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## COMMUNICATION

Enhanced light harvesting in mesoporous TiO<sub>2</sub>/P3HT hybrid solar cells using a porphyrin dye†Soo-Jin Moon,<sup>a</sup> Etienne Baranoff,<sup>a</sup> Shaik M. Zakeeruddin,<sup>a</sup> Chen-Yu Yeh,<sup>b</sup> Eric Wei-Guang Diau,<sup>c</sup> Michael Grätzel\*<sup>a</sup> and Kevin Sivula\*<sup>a</sup>

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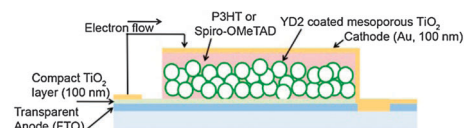
We report panchromatic light harvesting in hybrid TiO<sub>2</sub>/P3HT photovoltaic devices using a porphyrin dye that complements the light absorption of P3HT. The high short circuit photocurrent (12.1 mA cm<sup>-2</sup>) obtained is found to be due, in part, to Förster resonance energy transfer from the P3HT to the dye.

Hybrid organic–inorganic photovoltaic devices are extremely attractive for inexpensive solar energy conversion. A hybrid device can potentially combine the advantages of both classes of materials, for example, the manufacturing-friendly processability and tunability of organic semiconductors and the good chemical and physical stability of inorganic semiconductors.<sup>1</sup> In particular, the combination of regioregular poly(3-hexylthiophene)(P3HT) and nanostructured TiO<sub>2</sub> has been an important prototype for hybrid solar cells. In this system, excited states (excitons) generated in the light-absorbing P3HT are separated at the type II heterojunction formed with the TiO<sub>2</sub>. The discord between the average photon penetration depth and the exciton transport length in the P3HT is nominally overcome by using a bulk heterojunction—*i.e.* bicontinuous and interpenetrating phase domains of the two materials afforded by infiltrating the P3HT into a high-surface area, mesoporous TiO<sub>2</sub> thin film.<sup>2</sup> Despite this remedy, power conversion efficiencies of the TiO<sub>2</sub>/P3HT hybrid cells have remained very low (less than 1% under standard conditions).<sup>3,4</sup>

Critical concerns for these devices are the incomplete polymer infiltration into the mesoporous TiO<sub>2</sub> and the poor electronic communication between the organic and inorganic materials. These limitations conspire to give high charge recombination and low exciton harvesting. To improve device performance, numerous approaches have been employed. For example, optimizing the TiO<sub>2</sub> nanostructure using approaches such as tuning the pore size<sup>5</sup> or employing nanotube arrays<sup>6</sup> can facilitate infiltration and also direct charge transport.

In addition, surface modification of the TiO<sub>2</sub> by the chemisorption of molecular species containing carboxylate, phosphonate or sulfonate groups has been used to facilitate energy transfer.<sup>7,8</sup> In the last few years, a strategy of sensitizing the TiO<sub>2</sub> with light harvesting dyes containing carboxylate anchoring groups has been employed to improve the interfacial energetics between the TiO<sub>2</sub> and P3HT and to also enhance light absorption by the device.<sup>8–12</sup> These dyes exhibit highly efficient electron injection into TiO<sub>2</sub> as in the well known dye sensitized solar cell.<sup>13</sup> In addition, if a dye is chosen that absorbs light not captured by the P3HT (which absorbs light strongly between  $\lambda = 400$  and 600 nm), it could enhance the photocurrent of the TiO<sub>2</sub>/P3HT cell by achieving a more panchromatic light harvesting response. Recently, this concept was demonstrated with a TiO<sub>2</sub> nanotube array and a near-infrared absorbing squaraine dye (SQ1),<sup>14</sup> and also by using the near-UV absorbing dye D131 with nanostructured TiO<sub>2</sub> prepared from colloids.<sup>11</sup> In these reports, the device short circuit photocurrent ( $J_{SC}$ ) was improved to around 10 and 6 mA cm<sup>-2</sup> under standard illumination conditions, respectively, and power conversion efficiencies were reported to be around 3% in both of these cases.

In the present work we broaden the demonstration of this concept using a porphyrin sensitizer (coded as YD2) that enhances the light absorption in both the near-IR and near-UV regions. We achieve the highest  $J_{SC}$  reported for a TiO<sub>2</sub>/dye/P3HT based hybrid photovoltaic device (over 12 mA cm<sup>-2</sup>) and a high power conversion efficiency of 3.13% under standard conditions. Furthermore, we compare these photovoltaic performances to that of a solar cell with a non-light harvesting organic hole transport material (HTM), Spiro-OMeTAD. Their drastically different performances and an additional photoluminescence study suggest that Förster resonance energy transfer (FRET) between the P3HT and the sensitizer is contributing to the enhanced photocurrents in the TiO<sub>2</sub>/YD2/P3HT hybrid solar cell.



**Scheme 1** The architecture of the solid-state hybrid organic/inorganic devices investigated in this work.

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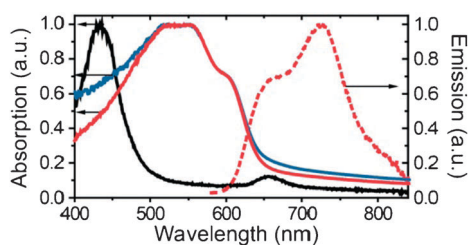
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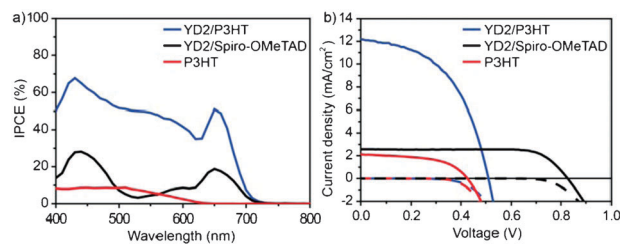
Devices with an architecture shown in Scheme 1 were fabricated according to the details given in the ESI.† Briefly, since P3HT is known to have difficulties in infiltrating the 20 nm pores traditionally used in TiO<sub>2</sub>-based solar cells,<sup>15</sup> we prepared our mesoporous TiO<sub>2</sub> layer with larger particles and larger pores (*ca.* 75 nm). Also, to compare the TiO<sub>2</sub>/YD2/P3HT based devices to devices without the benefit of the panchromatic light absorption, two types of control devices were prepared. First TiO<sub>2</sub>/P3HT devices were prepared, but without the YD2 dye. Also, a YD2 sensitized TiO<sub>2</sub> device with the transparent HTM, Spiro-OMeTAD, was assembled under optimized conditions as previously described.<sup>16</sup> In this case the mesoporous TiO<sub>2</sub> layer employed 20 nm particles as this morphology has been found to give the highest performance in Spiro-OMeTAD based devices.

The chosen dye, YD2 (for structure see Fig. S1, ESI†), exhibits the expected light absorption behaviour of a porphyrin-based dye with high molar extinction coefficients ( $\epsilon$ ) due to the Soret band ( $\epsilon = 217\,000\text{ M}^{-1}\text{ cm}^{-1}$  at 444 nm) and the Q-band ( $\epsilon = 33\,700\text{ M}^{-1}\text{ cm}^{-1}$  at 648 nm).<sup>17</sup> Fig. 1 shows the absorption spectra of a YD2 stained TiO<sub>2</sub> film (20 nm particles) compared to a TiO<sub>2</sub>/P3HT film (75 nm particles) with and without dye. The absorption bands of the YD2 dye in the near UV and the near IR complement the strong absorption of the P3HT in the spectral region of 400–630 nm. Their combination should lead to a broadening of the harvested wavelength bandwidth. Interestingly, the peaks of the dye cannot be resolved in the TiO<sub>2</sub>/YD2/P3HT film due to the reduced TiO<sub>2</sub> surface area and overpowering absorption of the P3HT. Finally, we note that the absorption peaks of the TiO<sub>2</sub>/P3HT films show no blue-shift in comparison to that of a pristine P3HT film, suggesting that a high degree of  $\pi$ - $\pi$  stacking of the chains is still occurring within the pores.<sup>2</sup>

In Fig. 2a, the incident photon-to-current conversion efficiency (IPCE) as a function of excitation wavelength of the three different photovoltaic devices is displayed. The IPCE spectrum of the TiO<sub>2</sub>/P3HT based device shows a maximum of about 10% despite the high absorptivity of the P3HT. Similarly for the TiO<sub>2</sub>/YD2/Spiro-OMeTAD cell, the IPCE values of the two main peaks corresponding to the absorption of Soret and Q-bands reach only 28% and 20%, respectively. Interestingly, in a liquid electrolyte based YD2 sensitized device using a 2.4  $\mu\text{m}$  thick TiO<sub>2</sub> film the IPCE reached over 80%.<sup>18</sup> This drastic difference in IPCE is not expected as similar high molar extinction coefficient dyes perform equally in liquid-based and Spiro-OMeTAD based devices



**Fig. 1** Normalized UV/Vis absorption of a YD2 (black) sensitized mesoporous TiO<sub>2</sub> film (20 nm particles) and a P3HT infiltrated TiO<sub>2</sub> film (75 nm particles) without (red) and with (blue) dye sensitization. The normalized emission (dashed red line) spectrum of a pristine P3HT film is also shown.



**Fig. 2** Photovoltaic device characteristics of a YD2 sensitized solid-state cell with Spiro-OMeTAD (black) and a TiO<sub>2</sub>/P3HT hybrid cell without dye (red) and with YD2 sensitization (blue). Panel (a) shows the IPCE spectrum and (b) shows the current–voltage ( $J$ - $V$ ) characteristics under full sunlight ( $100\text{ mW cm}^{-2}$ ) ( $0.20\text{ cm}^2$  of masked active area). Dashed lines representing the dark currents of the devices are shown.

(with similar TiO<sub>2</sub> film thicknesses).<sup>19</sup> These results suggest that the low IPCEs of the Spiro-OMeTAD based device are due to a limitation in charge transfer between YD2 and the hole transporter or the incomplete collection of photo-generated charge carriers. Furthermore, since Spiro-OMeTAD based devices fabricated with an identical procedure to that used here (but employing a different dye<sup>16</sup>) have shown both higher IPCEs and higher  $J_{SC}$ 's (*vide infra*), we can reason that charge collection is not limiting in the YD2/Spiro-OMeTAD system, leaving charge transfer at the interface as the likely limiting factor.

In stark contrast to both the TiO<sub>2</sub>/P3HT and the TiO<sub>2</sub>/YD2/Spiro-OMeTAD devices, the IPCE of the TiO<sub>2</sub>/YD2/P3HT based cell improved remarkably. Compared to the TiO<sub>2</sub>/P3HT device the photon conversion efficiency of the P3HT increased by about a factor of 5 in accordance with similar reports.<sup>9</sup> Compared to the TiO<sub>2</sub>/YD2/Spiro-OMeTAD device the response of the P3HT completely fills the valley where YD2 does not absorb light. In addition and in contrast to the UV/Vis data, the peaks of the dye (at 440 nm and 650 nm) can be clearly seen in the IPCE data and were also enhanced significantly *versus* the Spiro-OMeTAD device. At 440 nm, near the Soret band maximum, the IPCE reaches 69%, which is a 3-fold increase over the Spiro-OMeTAD based device. The IPCE value in the near infrared region is also about 50%. This increased IPCE of the YD2 can be attributed to an improved charge transfer at the YD2/P3HT interface compared with YD2/Spiro-OMeTAD. This view is supported by the discrepancy in performance between the liquid and solid-state cell performances with YD2 and suggests poor hole transfer from YD2 to Spiro-OMeTAD despite the higher expected driving force due to the HOMO level in this material ( $-4.8\text{ eV vs. vac}$ )<sup>20</sup> compared to P3HT ( $-5.0\text{ eV vs. vac}$ ).

The current–voltage behaviour of the three types of solar cells measured in the dark and under AM1.5 standard illumination conditions ( $100\text{ mW cm}^{-2}$ ) is shown in Fig. 2b and the device metrics are reported in Table S1, ESI.† The YD2/Spiro-OMeTAD cell possessed a very poor power conversion efficiency of 1.64% due to a low  $J_{SC}$  of  $2.56\text{ mA cm}^{-2}$ . However, the TiO<sub>2</sub>/YD2/P3HT hybrid cell generated much higher  $J_{SC}$  of  $12.1\text{ mA cm}^{-2}$  and solar power conversion efficiency,  $\eta$ , of 3.13%. To our knowledge, this represents the highest short-circuit photocurrent generated by a TiO<sub>2</sub>/dye/P3HT based device. In addition, we note that the high performance of this system was reproducible (see Table S1, ESI†), the IPCE spectra,

integrated over the AM 1.5G solar spectra, corroborates well with the observed solar photocurrent<sup>21</sup> and our device active area of 0.20 cm<sup>2</sup> is considerably larger than that of the recent reports of similarly high efficiencies reported by Mor *et al.*<sup>14</sup> and Zhang *et al.*<sup>11</sup> The high photocurrent of the TiO<sub>2</sub>/YD2/P3HT hybrid cell can be attributed to two factors: (1) a more panchromatic IPCE using the combination of the complementary light harvesters and (2) an improved IPCE of the both the YD2 and the P3HT. This second factor is discussed in more detail below. Despite the high photocurrent, the open circuit voltage,  $V_{OC}$ , and the fill factor (FF) of the P3HT based cells were much lower in comparison to the Spiro-OMeTAD cell. This is a common observation in P3HT based cells.<sup>9</sup> However, an annealing treatment<sup>15</sup> and more recently the addition of *t*BP or Li salts<sup>10,14</sup> have been reported to enhance both the  $V_{OC}$  and FF in TiO<sub>2</sub>/P3HT based devices. In addition the omission of the PEDOT:PSS layer has given devices with higher  $V_{OC}$ 's.<sup>12</sup> Unfortunately, in our experience the inclusion of additives, annealing, or the omission of the PEDOT:PSS layer led to very irreproducible device results. Hence, it is clear that the YD2 sensitized TiO<sub>2</sub>/P3HT hybrid cell has a potential for improvement by properly applying one of these techniques.

To better understand the increased IPCE of the dye and the P3HT in our hybrid device we now consider the two types of energy transfer that can occur at the dye/polymer interface: (1) direct electron transfer from P3HT to YD2 by exciton dissociation, and (2) exciton transfer by Förster resonance energy transfer (FRET).<sup>22</sup> The latter can take place from the P3HT to the YD2, given a significant spectral overlap between the absorption of the YD2's Q band and the emission of the P3HT. This is indeed the case presented here (see Fig. 1). Given that the FRET mechanism can occur over larger distances compared to the direct electron transfer in P3HT due to the small exciton diffusion length,<sup>23</sup> FRET from P3HT to YD2 could significantly contribute to the high photocurrent. To probe efficient electron transfer from P3HT to YD2, photoluminescence (PL) measurements were performed on pristine P3HT and the P3HT/YD2 dispersed in an inert poly(methyl methacrylate) matrix on a glass substrate. The PL intensity of the P3HT/YD2 mixture decreased remarkably compared to that of the pristine P3HT (see Fig. S2, ESI†). The P3HT/YD2 mixture leads to a PL quenching ratio of about 90%, indicating the efficient energy transfer from the P3HT to the YD2. Based on exciton harvesting calculations from McGehee and co-workers,<sup>23</sup> our device geometry, and the observed IPCE (*ca.* 50%), we can estimate a Förster radius of 2–3 nm. With this approximation we can estimate that in the absence of FRET an IPCE of only 20% would be expected for the P3HT assuming an exciton diffusion length of 5 nm. This strongly suggests that the FRET is playing an important role in the light harvesting in our YD2/P3HT hybrid device. However, as in similar work<sup>14</sup> it is difficult to quantitatively decouple the relative contributions of the different energy transfer mechanisms. Our future work will be directed toward understanding and directing this important aspect of TiO<sub>2</sub>/Dye/conjugated polymer hybrid solar cells, as well as increasing performance by improving the device voltage and fill factor.

In conclusion, for the first time we have demonstrated TiO<sub>2</sub>/Dye/P3HT hybrid solar cells with the porphyrin-based

YD2 dye. The cell generated a record photocurrent of 12.1 mA cm<sup>-2</sup> under standard illumination conditions due to the panchromatic light harvesting afforded from the two complementing absorbers, and achieved an overall power conversion efficiency of 3.13%. Efficient energy transfer from the P3HT to the YD2 was observed by photoluminescence quenching, suggesting that FRET energy transfer is playing an important role in the high IPCE observed. Our results further indicate that P3HT can successfully carry out dual functions as a HTM and a sensitizer in the cell. The continued development of these hybrid systems should eventually allow the fabrication of efficient but inexpensive solution-processed photovoltaic devices for solar energy conversion.

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