Supporting information for:

Enhanced light harvesting in mesoporous TiO₂/P3HT hybrid solar cells using a porphyrin dye

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Fig. S1. The molecular structures of the P3HT, Spiro-OMeTAD and YD2 are shown.

Table S1. Photovoltaic performance of YD2 sensitized cells with Spiro-OMeTAD and P3HT. Measured under AM1.5 conditions, 100 mW/cm². (0.20 cm² of masked active area)

<table>
<thead>
<tr>
<th>Device</th>
<th>(J_{SC}) (mA/cm²)</th>
<th>(V_{OC}) (mV)</th>
<th>F.F.</th>
<th>(\eta) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂/P3HT</td>
<td>2.12</td>
<td>425</td>
<td>0.53</td>
<td>0.49</td>
</tr>
<tr>
<td>TiO₂/YD2/P3HT</td>
<td>12.1</td>
<td>510</td>
<td>0.50</td>
<td>3.13</td>
</tr>
<tr>
<td>TiO₂/YD2/P3HT (duplicate)</td>
<td>10.62</td>
<td>534</td>
<td>0.53</td>
<td>3.03</td>
</tr>
<tr>
<td>TiO₂/YD2/Spiro-OMeTAD</td>
<td>2.56</td>
<td>827</td>
<td>0.77</td>
<td>1.64</td>
</tr>
</tbody>
</table>
Device fabrication details:

The fabrication of our hybrid solar cells employed a F-doped SnO2 glass substrate (15Ω/□, Pilkington) onto which a ~100 nm compact TiO2 layer was deposited by spray pyrolysis.\(^1\) Since P3HT is known to have difficulties infiltrating the 20 nm pores traditionally used in TiO2-based solar cells,\(^2\) we prepared our mesoporous TiO2 layer with larger particles and larger pores. A layer about 1 µm thick with 75 nm TiO2 particles was coated onto the FTO/compact TiO2 substrate using the spin coater. The 75 nm powder was received from Showa Titanium Co., and the TiO2 paste was prepared using a previously reported procedure.\(^3\) The electrode was then annealed at 500 °C for 30 min under oxygen flow, followed by treatment with a 0.02 M TiCl4 aqueous solution for 6 hours at room temperature. It was re-annealed at 450°C in air for 30 min and cooled before immersing it into a YD2 dye solution (0.2 mM in ethanol with 0.4 mM chenodeoxycholic acid to prevent aggregation\(^4\)) for 18 hours. The dye coated TiO2 electrodes were spin-coated at 250 rpm for 500 sec with a regioregular-P3HT solution (Reike Metals Co. 30 mg/ml in chlorobenzene). A poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) solution (2.8 wt% dispersion in water, Baytron P) diluted with two volumes of MeOH was spin-coated onto the TiO2/YD2/P3HT films at 2000 rpm for 30 sec. As a counter electrode, Au was deposited on top of the samples using thermal resistance evaporation to define an active device area of 0.20 cm². To compare the TiO2/YD2/P3HT based devices to devices without the benefit of the panchromatic light absorption, two types of control devices were prepared. First TiO2/P3HT devices were prepared as above, but without the YD2 dye. Also, a YD2 sensitized TiO2 device with the transparent HTM, Spiro-OMeTAD, was assembled under optimized conditions as previously described.\(^5\) In this case the mesoporous TiO2 layer had a thickness of 2 µm.

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**Fig. S2.** Photoluminescence spectra of the pristine P3HT film (red) and P3HT/YD2 mixture (black).
with 20 nm particles as this morphology has been found to give the highest performance in Spiro-OMeTAD based devices.

Additional experimental details:

Device characterization: The incident photon-to-current conversion efficiency (IPCE) was created by using the incident light from a 300 W xenon lamp (ILC Technology, U.S.A.), which had been focused through a Gemini-180 double monochromator (Jobin Yvon Ltd.). The irradiation source employed for the J-V measurements was a filtered (Schott 113) 450 W xenon light source (Osram XBO 450, USA) whose power was adjusted using a reference Si photodiode equipped with a color-matched filter (KG-3, Schott), thus reducing the spectral mismatch between the simulated light and AM 1.5G irradiation in the region of 350–750 nm to less than 4%.

PL Measurements: To probe efficient electron transfer from P3HT to YD2, photoluminescence (PL) measurements were performed using a time-correlated single photon counting (TCSPC) system from PicoQuant. Films were excited with a pulsed laser diode, (model LDH 485: 481nm, 70ps FWHM, 5MHz) detected with a single photon avalanche diode (PDM 100CT SPAD) attached to a monochromator and processed by a PicoHarp 300 correlating system. For the PL measurements we deposited the pristine P3HT and the P3HT/YD2 (P3HT:YD2=20:1 concentration ratio) in an inert poly(methyl methacrylate) (PMMA) matrix on a glass substrate using a spin coater.

References: