of phthalocyanines with other dyes having complementary absorption spectra is an interesting strategy to achieve panchromatic sensitization of TiO₂ films. Phthalocyanine dyes offer an optical window in the visible region that makes these molecules very appealing components of co-sensitizer blends. On the other hand, the use of long-range Forster resonance energy transfer (FRET) has been proposed as a new concept for increasing light harvesting in DSSCs using phthalocyanines in combination with unattached energy relay dyes (ERDs).

In this regard, novel highly conjugated panchromatic phthalocyanine based sensitizers, which bear peripheral triarylamine-terminated bithiophene and hexylbithiophene units, respectively, and bulky substituted phthalocyanines bearing alkynyl carboxy groups as anchoring ligands have been synthesised. Some of these compounds have been tested as sensitizers in DSSCs, giving power conversion efficiencies close to 6%.

Results and Discussion

A convergent synthetic strategy was used for synthesizing 2-Carboxy-9(10),16(17),23(24)-tris-[2-(*N,N*-bis-(9,9-dimethylfluoren-2-yl)-4-aminophenyl)-5,5'-bithiophene]phthalocyaninato Zinc(II) (**1**) based on the key step of preparing a carboxytri(iodo)-ZnPc for subsequent introduction of the peripheral π -conjugated substituents on the carboxy-containing ZnPc. The final Suzuki cross-coupling reactions with the appropriate boronate was performed using standard conditions.

2-Carboxyethynyl-9,10,16,17,23,24-hexakis(2',6'-diphenylphenoxy)-5,28:14,19-diimino-7,12:21,26-dinitrilotetrabenzo[*c, h, m, r*][1,6,11,16]tetraazacycloicosinato-(2⁻)-N²⁹, N³⁰, N³¹, N³² zinc (II) (**2**) was synthesized by means of two consecutive oxidation steps from the corresponding hydroxypropargyl derivative: the reaction with the periodinane derivative IBX in DMSO afforded the corresponding formylethynyl derivative, which was isolated and treated with NaClO₂ in water in the presence of sulfamic acid to yield the target compound. The synthesis of the corresponding mono (hydroxypropargyl) precursor was carried out by Shonogashira coupling between propargylic alcohol and the corresponding monoiodo Pc derivative. The effectiveness of peripheral substituents in suppressing Pc aggregation is confirmed by ¹H-NMR spectroscopy.

The photovoltaic device characteristics of **1** and **2** were measured under standard global AM 1.5 simulated solar conditions. The power conversion efficiency of a **1**-sensitized-cell was 2.65%. The IPCE of **1**-DSSC shows considerable high-energy photons absorption contribution, which is in agreement with absorption spectrum in solution. **2**-sensitized solar cell yielded PCE of 5.5% and 6.1% under 100 (1 sun irradiation) and 9.5 mW/cm², respectively in absence of CDCA (4).

Conclusions

A key compound, carboxytri(iodo) ZnPc has been synthesized and used in a convergent strategy for preparing highly conjugated panchromatic sensitizer **1**, which when tested as dye in dye sensitized solar cells gave power conversion efficiencies close to 3%. The panchromatic response of this dye is because of the complementary absorption in the visible region caused by the π -conjugated bithiophene peripheral substituents and the ZnPc near infrared absorption.

On the other hand **2**-sensitized solar cell yielded PCE of 5.5% and 6.1% under 100 (1 sun irradiation) and 9.5 mW/cm², respectively. The higher efficiency of this dye is due in part to the complete lack of molecular aggregates of this compound on the surface of the nanoparticles of TiO₂, this fact being a consequence of the peripheral substitution of the Pc macrocycle with bulky diphenylphenoxy moieties, as previously demonstrated (5), but mainly to the particular alkynyl carboxy group as an anchoring ligand.

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