Probing the role of anchoring ligands in charge separation dynamics of novel zinc phthalocyanine sensitized TiO_2 films through ultrafast spectroscopy

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Introduction

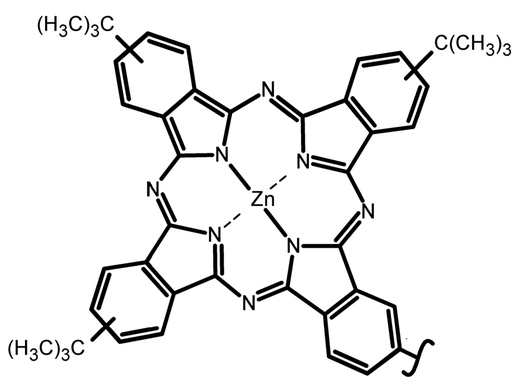
Zinc phthalocyanines (ZnPcs) are attractive photosensitizers in dye-sensitized solar cells (DSSCs) because of their strong absorption in the near-IR and excellent chemical stability. DSSCs based on phthalocyanines, however, have shown poor device efficiencies <1% for a long time[1]. Only recently efficiencies up to ~5% have been realized[2]. An important tool involves replacing a symmetric phthalocyanine by an asymmetric equivalent with one electron pulling group and three electron pushing groups. We have studied the electron transfer and recombination dynamics of ZnPcs with various electron-pulling groups anchored onto nanocrystalline TiO_2 using femtosecond transient absorption.

Conclusions

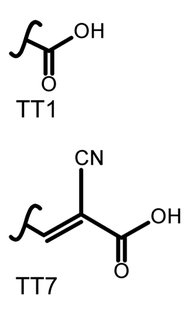
TT1 sensitized TiO_2 shows faster electron injection and slower recombination as compared to TT7, explaining the lower efficiency observed for a DSSC based on the latter (2.55% for TT7 and 3.56% for TT1)[2b]. Apparently the effect of the increased distance between the phthalocyanine core and the TiO_2 for TT7 is greater than the impact of the electronegative CN group, resulting in a slower electron injection. The presence of the electron pulling CN group might however promote the back electron transfer from the TiO_2 to the ZnPc core leading to faster recombination.

Molecular structures

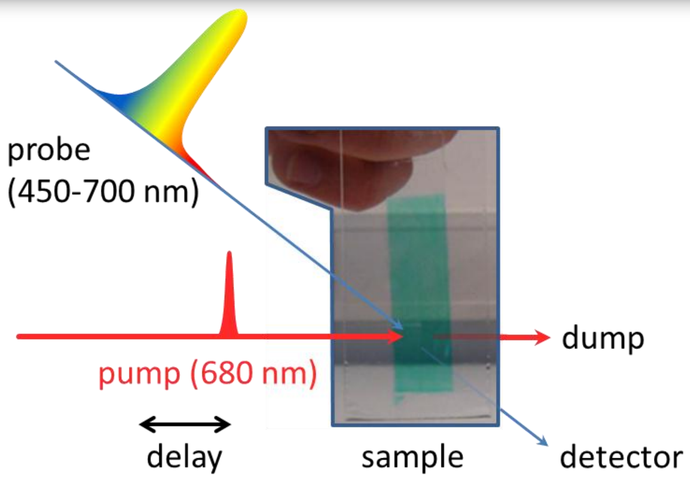
ZnPc core



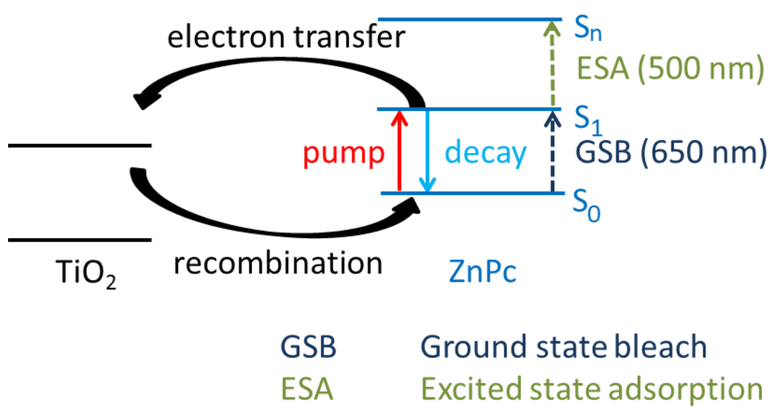
Electron-pulling group



Transient absorption setup

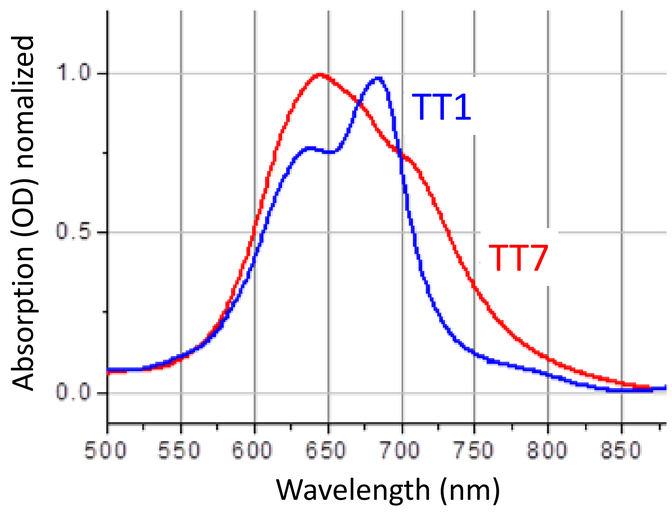


Photophysical pathways

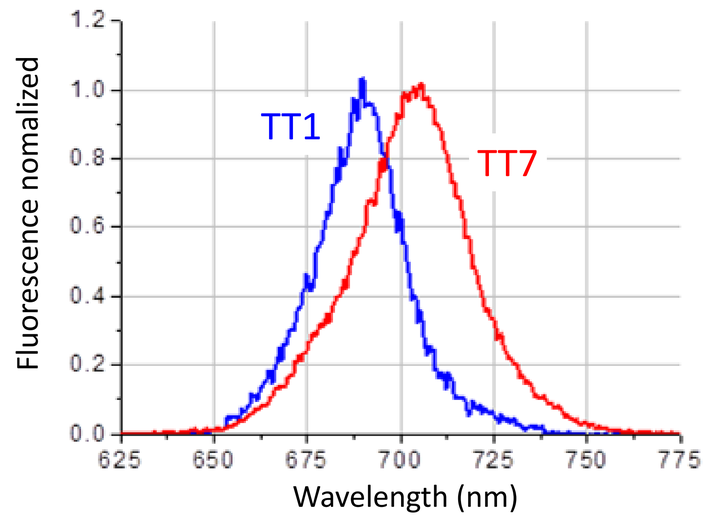


Results

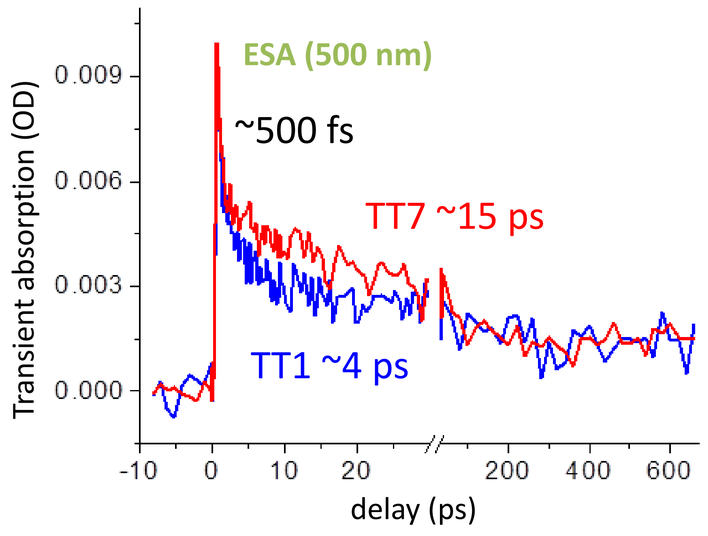
TT1 and TT7 onto TiO_2: Absorption spectra

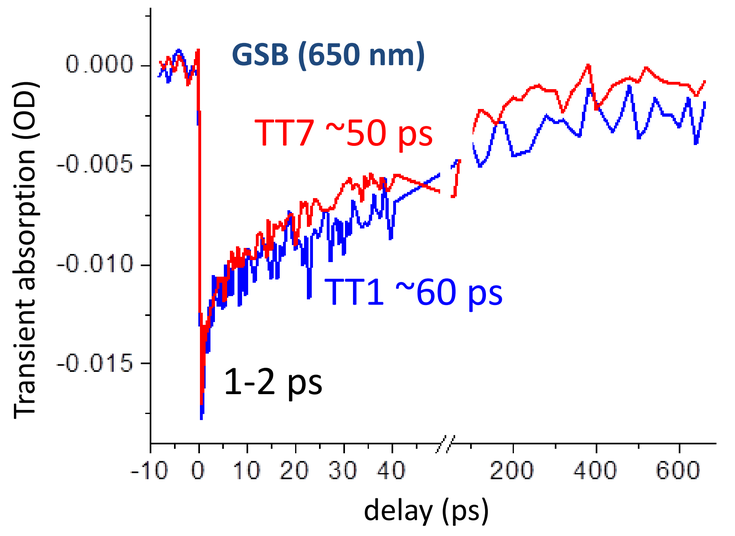


TT1 and TT7 in solution[3]: Fluorescence spectra



TT1 and TT7 onto TiO_2 : ESA (electron transfer) and GSB (recombination) dynamics





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References

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[2] (a) Reddy, P. Y.; Giribabu, L.; Lyness, C.; Snaith, H. J.; Vijaykumar, C.; Chandrasekharam, M.; Lakshmikantam, M.; Yum, J. H.; Kalyanasundaram, K.; Grätzel, M.; Nazeeruddin, M. K. *Angew Chem Int Edit* **2007**, *46*, 373(b) Cid, J. J.; Garcia-Iglesias, M.; Yum, J. H.; Forneli, A.; Albero, J.; Martinez-Ferrero, E.; Vázquez, P.; Grätzel, M.; Nazeeruddin, M. K.; Palomares, E.; Torres, T. *Chem-Eur J* **2009**, *15*, 5130.
[3] Solvent is Ethanol containng Cheno, λ_{exc}= 606 nm.

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