

Manipulation of electron transfer dynamics in zinc phthalocyanine sensitized TiO₂ nanoparticles by modification of the anchoring ligand

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1. Introduction

Photosensitizers are currently a topic of intense scientific research because of their photophysical properties that hold great promise for applications in photodynamic therapy (PDT), blood sterilization, sunlight-activated herbicides and insecticides, biomedical imaging and dye-sensitized solar cells (DSSCs) [1-4]. A photosensitizer should have a high absorption cross section at the wavelength suitable for the specific application and excellent photochemical and thermal stabilities. Amongst the most promising photosensitizers are zinc phthalocyanines (ZnPcs) (Fig 1(a)).

Zinc phthalocyanine (ZnPc) based DSSCs show great potential for efficient light harvesting and light to electrical energy conversion. However, they have exhibited poor device efficiencies (< 1%) for a long time [5]. Only recently efficiencies up to ~5% have been realized [6,7]. An important tool in the development towards higher efficiencies involves replacing a symmetric phthalocyanine by an asymmetric equivalent [7] with one electron pulling group (anchoring onto the TiO₂) and three electron pushing groups (Fig. 1(b)). This suggests that such an asymmetrical push-pull structure supports light-induced forward electron transfer from the ZnPc core into the TiO₂ and prevents back electron transfer. However, the ultrafast photodynamics have not been reported so far.

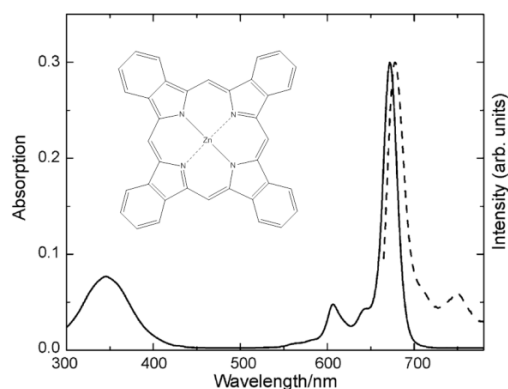


Fig. 1 (a) Absorption and fluorescence spectra of ZnPc in dimethyl sulfoxide (DMSO). Inset shows the molecular structure of ZnPc. (b) Asymmetric push-pull ZnPc photosensitizer with electron transfer directed towards the TiO₂, (c) Chemical structures of the molecules investigated.

2. Experimental Details

Here we report a systematic study to investigate the impact of modification of the anchoring electron-pulling group on the ultrafast dynamics of the forward and back electron transfer using femtosecond pump-probe spectroscopy. The experiments were performed on ZnPc derivatives deposited on TiO₂ substrates (Fig. 1(c)) serving as a model system of a DSSC. Figure 2(a) shows the steady-state absorption and fluorescence spectra of the systems studied. Transient pump-probe data were recorded upon excitation of ZnPc derivatives at 680 nm obtained from a Non-collinear Optical Parametric Amplifier (NOPA). The NOPA was pumped by second harmonic (387 nm) of the fundamental pulses (775 nm, 150 fs) from a commercial 1 KHz regeneratively amplified Ti:Sapphire laser system (CPA-2001, Clark MXR Inc.). Transient dynamics were probed by using a white light continuum (470 nm - 700 nm) generated by focusing a part of the fundamental into a 2 mm sapphire window. Forward electron injection dynamics were probed via evolution of the excited state absorption (ESA) (Fig. 2(b)). Back electron transfer was monitored through the ground state bleach (GSB) recovery (Fig. 2(b)).

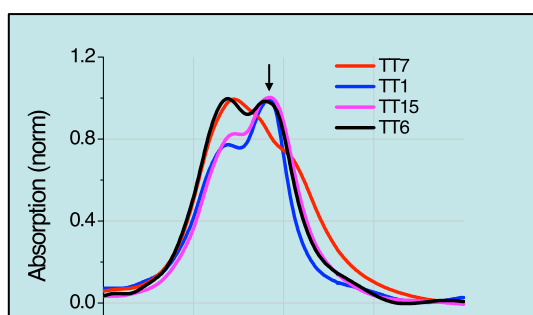


Fig. 2 : (a) Absorption spectra of ZnPc derivatives on TiO₂ substrates (b) Photophysical pathways in a ZnPc sensitized TiO₂ substrate.

3. Conclusions

Our results show that modification of the anchoring group does influence the dynamics of the forward and back electron transfer significantly. In particular, it provides a passive control of the rates of forward and back electron transfer and hence over the resulting DSSC efficiency. These observations are consistent with the reported differences [7] in DSSC efficiencies for these ZnPc derivatives.

4. References

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