



## Design of novel phenanthrocarbazole dyes for efficient applications in dye-sensitized solar cells

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### ABSTRACT

Phenanthrocarbazole (PC)-based organic dye-sensitized solar cells (DSSCs) have been recently reported in experiments with an impressive high power conversion efficiency of over 12%. In this paper we report a computational study of the electronic structures, optical parameters and electron injection properties of a series of five PC dyes and the dye-TiO<sub>2</sub> interfaces. Density functional theory (DFT) and time-dependent DFT (TDDFT) approaches were employed. We show that the incorporation of additional building blocks (indoline, carbazole, triphenylamine, or coumarin) to the PC donor moiety leads to obvious influence on the electronic structures and properties, compared to unitary electron donor PC dye. The binary electron-donor PC based dyes demonstrate better electronic properties and spectroscopic parameters. The calculated injection time of electrons from the excited state of dye to the conduction band of TiO<sub>2</sub> is ideal for DSSC applications. The newly designed coumarin-PC and indoline-PC dyes show desirable energetic, electronic, and spectroscopic parameters for DSSCs. Our results are useful for a better understanding on the design rule of PC based organic dyes for future DSSCs.

### 1. Introduction

The past three decades have witnessed the rapid progress of dye-sensitized solar cells (DSSCs) as clean and sustainable energy with improving power conversion efficiency. More and more attention has been paid to DSSCs, since the first demonstration in 1991 [1], due to the increasingly serious energy crisis and environmental problem.

The DSSC cells are composed of a wide band gap semiconductor (typically TiO<sub>2</sub>) deposited on a transparent conducting substrate, quasi-monolayer of dye sensitizers, and a redox electrolyte. As one of the major components of the DSSCs, the dye sensitizer adsorbs sunlight and plays a significant role for solar energy conversion efficiency. The dyes are chemically bonded to the surface of TiO<sub>2</sub> or other semiconductor. The following properties are required for efficient photosensitizers: (i) intense absorption in the visible-near infrared region; (ii) adsorption firmly on the surface of the TiO<sub>2</sub> or other surface of semiconductor; (iii) the lowest unoccupied molecular orbital (LUMO) of dyes lies above the TiO<sub>2</sub> conduction band edge, in order to guarantee enough thermodynamic driving force for desirable electron injection from the excited state dye to the TiO<sub>2</sub> conduction band edge; (iv) the highest occupied

molecular orbital (HOMO) of dyes lie below the iodide redox potential, to lead to a fast dye regeneration and avoid geminating charge recombination between oxidized dye molecules and photo-injected electrons in the nanocrystalline TiO<sub>2</sub> film; (v) good stabilities for long term cell operation.

Ruthenium polypyridine sensitizers [2] and zinc porphyrin complexes [3] have demonstrated impressive power conversion efficiencies of larger than 11%. However, the ruthenium dye based DSSCs suffer from the limitation of ruthenium resources and the subsequent environmental issues. The zinc porphyrin sensitizers have the disadvantages of low synthesis yield and the highly toxic raw materials used during the preparation.

As possible substituents for the ruthenium dyes, metal-free organic sensitizers have been developed in the past several decades, with desirable advantages of high molar extinction coefficients, low cost, good flexibility in tailoring molecular geometries, and environmental compatibility [4]. Polyaromatic hydrocarbons (PAHs) are composed of multiple aromatic rings with sole carbon and hydrogen atoms. PAHs based compounds have been used as the central block of the donor-accepter organic sensitizers [5]. The delocalization of the extended  $\pi$

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electrons in PAH based dyes contribute to better excited state properties and improved power conversion efficiency [5]. Continuous development of PAH based dyes has brought forth new opportunities for efficient enhancement of novel DSSCs [6]. Among the PAH materials, perylene is an important pigment/dye. Because of the facile preparation, good stabilities, desirable spectral properties and excellent fluorescence quantum yield, perylene dyes have been used as promising candidates for many applications, including DSSCs [7,8].

The polycyclic aromatic hydrocarbon N-annulated perylene (1H-phenanthro[1,10,9,8-cdefg]carbazole, PC) shows high level of  $\pi$ -conjugation and charge delocalization, and it has been used as electron-releasing moiety in dye sensitizers. Experimentally the PC unit has been added to the porphyrin-based dyes as an efficient electron-releasing moiety to enhance the light-harvesting efficiency and the absorption of infrared solar photons [9]. Recently, Wang group has reported a series of PC-based organic dyes with more complicated PAH segments as the central building blocks, [8,10–14] and high-power conversion efficiencies up to 13.0% has been achieved [15].

Currently, density functional theory (DFT) and time-dependent DFT (TDDFT) have been adopted as standard methods to study the ground and excited-state geometries, electronic and spectroscopic properties of some PC dyes [11,13,14]. However, the PC dye-TiO<sub>2</sub> interface has not been investigated so far, probably due to the heavy computational consumption. The structure and electronic properties of dye-TiO<sub>2</sub> surface interface are very important to reveal the basic feature of electron injection from the excited state dye into the conduction band of the semiconductor, which provides crucial guidance for the future optimization of DSSCs.

The aim of this paper is to give theoretical insights into the effect of the electron-donor on the electronic structure, optical properties and electron injection features for the PC-based organic dyes. We will focus on the organic dye monomer -TiO<sub>2</sub> interface. We considered five dyes in total, and the dyes are named in their donors. Specifically, we studied pristine PC (named HW-1 in Wang's paper [14]), triphenylamine-functionalized PC (TPA-PC), phenyl-functionalized PC (named C272 in Wang's paper [8]), indoline-functionalized PC (Indo-PC), and coumarin-functionalized PC (Cou-PC). Dye PC is the reference dye with single electron-donor. The other four dyes involve ancillary electron-donors. Scheme 1 illustrates the molecular structures of the organic dyes considered in this article. The 4-(7-ethynylbenzo[c][1,2,5]thiadiazol-4-yl)

benzoic acid is the electron-acceptor for all the dyes considered in this paper.

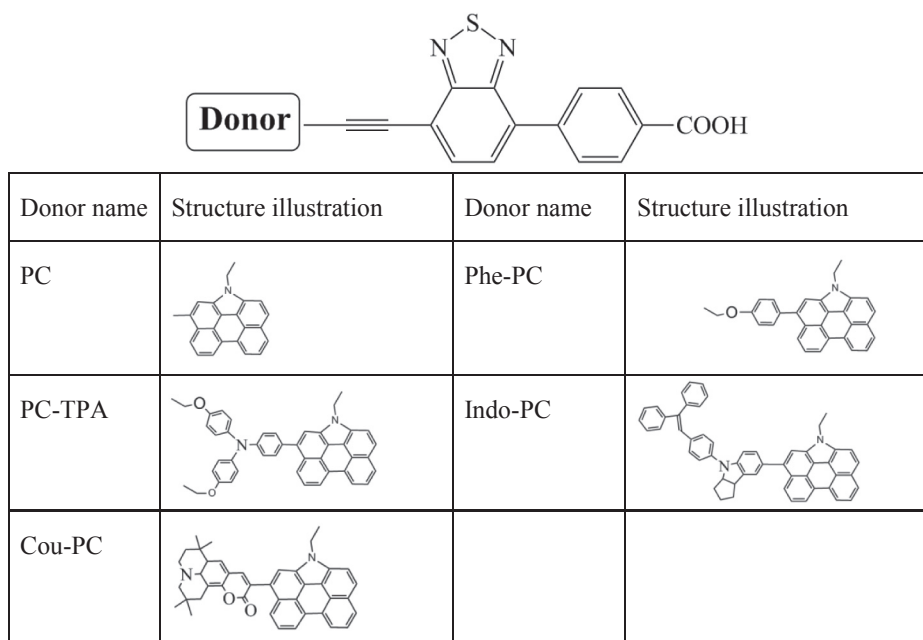
## 2. Computational details

### 2.1. Details of the computation

We optimized the ground state structures of pure dyes by using B3LYP/6-31G(d, p) methods, which has been demonstrated reliable for structural optimizations of organic sensitizers [16–18]. Traditional DFT methods are used to calculate the electronic properties of the dyes and dye-TiO<sub>2</sub> interface. The time-dependent DFT simulation was performed to simulate the optical properties (excitation energies of the lowest excited state, adsorption and emission spectra) of the lowest excited state organic dyes.

We adopt a (TiO<sub>2</sub>)<sub>46</sub> nanocluster model to simulate the TiO<sub>2</sub> surface. The dye-(TiO<sub>2</sub>)<sub>46</sub> model and the DFTB method have been widely used to simulate the geometries of the dye-TiO<sub>2</sub> interacting systems with desirable accuracies and computational efficiencies [17,19]. This cluster model was obtained by appropriately 'cutting' an anatase slab exposing the majority (1 0 1) surface. In the surface of (TiO<sub>2</sub>)<sub>46</sub> nanocluster, there are 3 rows of 5- coordinated (Ti<sup>V</sup>) or 6- coordinated (Ti<sup>VI</sup>) titanium sites. The penta-coordinated surface Ti<sup>V</sup> atoms in the (TiO<sub>2</sub>)<sub>46</sub> nanocluster will interact with the carboxylic oxygen atoms in the organic dye to form new Ti-O bonds. The bidentate adsorption is energetically favored compared to the monodentate mode for some organic dyes, so we only consider the bidentate adsorption mode here.

The self-consistent-charge density-functional tight-binding (SCC-DFTB) method were performed to simulate the structures of the (TiO<sub>2</sub>)<sub>46</sub> nanocluster and the dye-(TiO<sub>2</sub>)<sub>46</sub> interface, as implemented in the DFTB + program package [20]. A comprehensive description of the DFTB method can be found in the literature [20,21]. The carboxylic oxygen atoms of organic dye was originally put almost perpendicularly to the penta-coordinated surface Ti<sup>V</sup> atoms, and then full geometric optimizations were performed. The convergence criterion is 10<sup>-5</sup> electrons for charge and 5 × 10<sup>-4</sup> au for residual forces. The DFTB method has been widely used to simulate the geometries of the dye-TiO<sub>2</sub> interacting systems with desirable accuracies and computational efficiencies [17,18,22,23]. The DFTB optimized dye/(TiO<sub>2</sub>)<sub>46</sub> nanoparticle were followed by single point electronic structure calculations



**Scheme 1.** Molecular structures of the organic dyes considered in this article with different electron-donors.

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