

Cite this: *J. Mater. Chem.*, 2011, **21**, 1693

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## COMMUNICATION

Co-sensitized DSCs: dye selection criteria for optimized device  $V_{oc}$  and efficiency†John N. Clifford,<sup>a</sup> Amparo Forneli,<sup>a</sup> Huajie Chen,<sup>b</sup> Tomas Torres,<sup>c</sup> Songting Tan<sup>b</sup> and Emilio Palomares<sup>\*ad</sup>

Received 27th October 2010, Accepted 2nd December 2010

DOI: 10.1039/c0jm03661g

Co-sensitization of nanocrystalline  $\text{TiO}_2$  with the organic dye **D2** and the zinc phthalocyanine dye **TT1** improves light harvesting,  $J_{sc}$  and efficiency of DSC devices. However, the  $V_{oc}$  of the co-sensitized cell is markedly inferior ( $\sim 130$  mV) when compared to the reference device made with **D2** only. We discuss the implications of our results with regard to selection criteria for dyes for co-sensitized DSCs.

It is hoped that photovoltaics will make a significant contribution to the renewable energy sector in the coming years. Dye sensitized solar cells (DSCs)<sup>1,2</sup> are currently the leading challenger to the silicon cell, with efficiencies of 11% recorded with  $\text{Ru}(\text{II})$  polypyridyls<sup>3,4</sup> and porphyrins<sup>5</sup> and 10% with donor-( $\pi$ -bridge)-acceptor organic dyes.<sup>6</sup> This technology is not only attractive due to the encouraging efficiencies observed but also because it is based on low cost materials indicating lower production costs, especially when compared to silicon cells.

Among the many ways to optimize DSC efficiency is to maximize the light-harvesting capacity of the cell. This can be achieved through sensitization of the  $\text{TiO}_2$  electrode with panchromatic dyes which have broad absorption bands in the UV-Visible and Near-IR which better match the solar spectrum.<sup>7,8</sup> Another method is to co-sensitize the metal oxide with more than one dye sensitizer as has been demonstrated on many occasions.<sup>9–13</sup> Our own co-sensitization studies have shown the possibility of improving light-harvesting with a subsequent improvement in the cell efficiency.<sup>11,12</sup>

Concerning the light-induced processes occurring at the  $\text{TiO}_2$ /dye/electrolyte interface, co-sensitization adds an extra degree of complexity as the possibility of dye-dye electron and/or energy transfer must be considered. Indeed, in a previous study we took advantage of such inter-dye processes to construct a hole-transfer cascade by sensitizing  $\text{TiO}_2$  with two layers of two different organic

dyes separated by  $\text{Al}_2\text{O}_3$ .<sup>11</sup> The  $\text{Al}_2\text{O}_3$  allowed more than one monolayer of dye to be adsorbed onto the  $\text{TiO}_2$  film and furthermore increased the charge separation distance between electrons in the  $\text{TiO}_2$  and dye cations on the film as holes were channeled to the outer layer of dye. Other studies have shown that if there is strong overlap of the absorption spectrum of one dye with the emission spectrum of the second dye, co-sensitization can result in efficient Förster Resonance Energy Transfer (FRET) between the two resulting in an improvement in both light-harvesting and efficiency.<sup>14</sup>

In the present communication we investigate the charge transfer processes occurring in co-sensitized DSCs including inter-dye charge transfer processes and moreover we discuss the importance of these findings with regard to selection criteria for dyes for optimized DSCs. The dyes used in this study were the organic dye **D2** and the zinc phthalocyanine dye **TT1**. Organic dyes and dyes with strong absorbance in the Near-IR such as phthalocyanines are good candidates as sensitizers in DSCs for many reasons (*e.g.* high molar extinction coefficients).<sup>15</sup> Their structures and absorption spectra in solution are shown in Fig. 1 and both are discussed in more detail elsewhere.<sup>16,17</sup> These dyes leave a large gap in the UV-Visible and in combination in a DSC device leave unharnessed the incident photons in this region. However, for the purposes of the present study they were chosen as they display the desired electrochemical properties with oxidation

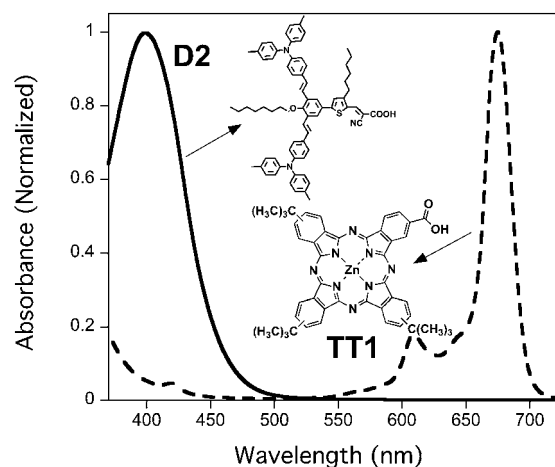


Fig. 1 The chemical structures of **D2** and **TT1** and their absorption spectra recorded in dichloromethane (—) and ethanol (---) respectively.

<sup>a</sup>Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans, 16, Tarragona, 43007, Spain. E-mail: epalomares@iciq.es; Fax: +34 977 920 224; Tel: +34 977 920 241

<sup>b</sup>College of Chemistry, Xiangting University, Xiangting, 411105, China. E-mail: tanst2008@163.com

<sup>c</sup>Departamento de Química, Orgánica, Universidad Autónoma de Madrid (UAM), E-28049, Madrid, E-28049, Spain. E-mail: tomas.torres@uam.es; Fax: +34 914 973 966; Tel: +34 914 974 151

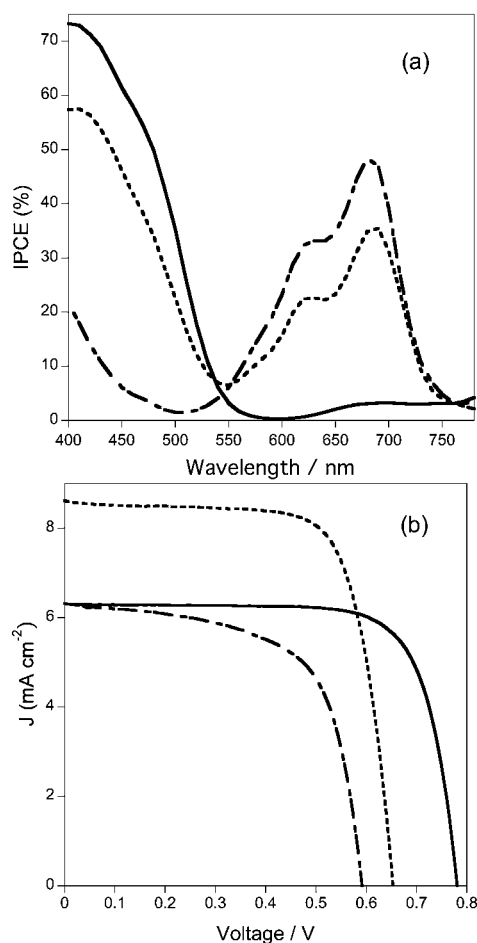
<sup>d</sup>ICREA, Passeig Lluís Companys 28, E-08012 Barcelona, Spain

† Electronic supplementary information (ESI) available: Electrochemistry and charge extraction data. See DOI: 10.1039/c0jm03661g

potentials at 1.35 and 1.04 *versus* NHE for **D2** and **TT1** respectively (see Fig. S1† and ref. 16 for **D2** and **TT1** cyclic voltammetry data respectively). TiO<sub>2</sub> films were sensitized first in a 300 mM **D2** solution in ethanol followed by sensitization in a 100 mM **TT1** solution in dichloromethane. Cells were constructed using Pt counter electrodes and the electrolyte used was composed of 0.03 M I<sub>2</sub>, 0.05 M LiI, 1 M BMII (or DMII), 0.1 M GuNCS, 0.5 M *tert*-butylpyridine in 85 : 15 acetonitrile : velenonitrile.

Cells made using co-sensitized films show improved light-harvesting when compared to cells made from films sensitized with a single dye only (Fig. 2(a)). Co-sensitized **D2** + **TT1** cells also show the best efficiencies (Fig. 2(b)) of 4.08% ( $J_{sc} = 8.6 \text{ mA cm}^{-2}$ ;  $V_{oc} = 643 \text{ mV}$ ; ff = 72.44%) when compared to 3.43% for **D2** cells ( $J_{sc} = 6.3 \text{ mA cm}^{-2}$ ;  $V_{oc} = 780 \text{ mV}$ ; ff = 73.96%) and 2.37% for **TT1** cells ( $J_{sc} = 6.3 \text{ mA cm}^{-2}$ ;  $V_{oc} = 588 \text{ mV}$ ; ff = 63.31%).<sup>18</sup> The significant increase in  $J_{sc}$  for **D2** + **TT1** can be ascribed to the increased light-harvesting efficiency of this cell. The authors are aware that better device performances have already been reported elsewhere for DSCs utilizing organic dyes yet combinations of different dyes present together often result in lower device efficiencies when compared to devices constructed with the individual dyes only. However, this is not the case in this work.

To understand the differences in  $V_{oc}$  observed in the cells we conducted charge extraction and transient photovoltage experiments.<sup>19</sup> In charge extraction measurements pulses of white light are



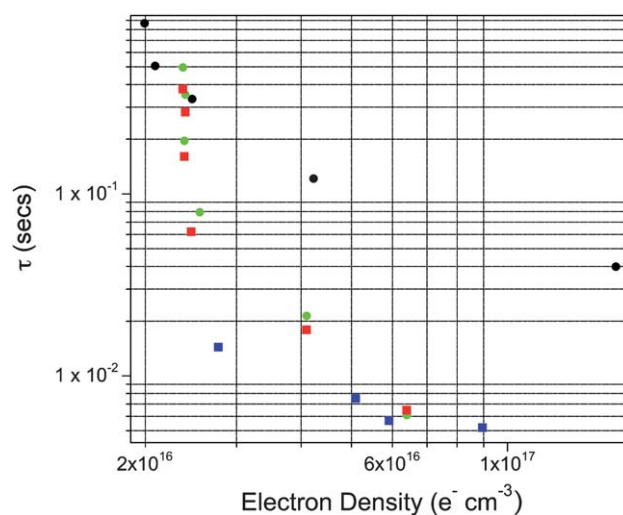
**Fig. 2** IPCE spectra (a) and  $J$ - $V$  curves (b) of **D2** (—), **TT1** (---) and **D2** + **TT1** (...) DSC devices.

applied to the cell that are large enough to reach a steady state under open circuit conditions. When the pulses cease, the cell is immediately short circuited and the charge extracted allowing electron density in the TiO<sub>2</sub> to be calculated. In transient photovoltage measurements a constant background voltage is applied to the cells using a series of white photodiodes. Short pulses of green (535 nm) or red (635 nm) light from a second series of photodiodes are then applied. The resulting photovoltage decay transients are collected and the  $\tau$  values determined by fitting the data to the equation  $\exp(-t/\tau)$ . Fig. 3 shows the  $\tau$  values plotted *versus* TiO<sub>2</sub> electron density for **D2**, **TT1** and **D2** + **TT1** devices.

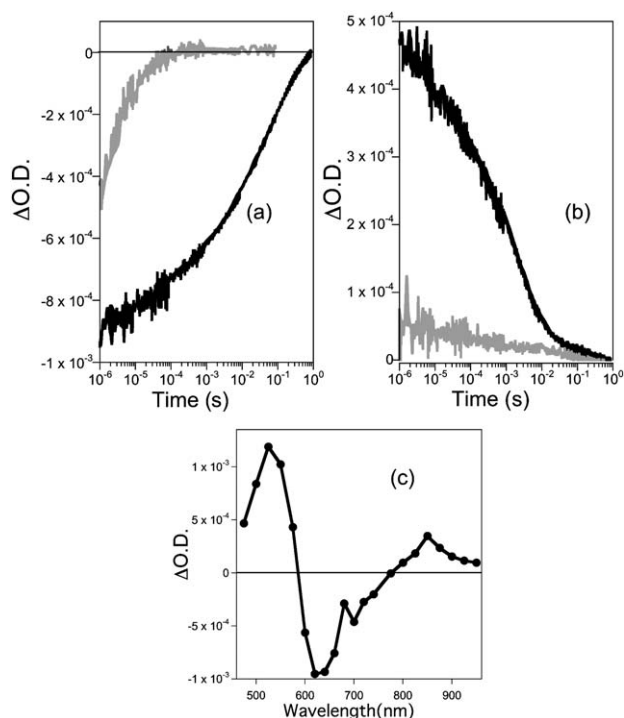
Charge extraction data (see Fig. S2†) show TiO<sub>2</sub> electron densities which indicate the conduction band edge position of the order **D2** > **D2** + **TT1** > **TT1** for these devices. This trend matches the cell voltages shown in Fig. 2, however, the differences in the TiO<sub>2</sub> conduction band edge alone cannot account entirely for the differences in  $V_{oc}$  observed for the cells *e.g.* charge extraction data indicate a difference in conduction band edge of  $\sim 80 \text{ mV}$  for **D2** and **D2** + **TT1** cells whereas the difference in cell  $V_{oc}$  is in fact  $\sim 130 \text{ mV}$ . Transient photovoltage data indicate that recombination of TiO<sub>2</sub> electrons with the electrolyte may also determine  $V_{oc}$ . Electron lifetimes are much longer in the **D2** device compared to the **TT1** device which correlates well with their  $V_{oc}$ . Electron lifetimes in the co-sensitized **D2** + **TT1** cell are somewhat intermediate between **D2** and **TT1** cells which again correlates well with  $V_{oc}$ . Furthermore lifetimes in **D2** + **TT1** are similar regardless of which diode is used (indeed when both green and red diodes are used simultaneously lifetimes are quite similar).

Transient absorption spectroscopy (TAS) was used to investigate the light induced processes occurring at the TiO<sub>2</sub>/dye/electrolyte interface. TiO<sub>2</sub> films sensitized with **D2** and **TT1** show typical stretched exponential kinetics as observed previously.<sup>20</sup> The kinetics in a **D2** + **TT1** device in the presence and absence of electrolyte are shown in Fig. 4.

Excitation at 430 nm in **D2** + **TT1** results in almost exclusive excitation of the **D2** sensitizer as **TT1** has a negligible absorbance at



**Fig. 3** Electron lifetimes calculated from photovoltage decays in **D2** (black circles) and **TT1** (blue squares) cells following excitation by green and red photodiodes respectively and in a **D2** + **TT1** cell following excitation by a green (green circles) and red photodiode (red squares).



**Fig. 4** Transient absorption kinetics of (a) a **D2** + **TT1** cell at 680 nm following excitation at 430 nm and (b) a **D2** cell at 520 nm following excitation at 430 nm in the presence (grey) and absence (black) of electrolyte. (c) The difference absorption spectrum of the **D2** + **TT1** cell recorded at 8  $\mu$ s in the absence of electrolyte following excitation at 430 nm. Measurements were conducted with semi-transparent DSC cells consisting of 4  $\mu$ m  $\text{TiO}_2$  films.

this wavelength (see Fig. 1). These kinetics are shown in Fig. 4(a). The difference absorption spectrum recorded (Fig. 4(c)) indicates that the kinetics being monitored are in fact those of the decay of the **TT1** cation, *i.e.* following optical excitation, **D2** injects an electron into  $\text{TiO}_2$  and the hole on **D2** is subsequently shuttled to **TT1**. The electrochemical properties of the two sensitizers indicate that this hole-transfer is energetically possible. We have already demonstrated similar kinetics previously.<sup>11</sup> Hole-transfer between **D2** and **TT1** is clearly too fast for our TAS system to monitor and appears complete by the onset of our system response. The kinetics in Fig. 4(a) in the presence of electrolyte indicate efficient regeneration of the **TT1** cation meaning the possibility of this process limiting  $V_{oc}$  in **D2** + **TT1** devices can be discarded. Furthermore, kinetics recorded in the presence of the  $\text{I}^-/\text{I}_3^-$  electrolyte show that hole-transfer from **D2** to **TT1** is much faster than the regeneration of **D2**<sup>+</sup> by the electrolyte, which is in itself an extremely fast reaction, also too fast for our system to monitor (Fig. 4(b)). The long-lived flat signal is ascribed to electrons in the  $\text{TiO}_2$  and/or the oxidized species of the  $\text{I}^-/\text{I}_3^-$  electrolyte.<sup>21,22</sup> One can therefore assume that in **D2** + **TT1** cells the majority of holes will be located on **TT1** either directly through excitation of **TT1** or indirectly through excitation of **D2**.

To conclude, co-sensitized **D2** + **TT1** cells show increased light-harvesting and overall improvement in cell efficiency compared to reference cells made with either **D2** or **TT1** only. The  $V_{oc}$  for these devices can be explained from both the charge extraction and transient photovoltage data where the position of the  $\text{TiO}_2$  conduction

band and electron lifetimes are of the order **D2** > **D2** + **TT1** > **TT1**. Transient absorption data show that hole-transfer occurs from **D2** to **TT1** in **D2** + **TT1** devices which does not, however, lead to inferior efficiencies when compared to **D2** and **TT1** reference devices. This study indicates that when considering dyes for use in co-sensitized DSCs, they should not only display complimentary absorption bands but also large  $V_{oc}$  and long electron lifetimes under operating conditions. Though **TT1** improves the light-harvesting in the **D2** + **TT1** cell compared to the **D2** device the  $V_{oc}$  of the co-sensitized device is greatly inferior ( $\sim 130$  mV). Engineering dyes (especially Near-IR absorbing dyes) which fulfill these criteria will be crucial to exploiting co-sensitization as a viable means to optimize DSCs.

Finally, it has been shown that inter-dye charge transfer processes do not necessarily limit cell efficiency. Several studies have aimed at limiting the contact and therefore possible charge transfer reactions between the different dye species in co-sensitized DSCs.<sup>23,24</sup> However, such reactions may not necessarily limit efficiency, as demonstrated in this work.

## Acknowledgements

This work has been supported by the Spanish MICINN (CTQ-2008-00418BQU, CTQ2007-60746/BQU, CONSOLIDER 2010, Nano-Mol-CSD2007-00010 and HOPE-CSD-0007-2007), Comunidad de Madrid (S-0505/PPQ/000225), EU (ROBUST, Collaborative Research Project, FP7-ENERGY-2007-1-RTD) and the National Nature Science Foundation of China (Grant Nos. 50873045). JNC acknowledges the MICINN for his Juan de la Cierva Fellowship.

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