Supporting Information

Silicon-based triarylamines as redox mediator in dye-sensitized solar cells

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A. Experimental details and supporting figures/scheme

A1. Materials

All chemicals were of analytical grade and purchased from Sigma Aldrich and are used as receive unless mentioned otherwise. TiO_2 (P25) powder was provided by Degussa Co. Fluorine-doped tin oxide (FTO) conducting glass (Tec 7, 8 Ohm/cm^2) was purchased from Pilkington Co. Ltd. The N3 dye was purchased from Solaronix SA and is used as received. Solutions of N3 were prepared in anhydrous ethanol (Commercial Alcohols Inc., USP). Z907 was purchased from Sigma Aldrich and the solution was prepared by dissolving the crystals in acetonitrile and t-butanol (1:1 v:v).

The so called "compact layer" of TiO_2 on fluorine-doped tin oxide (FTO) conducting glass (10cm × 5cm) and subsequent nanoporous TiO_2 layer were prepared following a literature procedure.[S1]

The thickness of the TiO_2 films was controlled by adjusting the thickness of the adhesive tape spacer and the concentration of the TiO_2 suspension. The thickness of the films is measured with SEM by taking images from the cross section of the films. The thicknesses are mentioned wherever necessary.

A2. Photoelectrochemical experiments

The Pt-coated conducting glass was prepared through sputtering. An adhesive layer of Cr was deposited on the glass piece prior to the sputtering of Pt. The thickness of the sputtered Pt layer was ca. 1.5 μm. After being left at 120°C for 30min in air, the TiO_2 films were directly

soaked in a solution of 0.3mM of N3 or Z907 for 48 hours. Then the films were taken out and were washed with copious amount of dry ethanol. The films were dried under inert atmosphere in the dark before use. Iodide-triiodide (I_3^-/I^-) electrolyte was prepared by making a solution of LiI (0.5M), iodine (0.05M), 4-tert-Butylpyridine (0.1M) using 3-Methyl-2-Oxazolidione and dry acetonitrile (3:7 v:v) as solvents. The HTM solutions were prepared by making a solution of the HTM (0.26M), tertiary-butyl pyridine (TBP) (1.6M), Bis (trifluoromethane) sulfonimide lithium salt (LiTFSI) (2.8×10^{-2}M) in dichloromethane (DCM). The silyl ether HTM (N, N'-diphenyl-1, 4-phenylenediamine, 4-tetra-triisopropylsilyl ether, abbreviated as 1,4 PDATIPS) is denoted as triarylamine **1** and the methyl ether substituted HTM is denoted as triarylamine **2**.

The cells were fabricated by sandwiching the Pt counter electrode with the sensitized TiO_2 films using Kapton tape (7.6μm) as a spacer. The HTM solution was inserted between the electrodes using a micropipette and the cells were sealed properly using the Kapton tapes. In photoelectrochemical (PEC) experiments, a Melles Griot 13 PEM 001 power/energy meter was used to measure the light intensity of the xenon lamp (USHIHO xenon short arc lamp) to be $100mW/cm^2$ at the illuminated surface of the prepared DSSC ($0.581cm^2$) after the incident light was filtered using IR (Edmund Optics) and UV (Andover Corp.) cut-off filters. The photoelectrochemical characterizations of the DSSCs were carried out using radiation of AM 1.5 simulated light (PTI) equipped with a 450-W Xe lamp (short-arc lamp, USHIHO), IR (Edmund Optics) and UV (Andover Corp.) filters. A power meter (13 PEM 001, Melles Griot) was also used to measure the light intensity prior to experiments.For incident photon to current conversion efficiency (IPCE) experiments a monochromator (101/102, PTI) combined with the as-mentioned xenon lamp was used. The light intensity at each specific wavelength was measured with the mentioned power/energy meter and spectrum resembles that of sunlight. The open-circuit photovoltage decay (OCVD) measurements were performed using the same method introduced by Zaban et al.[S2] at an intensity of 100 mW/cm^2. A Voltalab PGZ 402 potentiostat (Radiometer, Copenhagen) was used in PEC, IPCE and OCVD measurements to apply the desired electrochemical wave function. for the IPCE measurements, the wavelength sweep rate was typically 5nm s^{-1}. The monochromator and the potentiostat were triggered simultaneously so that the wavelength and the corresponding current densities were collected using the VoltaMaster 4 solftware as the interface. In all the measurements, the light entered the cell through the anode side where an area of 0.581 cm^2 was illuminated.

A3. UV-Vis spectroscopy

All UV-Vis spectra of solutions were obtained using Ultraspec 4300 pro (Biochrom) UV-Vis instrument. UV-Vis spectroscopy of the sensitized TiO_2 films was performed by using a Perkin-Elmer (Lambda 1050) instrument equipped with an integrating sphere accessory.

To measure the amount of the dyes adsorbed on TiO_2 the procedure described in reference S3 was followed. The dyes were desorbed from the TiO_2 using a slightly alkaline mixture of water and ethanol.

A4. Cell performance characterization

As mentioned values reported in Table 1 and Fig. 1 are for cells that displayed the best behaviors while Table 2 displays the average performance for these cells. Below the data for all the cells tested with triarylamine **1** using N3 and Z907 as sensitizers are reported (Figs. S.1a and S.1b, respectively). Cells prepared with triarylamine **2** (Scheme S.1) displayed very poor performances under illumination, while triarylamines **1** and **2** displayed very similar dark currents (Fig. S.2).
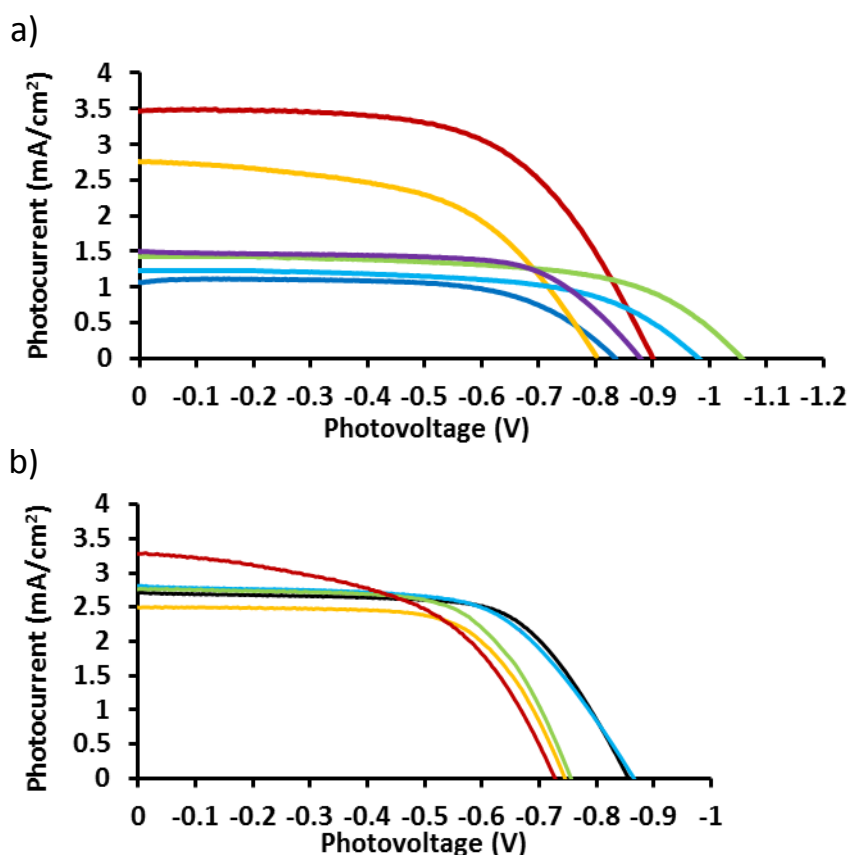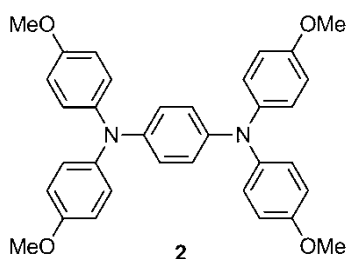
Fig. S.1. Photoelectrochemical J-V curves for all a) N3 and b) Z907 sensitized solar cells fabricated with thin TiO_2 film and using a solution of triarylamine **1** as redox mediator.

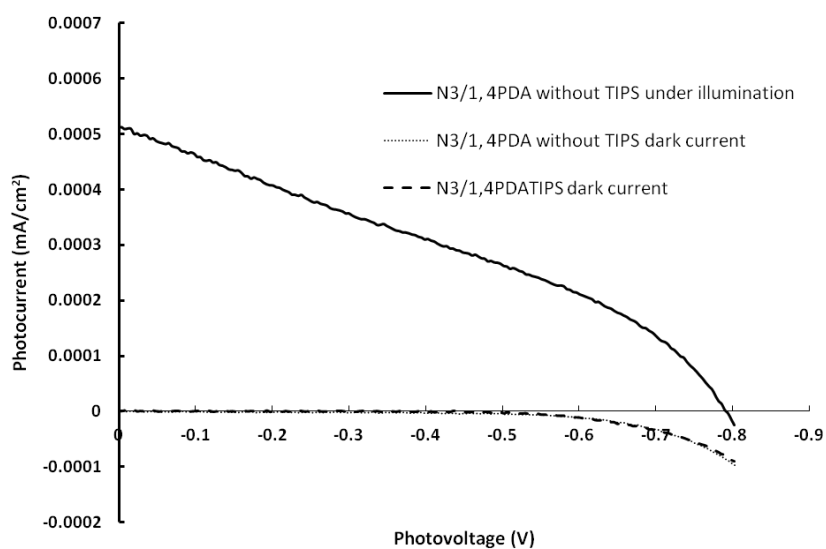**Scheme S.1** Structure of compound **2**.

Fig. S.2. Photoelectrochemical J-V curve for N3 sensitized solar cells fabricated with thin TiO_2 film and using a solution of triarylamine **2** (solid line). Also shown in this graph is the dark current for two N3 sensitized TiO_2 cells using solutions of triarylamines **1** (dash line) and **2** (dotted line). The dark current for both HTMs are identical.

A.5. DFT Calculations

Density functional theory calculations were performed using Sparten '06 for windows. Geometry optimizations were carried out using the Becke-Lee-Yang-Parr exchange correlation functionwith a 6-31G(D) basis set.[S4]

Table S.1 Calculated HOMO and LUMO energy levels for triarylamines **1** and **2**.

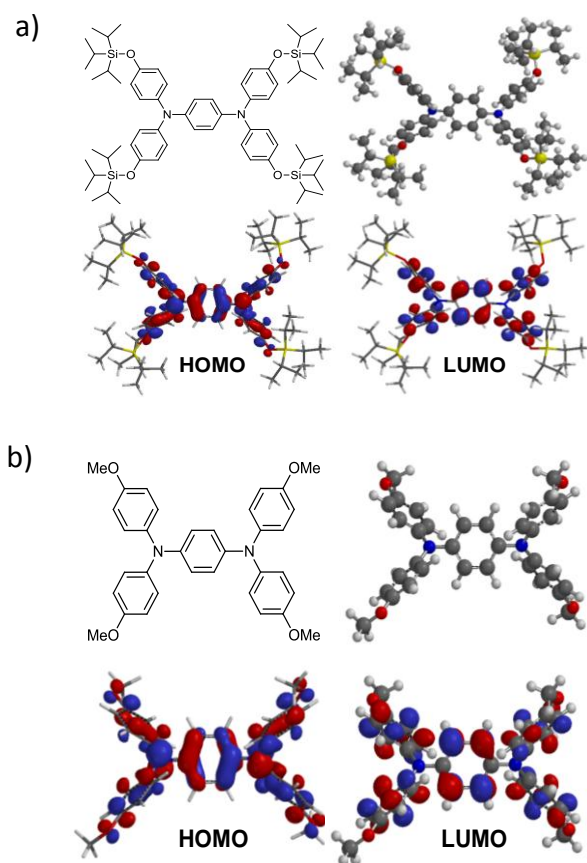| Compound	Calculated HOMO (eV)	Calculated LUMO (eV)
1	-4.32	-0.39
2	-4.24	-0.32

Fig. S.3. Optimized geometry of triarylamines a) **1** and b) **2** as calculated by DFT with predicted HOMO and LUMOs shown.

B. *Effect of hydrolysis on the performance of triarylamine 1.*

In order ensure that the performance of our HTMs was not related to the presence of some hydrolysis products. The effect of hydrolysis was monitored as follows: a 0.26 M solution of triarylamine **1** or **2** was prepared in dichloromethane (DCM). 0.5mL of this solution was transferred into a glass vial and 2mL of 0.1M HCl was added. The mixture was shaken for ca. 15 minutes and then HCl layer was decanted. A fresh portion of the same HCl solution was then added to the vial and again shaken for ca. 15 minutes. After the aqueous solution was decanted, the HTM solution was kept in a sealed glass vial for further use. In order to compare the TLC of the resultant solution to that of the non-hydrolyzed compounds, TLC were performed with a solvent mixture of chloroform and ethylacetate (9:2 v:v). Evidence of hydrolysis was detected from TLC after the first cycle of exposure to HCl.

The solutions of the hydrolyzed compounds were then prepared as it was described for non-hydrolyzed alternatives.
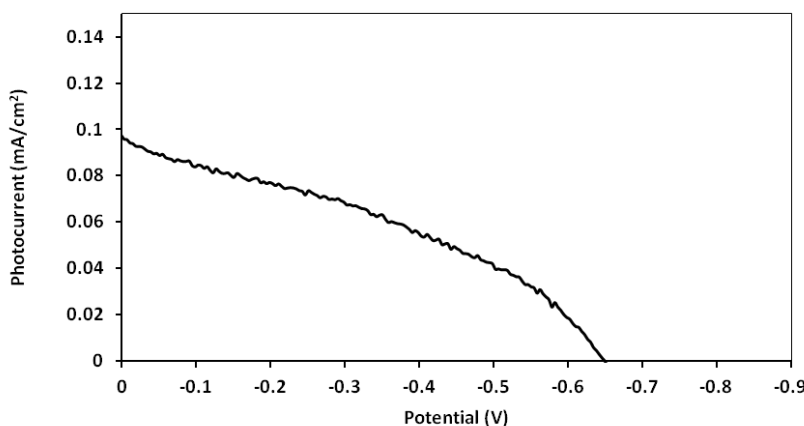

Fig.S.4. Photoelectrochemical i-V curves for N3 sensitized solar cells fabricated with thin TiO_2 film and using a solution of **1** after hydrolysis (see text for experimental conditions).

C. *Determination of the lifetime (τ_n) of the injected electrons*

According to Eq. S.1, IPCE values are mainly dependent on three factors, i.e., light harvesting efficiency (LHE), electron injection efficiency (φ_{inj}) and charge collection efficiency (η_c) where λ is the desired wavelength.[S5]

$$IPCE(\lambda) = LHE(\lambda)\ \varphi_{inj}\eta_c \qquad\qquad\qquad Eq.\ (S.1)$$

The low IPCE values obtained for the cells with triarylamine **1**, can be due to inefficient electron injection or charge collection. In order to better evaluate the loss mechanisms in cells with triarylamine **1**, open-circuit photovoltage decay (OCVD) were employed to understand these losses. As discussed previously, recombination of electrons and holes are caused by shorter diffusion length of electrons and poor pore-filling in the TiO_2 layer. According to Bisquert *et al.*[S6], OCVD measurements are informative in describing the abundance and mechanisms of recombination of electrons and their lifetime in DSSCs. This technique is a simple and powerful tool to compare the lifetime (τ_n) of the injected electrons in DSSCs with different components and structures. In these measurements, the V_{oc} decay was followed for cells with different redox mediators and TiO_2 film thicknesses. This rate of decay is a direct indication of how fast the recombination processes take place when using triarylamine **1** as redox mediator.

Fig.S.5 shows the V_{oc} decays curves for cells fabricated with triarylamine **1** and I_3^-/I^- when the TiO_2 is sensitised with N3 and Z907 (Fig. S.5a) and S.5b), respectively). The cells fabricated with triarylamine **1** have a very fast V_{oc} decay upon cutting off the illumination, in comparison to the cells prepared with I_3^-/I^-. This suggests slower recombination for the I_3^-/I^- electrolyte. Therefore, the recombination of electrons from the CB of TiO_2 back to the redox mediator, is faster on our HTM than the ordinary I_3^-/I^- electrolyte.[S7,S8] This result is in harmony with a "shorter diffusion length" of the electrons in triarylamine **1**.
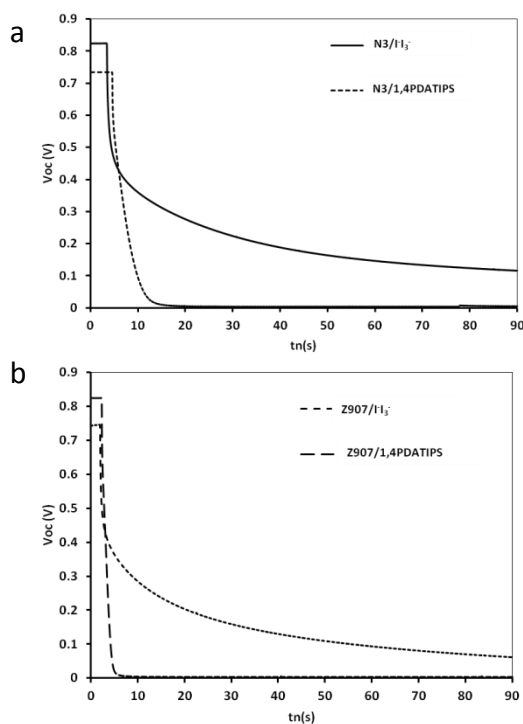
Figure S.5. Comparison of the OCVD of a) N3 and b) Z907 sensitized solar cells prepared using triarylamine **1** and I_3^-/I^-.

The lifetime (τ_n) versus V_{oc} were calculated and are reported for both N3 (Fig. 3) and for Z907 (Fig.S.6) below.[S2, S7] The data for both dyes from these measurements is almost identical and suggest much faster recombination from CB of TiO_2 back to the redox mediator when triarylamine **1** is used versus the I_3^-/I^- electrolyte.
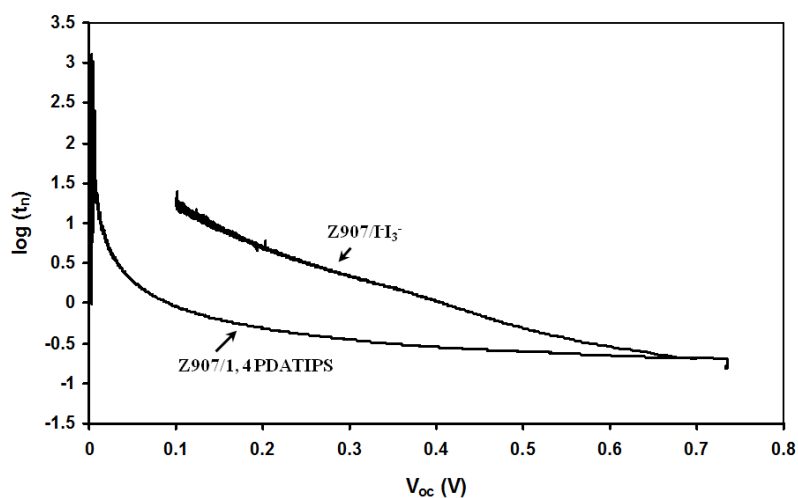

Fig.S.6. Lifetime (τ_n) versus V_{oc} plots derived from corresponding open circuit voltage potential decays (see Fig.S.5b OCVD data) for Z907 sensitized TiO_2 in contact with triarylamine **1** and I_3^-/I^- as redox mediators.

References

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