



# Symmetrically substituted phenothiazine as prospective candidate for UV responsive dye sensitized solar cells



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## ABSTRACT

A hybrid layer system consisting of anatase, an N-substituted dithienylated phenothiazine (DTPT) with a carboxylic anchor group as molecular donor– $\pi$ -acceptor-system and poly(3-hexylthiophene) as hole transporting material is studied by means of X-ray and UV-photoelectron spectroscopy and UV/vis spectroscopy. The optoelectronic properties of the DTPT and the energy level alignment at the interface DTPT/TiO<sub>2</sub> enable the design of an UV-responsive hybrid solar cell, which is conceptually presented.

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## 1. Introduction

In modern society, the quality of life of an ever growing population depends on the reliable access to energy. But with the need for energy, responsibility grows to preserve our environment with the help of renewable energy sources. Photovoltaics is still one of the most promising alternatives to traditional energy sources and hybrid bulk heterojunction solar cells are emerging as innovative and cheap antagonists to silicon-based concepts [1,2].

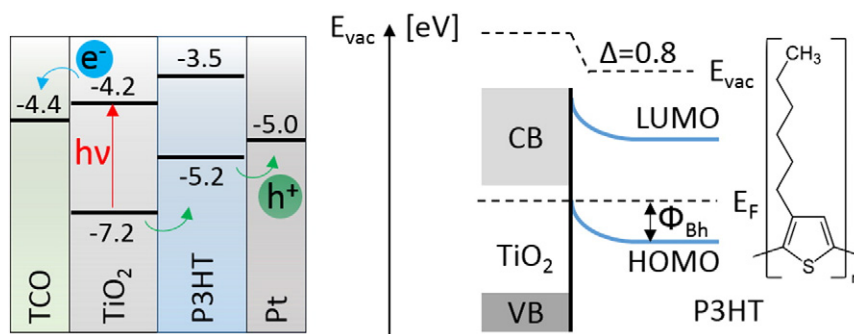
Because of their ability for efficient intramolecular charge transport organic donor– $\pi$ -acceptor systems are well suited for application as photosensitive chromophores. Substituted molecules with phenothiazine moieties have proven themselves as metal-free alternatives to the prominent ruthenium-complexes [3–7]. The redox active and photostable phenothiazine possesses a large photo induced oxidation potential, which catalyzes the generation of free charges through sunlight. An often pursued approach so far was to create spaced donor and acceptor groups by asymmetric substitution of the phenothiazine's aromatic carbon matrix. Recently, a new class of phenothiazine composites was reported [8–10], where two symmetrically substituted thiophene units act as donor and the functionalized substituent, linked to the monomer over

the thiazine's central nitrogen atom, acts as an acceptor. In particular, a nitrogen anchored carboxylic group can chemically bind to TiO<sub>2</sub> nanoparticles and makes the dithienylated 3,8-phenothiazine (DTPT) feasible for application in organic photovoltaics (see Fig. 2 below).

The utilization of the ultraviolet region for the design of solar cells has been scarcely covered so far [11]. The prototype of an UV-responsive hybrid solar cell based on a heterojunction between poly(3-hexylthiophene) (P3HT) and TiO<sub>2</sub>, schematically drawn in Fig. 1, was introduced and discussed by Wu et al. [11]. Encapsulated by a fluorine doped tin oxide anode and a platinum cathode, the process of photogeneration and transport of free electrons is fully accomplished by a nanoparticulate anatase TiO<sub>2</sub> layer, which absorbs in the ultraviolet region, while the polymer P3HT only acts as an organic hole transporting layer, regenerating the metal oxide. The cell marked an energy conversion efficiency of only around 1% under ultraviolet light irradiation of 100 mW cm<sup>-2</sup>. It was shown, that the electronic level alignment of the hole conducting polymer P3HT isn't over all beneficial for the regeneration of the TiO<sub>2</sub>, due to an upward band bending in the organic layer [12]. In addition, the thiophene-based polymer doesn't have a functionalized group, which would allow chemisorption to the coated surface and supports charge separation and transfer [13]. TiO<sub>2</sub> is already a very good n-type semiconductor for UV-light absorption [14,15] and P3HT is a well-known organic hole transporting material with a high hole mobility [16]. So one option left to optimize the charge

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**Fig. 1.** Schematic energy level diagram of the poly(3-hexylthiophene) (P3HT)/TiO<sub>2</sub> hybrid solar cell of Wu et al. [11] (left) and energy level alignment at the P3HT/TiO<sub>2</sub> interface (right), based on [12].  $\Delta$  denotes the surface dipole and  $\Phi_{\text{Bh}}$  the hole injection barrier.

transfer kinetics and photoactivity of this setup is to add an organic intermediate layer, that

- sensitizes the TiO<sub>2</sub>-layer further for light absorption in the UV-region of the solar spectrum
- features molecules that can chemically anchor on the TiO<sub>2</sub> surface
- has a beneficial electronic level alignment at the TiO<sub>2</sub> and P3HT interface.

It will be demonstrated in the following, that due to the investigated sensibility for the near UV and blue region of the solar light spectrum and the good hole conducting properties the DTPT molecule meets the pointed out requirements, making the realization of the concept shown in Fig. 2 feasible: with a transparent conducting oxide as anode, a nanocrystalline anatase TiO<sub>2</sub> layer is sensitized with a monolayer of DTPT, followed by P3HT as hole transporting layer and a gold cathode.

In this context the electronic properties of the components' interfaces were studied by means of X-ray and UV-photoemission (XPS and UPS). UV-Vis spectroscopy was used to determine the light absorption of the sensitized TiO<sub>2</sub>.

## 2. Experimental details

### 2.1. Photoelectron spectroscopy

The photoemission studies were performed in situ in an ultrahigh vacuum (UHV) system with a base pressure below  $2 \times 10^{-8}$  Pa. The XPS and UPS spectra were recorded with a commercial Phoibos 150 MCD9 hemispherical energy analyzer (Specs, Berlin). The employed Mg K<sub>α</sub> radiation (1253.6 eV) and He I radiation (21.2 eV) was provided by standard laboratory excitation sources (XR-50 and UVS-10/35, Leybold). From measuring the 3d5/2 peak of an Ag(111) crystal, the

energy resolution of XPS was estimated to be better than 1 eV and for UPS better than 100 meV estimated from measurements of the Fermi edge. The energy scale was aligned by initial determination of the 4p3/2, 4d5/2, 4f5/2, and 4f7/2 peaks of an Au(111) crystal. The background of the acquired spectra was subtracted using the Shirley method [17] for XPS and the method of Li [18] for UPS. For all spectra satellite-correction was applied. For UPS the sample was biased with -6 V.

### 2.2. UV/vis

The UV/vis-spectra were recorded using a Genesys 10S Bio spectrophotometer (ThermoFisher Scientific, Waltham, USA).

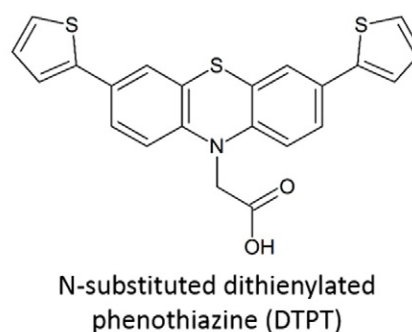
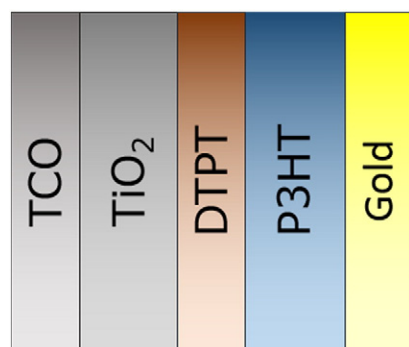
### 2.3. Density functional theory

To obtain the static dipole of the DTPT, geometry optimization for the single molecule was performed with density functional theory DFT (B3LYP) approach using the standard diffusion and polarized 6-31 + G(d,g) basis set. All calculations were made using the Spartan'14 software (Wavefunction Inc., Irvine, USA).

### 2.4. Sample preparation

Nanocrystalline anatase TiO<sub>2</sub> films were prepared using a suspension of the colloidal TiO<sub>2</sub> powder Hombikat II (Sachtleben, Duisburg, Germany) with a nominal particle sizes of 18 nm in ethanol. The suspension was spin-coated with 3000 rpm under ambient conditions on cut out 10 mm × 10 mm plates of a natively oxidized silicon wafer. The milky white thin films were then dried in air at room temperature and annealed at 720 K for 2 h in a muffle furnace to create an n-type doping of the surface through oxygen vacancies. The structural properties of such films are subject to several publications [19–23].

The DTPT was prepared following the synthesis as described in [9,10]. It was then solved in acetone 1 g/10 ml and spin-coated onto the TiO<sub>2</sub>



**Fig. 2.** Schematic concept of a UV-responsive hybrid solar cell consisting of the layers (from left to right): transparent conducting oxide (TCO), anatase TiO<sub>2</sub>, intermediate DTPT layer, P3HT as hole transporting material and gold cathode.

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