

# Effect of the structure of substituents on charge separation in *meso*-tetraphenylporphyrin/TiO<sub>2</sub> bilayers

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## Abstract

The efficiency of photo-induced charge separation in smooth *meso*-tetra(alkylphenyl)porphyrin/TiO<sub>2</sub> bilayers has been investigated using the Time-Resolved Microwave Conductivity (TRMC) technique. Particular attention has been paid to the effect of the structure of the substituents on the charge separation efficiency. The chemical structure of the substituents is found to affect the charge separation efficiency significantly. Ethyl-substituted *meso*-tetraphenylporphyrin/TiO<sub>2</sub> bilayers exhibit a charge separation efficiency of 6.2% at the absorption maximum, which is considerably higher than the efficiencies near 1% or even lower found for the other porphyrin derivatives. The low charge separation efficiencies of these porphyrin/TiO<sub>2</sub> bilayers are discussed in terms of a short exciton diffusion length and/or a low interfacial electron injection yield ( $\phi_{inj}$ ). The short exciton diffusion lengths are related to a short lifetime of the singlet state and a low energy transfer rate between porphyrin molecules due to a low fluorescence rate constant. The results suggest that the value of  $\phi_{inj}$  is affected by the presence of alkyl substituents on the phenyl groups.

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## 1. Introduction

Dye-sensitized solar cells, based on an electron accepting inorganic semiconductor coated with a light absorbing dye, exhibit advantages over silicon-based solar cells such as cheap processing, chromatic flexibility and a practically infinite variety of materials [1]. The wide bandgap inorganic semiconductor such as TiO<sub>2</sub> does not absorb visible light, but is photosensitized by the dye layer. Absorption of a photon by the dye results in the formation of a strongly bound electron–hole pair, also referred to as an exciton. The exciton may migrate to the interface with the semiconductor, where charge separation can occur by injection of an electron from the dye into the conduction band of the semiconductor. The separated electron and hole formed at the interface can either recombine or escape from each other. Application of such a bilayer in a sandwich configuration yields a photovoltaic device in which the charge carriers can be collected by the electrodes.

A major problem in using organic dye layers is the small distance an exciton is able to travel by diffusion. The penetration depth of visible light in organic dye layers is typically 100 nm, while the exciton diffusion length ( $A_E$ ) is usually found to be only a few nanometers [2,3]. The exciton diffusion length depends on the exciton diffusion coefficient ( $D_E$ ) and the exciton lifetime ( $\tau_E$ ) according to:

$$A_E = \sqrt{D_E \tau_E} \quad (1)$$

Because of this short exciton diffusion length, the photoactive part of the dye layer is restricted to a few monolayers near the interface with the semiconductor. Excitons formed further away from the interface decay before reaching the interface by radiationless processes or under emission of a photon. The short exciton diffusion length results in a low charge separation efficiency and hence in a low cell performance.

One way to overcome this problem is the use of nanocrystalline semiconductor films, thus reducing the mean distance excitons need to diffuse to reach the interface [1,4,5]. A performance over 10% has been achieved for a cell based on an interpenetrating network of dye-coated nanocrystalline TiO<sub>2</sub> particles and a hole transporting electrolyte [4]. However, due

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to complications involved in the use of a liquid electrolyte [6], there is currently a great interest in the development of total solid-state organic/inorganic solar cells, for which a maximum performance of 3–4% has been realized so far [7–9].

Another approach to enhance the charge separation efficiency involves an increase of the exciton diffusion length. According to Eq. (1) this can be achieved by a longer exciton lifetime and/or a larger exciton diffusion coefficient.

Porphyrin-based dyes have attracted considerable attention to be applied in solar cells because of their very strong light absorption in the visible part of the solar emission spectrum. Combined with TiO<sub>2</sub> as an electron acceptor, efficient charge separation has been observed [10–14]. Current research on porphyrin/TiO<sub>2</sub> combinations is focussed on improvement of the exciton diffusion length [2,3,15,16], enhancement of the interfacial electron injection yield [16,17], and improvement of the charge transport properties [18–20].

Previous studies have shown that changes in the chemical structure of *meso*-tetraphenylporphyrins strongly affect the charge separation efficiency of these porphyrins in a bilayer with TiO<sub>2</sub>. The introduction of a Pd atom [21] or an octyl substituent at the *para*-positions of the phenyl groups [15] results in an almost 10 times increased charge separation efficiency since the exciton transport in these dye films occurs via the triplet level. Exciton transport via the triplet route, however, is less attractive as compared to transport via the singlet route because of unwanted chemical degradation of the dye [22,23].

The aim of the present work is to provide information about the influence of substituents on the photo-induced charge separation efficiency. Fig. 1 shows the chemical structures of the porphyrins investigated. Differences in charge separation efficiency will be discussed in terms of the exciton diffusion length and the interfacial electron injection yield.

## 2. Experimental

### 2.1. Sample preparation

Thin smooth TiO<sub>2</sub> films with a thickness of ca. 100 nm, prepared by chemical vapor deposition onto 1 × 12 × 25 mm<sup>3</sup> quartz substrates, were purchased from Everest Coatings,

Delft, The Netherlands. *meso*-tetraphenylporphyrin (TPP) was purchased from Porphyrin Systems, Lübeck, Germany. *meso*-tetra(4-methylphenyl)porphyrin (TMePP), *meso*-tetra(4-ethylphenyl)porphyrin (TEtPP), *meso*-tetra(4-tert-butylphenyl)porphyrin (TtBuPP) and *meso*-tetra(2,4,6-trimethylphenyl)porphyrin (TtriMePP) were purchased from Frontier Scientific, Logan, USA. The chemical structures of these porphyrins are shown in Fig. 1. Porphyrin films with a thickness in the order of 30 nm were prepared by spin-coating from the corresponding solution in CHCl<sub>3</sub> (Anhydrous, 99+%, Aldrich) at 2500 rpm under N<sub>2</sub> atmosphere onto either a quartz or a TiO<sub>2</sub> substrate. The thickness of the porphyrin films was determined using a Veeco Dektak 8 Stylus Profiler.

### 2.2. Optical characterization

Optical transmission and reflection spectra were recorded with a Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer. From the transmission and reflection spectra, the optical density (OD) and the fraction of absorbed light ( $F_A$ ) were calculated according to Eqs. (2) and (3), with  $I_T$  the intensity of the transmitted light,  $I_0$  the incident light intensity and  $I_R$  the intensity of the reflected light [14]:

$$OD = -\log\left(\frac{I_T}{I_0 - I_R}\right) \quad (2)$$

$$F_A = 1 - \left(\frac{I_T + I_R}{I_0}\right) \quad (3)$$

The wavelength dependences of OD and  $F_A$  are denoted the “absorption spectrum” and the “attenuation spectrum”, respectively. Steady-state and time-resolved fluorescence spectra were recorded with a Lifespec-ps setup using a 405 nm excitation source (Edinburgh Instruments) and related to the optical attenuation.

### 2.3. TRMC measurements

The Time-Resolved Microwave Conductivity (TRMC) technique and experimental setup have been described previously [3,24]. The porphyrin/TiO<sub>2</sub> bilayers were mounted in an

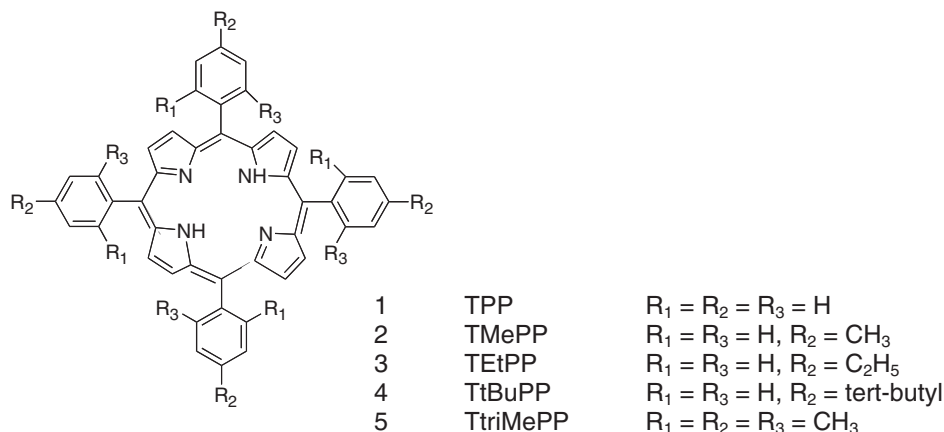


Fig. 1. Chemical structures of the porphyrins investigated.

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