

Supporting Information

Excitation Energy Dependent Charge Separation at Hole-Transporting Dye/TiO₂ Hetero-Interface

Eva L. Unger¹, Tomas Edvinsson¹, Joseph D. Roy-Mayhew², Håkan Rensmo³, Anders Hagfeldt¹, Erik M. J. Johansson¹ and Gerrit Boschloo^{1*}

¹ Department of Chemistry, Uppsala University, Sweden

² Department of Chemical and Biological Engineering, Princeton University, USA

³ Department of Physics, Uppsala University, Sweden

S.1 Electrochemical measurements

The electrochemical oxidation and reduction potentials of **TDCV-TPA** were measured using differential pulse voltammetry (DPV). To distinguish molecular properties from properties of the molecular assembly in the films, measurements were carried out both on the dye in CH₂Cl₂ solution (Figure S1, top) and on films spin-cast on fluorine-doped tin-oxide covered glass (Figure S1, bottom) used as working electrode in the electrochemical setup. The values for the first ($E_{ox,1}$) and second oxidation ($E_{ox,2}$) and reduction peaks ($E_{red,1}$ & $E_{red,2}$) are summarized in Table S1 for TDCV-TPA in solution and measured on a solid film. Measurements in solution were carried out in dichloromethane using TBAPF₆ as supporting electrolyte. Measurements of solid films were carried out using the ionic-liquid. All measurements were referenced vs ferrocene. Voigt fits to the DPV-peaks are included in Figure S1.

It seems that the oxidation potential of **TDCV-TPA** is less affected by the aggregation of the dye molecules into films while the reduction potentials for the dye in solid state occurred at more positive potentials. Compared to the optical band-gaps ΔE_{opt} (Table 1) of the dye in PMMA or solid film, the electrochemical bandgap ΔE_{el} determined in solution is about 0.3 eV lower in energy. Optical excitation leads to bound electron-hole pairs while in electrochemistry separated ions are created. The difference in the bandgap is due to the excitation binding energy and solvation energy of the free ions.

Converted to energy scale, the oxidation potentials were measured to be more negative compared to the results for the dye HOMO measured by PES which is often the case due to different environmental conditions during the measurements.¹ Electrochemical measurements are affected by solvent and polarization effects which is often expressed in terms of the

reorganization energy λ . As TDCV-TPA is a rather polar molecule, differences in reorganization energy are expected to have a large effect on the electronic properties of the molecule and environment.

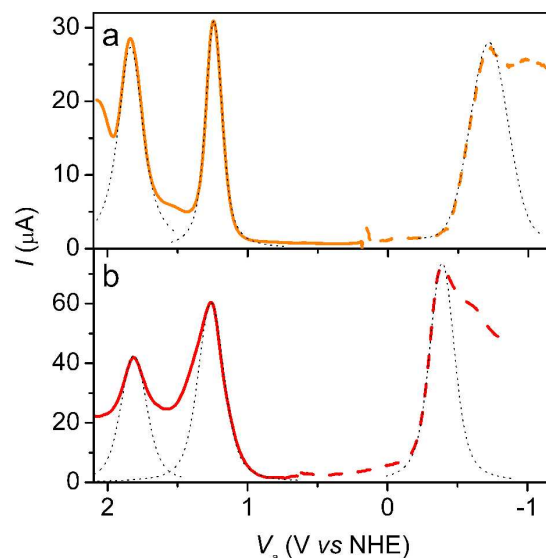


Figure S1: Electrochemical differential pulse voltammetry (DPV) of **a** TDCV-TPA in dichloromethane solution and **b** as a spin-cast film on FTO in ionic liquid; measured using ferrocene as a common reference.

S.2 IR measurements

To investigate the interaction of **TDCV-TPA** with TiO₂ we carried out IR-spectroscopy on meso-porous TiO₂ films sensitized with TDCV-TPA in comparison with the dye in a film and in a KBr matrix (Figure 7). The meso-porous films were used to increase the interfacial area between TDCV-TPA and TiO₂ for the purpose of increasing signal intensity. To investigate the interaction with TiO₂ the dye was left to phy-

isorb from a dilute solution (~ 0.2 mM), briefly rinsed and dried in vacuum prior to the measurements.

FTIR-spectra were recorded of **TDCV-TPA** as a solid film on glass, in a KBr window and adsorbed to mesoporous TiO_2 films (sintered Dyesol NT18 paste ~ 4 μm) on a Nicolet Avatar 370 DTGS spectrometer equipped with a Smart MIRacle™ accessory to measure single reflection ATR.

The signals between 1600 and 1300 cm^{-1} were found to be vibrations originating from the $\text{C}=\text{C}$ bonds in the benzyl and thiophene rings. The signals between 1600 and 1300 can be assigned to vibrations from the TPA and thiophene rings of the molecule (1566 cm^{-1} : ring-stretch; 1437 cm^{-1} : $\text{C}-\text{N}$ str., $\text{C}-\text{H}$ bend, ring str. & thiophene-ring; 1319 cm^{-1} : $\text{C}-\text{H}$ bend, ring str & $\text{C}-\text{N}$ str).²

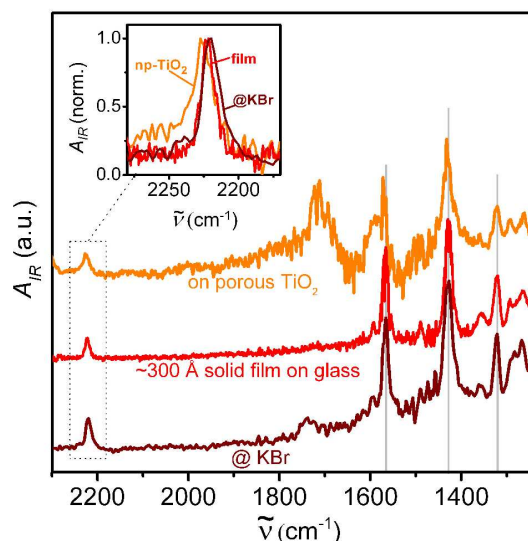


Figure S2: Comparison of FT-IR absorbance spectra of TDCV-TPA under different conditions (indicated in figure). The shift in the CN-signal indicates interaction with the TiO_2 surface (inset).

The $\text{C}\equiv\text{N}$ vibration is shifted to higher wavenumbers by 4 cm^{-1} with respect to the signal measured in a KBr pellet and on **TDCV-TPA** films. In addition, a shoulder in the signal is observed. We interpret this effect to be caused by an interaction between the CN -groups and the titania surface.

REFERENCES

- (1) Andrade, B. W.; Datta, S.; Forrest, S. R.; Djurovich, P.; Polikarpov, E.; Thompson, M. E. *Org. Electronics* **2005**, *6*, 11.
- (2) Reva, I.; Lapinski, L.; Chattopadhyay, N.; Fausto, R. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3844.