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Abstract. Carboxylic acid functionalized pentacene-based dyes are synthesized and tested in dye-sensitized solar cells utilizing titania (rutile) nanowire arrays as the electron transporting photoanode. Functionalization on both chromophore and solubilizing substituents leads to materials demonstrating promising light-harvesting and energy-conversion properties in these large polycyclic aromatic compounds. © 2011 Society of Photo-Optical Instrumentation Engineers (SPIE).

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1 Introduction

The quest for low-cost photovoltaic devices has led to the utilization of organic materials in a variety of roles. Along with the rapid advances in bulk-heterojunction solar cells, which are slowly advancing toward 10% power-conversion efficiency (PCE), dye-sensitized solar cells (DSSCs) are also a promising technology because of their low cost and relatively high efficiency. Introduced in 1991, initial DSSCs exhibited a 7% PCE and quickly achieved ∼10% with the development of new sensitizers. Despite these good efficiencies, disadvantages associated with rare-metal dyes and redox shuttle (I−/I3−) carried by volatile organic solvent have slowed commercialization. To further improve DSSC performance, and potentially circumvent issues with metal-based dyes, all-organic sensitizers have been the focus of recent research efforts. Organic dyes are rapidly gaining in efficiency, approaching the PCE record (∼11%) set by the current top performing rare-metal dye N719.

Our group has developed a class of soluble pentacene derivatives with excellent hole mobility. With the eventual aim of developing materials for solid-state DSSCs, we endeavored to engineer a pentacene chromophore according to the general requirements for a dye to be used as a sensitizer in DSSCs. A functional sensitizer typically consists of a chromophore and an anchoring group, sometimes coupled by a conjugated linker (bridge). As the light-harvesting component, the chromophore is critical to device efficiency. Although the absorption breadth is not the only factor determining overall device performance, a general goal in sensitizer design is to cover as broad a spectrum as possible in the visible and near-IR region, where solar radiation at the planet surface is most intense. Most organic sensitizers absorb light below 600 nm, while reasonably efficient near-IR/IR dyes used in DSSCs are only occasionally seen in literature. Pentacene chromophores, with potential absorption out to 750 nm, could
extend the window of performance for DSSCs, provided that there is efficient coupling between the acene and the inorganic matrix. We report here the synthesis of a series of pentacene dyes (Fig. 1) and the evaluation of their sensitizing efficiencies in liquid-junction DSSCs.

2 Experimental

Pentacene dyes P1–P6 were prepared as shown in Fig. 2. They feature solubilizing triisopropylsilylethynyl (TIPS) groups at the C-6 and C-13 positions and a –COOH anchoring group that is bridged by various conjugated linkers at the C-2 position. P7 and P8 share the core structure with P3, but the solubilizing trialkylsilylethynyl groups are engineered to enhance the solubility of resulting sensitizer.

2.1 Synthesis Details

As the simplest dye in this series, P1 has a –COOH group connected directly to the pentacene backbone. We were unable to prepare this compound by straightforward halide/CO2 carboxylation of a 2-halopentacene in the presence of BuLi or Grignard reagent. Instead, a catalytic formylation31 of iodide 1 (Ref.32) afforded aldehyde 2 in reasonable yield, which was followed by Ag2O oxidization to acid P1. Dye P2 was obtained in two steps; a Heck reaction between 1 and t-butyl acrylate yielded ester 3, which was hydrolyzed to acrylic acid P2. Cyanoacrylic acid P3 was obtained by Knoevenagel condensation between aldehyde 2 and cyanoacetic acid. P7 and P8 were prepared in the same manner. Alkyne-linked dye P4 was prepared by hydrolysis of methyl ester 4, which was accessible by Sonogashira coupling between 1 and methyl propiolate. Dye P5 was also made by Sonogashira coupling using 4-ethynyl benzoic acid. Thiophene aldehyde 5 was obtained by Suzuki coupling of a thiophene carboxaldehyde in moderate yield and then oxidized to provide dye P6.

2.2 Device Fabrication

Vertically oriented TiO$_2$ nanowire arrays were synthesized by a hydrothermal method on fluorine doped tin oxide (FTO)-coated glass (TEC-8, 8 ohm/square) substrates. The substrates were initially cleaned by sonication in acetone, 2-propanol, and methanol, rinsed with deionized water, and dried in a nitrogen stream. These substrates were dipped in 0.1 M TiCl$_4$ solution for 8 h and then heated at 500°C for 1 h to obtain a layer of TiO$_2$ ~ 20 nm thick. To grow
nanowire arrays, these treated FTO substrates were loaded into a sealed Teflon® reactor (23 ml volume) containing 10 ml of toluene, 1 ml of titanium tetrachloride (1 M in toluene), 1 ml of tetrabutyl titanate, and 1 ml of hydrochloric acid (37%). We conducted the growth of single-crystalline nanowires on transparent conducting oxide (TCO) solid substrate by a nonpolar solvent/hydrophilic solid interfacial reaction mechanism. (A very different alkali hydrothermal growth process has also been used to synthesize single-crystalline rutile nanowire arrays.) Because it is desirable to have a high surface area and close packing of the nanowires for liquid solar cell applications, a high concentration of Ti⁴⁺ precursor was used. The reaction
took place at 160°C for 10 h. After the reaction was completed, the nanowire-covered FTO substrates were carefully washed with ethanol and annealed at 450°C for 30 min in air to remove the surface-adsorbed organic species. The nanowire arrays were ~3.5 μm in length, 20 nm in width, and 5–10 nm in interwire spacing. All samples were further treated with oxygen plasma for 5 min at an RF power of 80 W to clean and hydroxylate the surface for better dye adhesion. The DSSCs were prepared using the following two procedures:

**Method A**: Nanowire array samples were coated with dye by immersion for 30–60 min in a 1-mM tetrahydrofuran (THF) solution of the respective pentacene dye (P1–P6). Liquid-junction solar cells were prepared by infiltrating the dye-coated TiO2 electrode with redox electrolyte containing lithium iodide (0.1 M), iodine (0.01 M), tri-n-butyl phosphate (0.4 M), butyl methyl imidazodium iodide (0.6 M), and guanidinium thiocyanate (0.1 M) in a mixture of acetonitrile and valeronitrile (v/v = 15/1). Conductive glass slides, sputter coated with 100 nm of Pt were used as the counter electrode. Electrode spacing between the nanowire and counter electrodes was ensured by using a 25-μm-thick SX-1170 spacer (Solaronix Inc., Aubonne, Switzerland). Photocurrent density and photovoltage were measured with active sample areas of 0.2 cm2 using AM-1.5 simulated sunlight produced by a 500-W Oriel Solar Simulator, calibrated with a national renewable energy laboratory (NREL)-certified silicon solar cell.

**Method B**: Similar to method A except that nanowire array samples were coated with dye by immersion for 5 h in a 0.4-mg/mL toluene solution of the respective pentacene dye (P3, P7, and P8) at 70°C.

### 2.3 Computational Details

Density functional theory (DFT) calculations were performed in the Gaussian03 program package.[36] The geometries of P1–P6 were optimized at the B3LYP level using a 3–21G* basis set in vacuum using without any symmetry constraints. Electronic structure calculations were performed using a 6–31G* basis set. Molecular orbitals were visualized by GaussView 3.0 software.

### 3 Results and Discussion

P1–P6 were used to fabricate DSSCs but did not show impressive sensitizing results as their electronic characters indicate. Therefore, further molecular modifications and computational studies were applied to understand the possible reasons for their poor performance. Details will be presented in the following sections.

#### 3.1 Solar Cell I–V Characterization

P1–P6 did act as effective sensitizers in DSSCs. Although their sensitizing capabilities seem to be limited, structure-property relationships are obvious. The linker that couples the pentacene chromophore and the anchor group plays a critical role in determining the sensitizing effect. The solubility of these dyes seems to be another important factor.

##### 3.1.1 Linker effect

Initially, the solar cells were fabricated using method A. The subtle change in linker structure of sensitizers P1–P6 dramatically affects their performance in the devices (Fig. 3). Table summarizes the key photovoltaic parameters for these materials. P1, which has no linker, shows the highest short-circuit current density (Jsc = 1.49 mA/cm²) as well as the highest open-circuit voltage (Voc = 0.6 V); however, its fill factor (FF) is only 0.38, the lowest in the group. In the case of P2 where a simple –C≡C– linker is introduced, comparable PCE (η = 0.30%) is seen, although Jsc drops and FF rises. It is surprising to see a poor result from P3, which has an
extra cyano group on the vinyl linker. Incorporating cyanoacrylic acid is a well-known strategy in organic sensitizer development because the strong electron-withdrawing nature of –C≡N has been demonstrated to facilitate the electron-injection process. The unexpected low $J_{SC}$ leads to overall poor performance by P3, indicating that a characteristic electronic property of the pentacene chromophore may mitigate the impact of the nitrile substituent. Switching to an alkyne linker (P4) results in the lowest PCE, arising from both poor $J_{SC}$ and $V_{OC}$. This poor performance is also seen in alkyne-containing P5. Direct aryl attachment (P6), however, exhibits sensitizing ability similar to that observed in vinyl-linked P2, indicating that heteroacenes could serve as efficient electron donors to titania.

### 3.1.2 Dye solubility

The poor performance of P1–P6 arises mainly from low photocurrent, which indicates either low concentration of dye, poor light-harvesting abilities and/or inefficient electron injection. Dye loading of P1–P6 is less than ideal due to their poor solubility in the solvents most commonly used for DSSC loading, such as acetonitrile and methanol. These pentacene dyes are only sufficiently soluble in THF, which unfortunately destroys the polymer spacer specifying the active cell area. Therefore, the soaking time for the TiO$_2$ thin film in dye solution was limited, typically between 30 min and 1 h, which may result in an unsaturated concentration of sensitizer on the titania surface. To improve the solubility and enhance absorption, two more dyes were prepared, namely, P7 and P8. These two compounds have the same cyanoacrylic acid anchor as P3, while their greasier substutients, tri-$n$-propylsilylethynyl (TNPS) and tri-isobutylsilylethynyl (TIBS) respectively, provide them greater solubility. Indeed, in toluene the solubility of P3 at

<table>
<thead>
<tr>
<th>Methods</th>
<th>Dye</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$ff$</th>
<th>$\eta$ (%)</th>
</tr>
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<tr>
<td>A</td>
<td>P1</td>
<td>0.60</td>
<td>1.49</td>
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<td>0.34</td>
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<td>P2</td>
<td>0.60</td>
<td>1.05</td>
<td>0.47</td>
<td>0.30</td>
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<td></td>
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<td>0.45</td>
<td>0.48</td>
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<td>0.51</td>
<td>0.36</td>
<td>0.52</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>P5</td>
<td>0.55</td>
<td>0.42</td>
<td>0.59</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>P6</td>
<td>0.57</td>
<td>0.95</td>
<td>0.53</td>
<td>0.29</td>
</tr>
<tr>
<td>B</td>
<td>P3</td>
<td>0.59</td>
<td>1.02</td>
<td>0.52</td>
<td>0.31</td>
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<tr>
<td></td>
<td>P7</td>
<td>0.61</td>
<td>1.69</td>
<td>0.49</td>
<td>0.50</td>
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<tr>
<td></td>
<td>P8</td>
<td>0.58</td>
<td>1.74</td>
<td>0.47</td>
<td>0.47</td>
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<td>7.79</td>
<td>0.56</td>
<td>3.34</td>
</tr>
<tr>
<td></td>
<td>N719</td>
<td>0.76</td>
<td>6.57</td>
<td>0.66</td>
<td>3.30</td>
</tr>
</tbody>
</table>
room temperature is 0.3 mg/mL, while that of P7 and P8 is 0.5 and 0.4 mg/mL, respectively. It needs to be pointed out that it would make more sense to focus molecular optimization on P1, the top-performing dye in the series. However, different trialkylsilylethynyl groups have very different chemical tolerance toward conditions leading to P1-type chromophore, which made the TNPS and TIBS versions of P1 inaccessible.

The modification of trialkylsilyl groups should only optimize the staining process (method B) while leaving the sensitizing property unchanged due to the identical electronic structure of chromophore. Table I clearly demonstrates the solar cell performance (PCE) increased from 0.1 to 0.3% for P3 when the new fabrication method was used. Moreover, when the solubility of dye rises, PCE was enhanced even further, to 0.5% for P7 and 0.47% for P8. This improvement mainly results from a gain in $J_{SC}$, most likely due to the increase in concentration of chemisorbed dye afforded by the greater solubility.

It is worth noting that the low PCEs seen in our pentacene sensitizers also result from the device configuration: in these studies, particularly thin films of titania (3.5 $\mu$m) were employed, which limits the current produced by these dyes due to the short optical path. To have a meaningful comparison with traditional dyes, DSSCs based on N719 and organic dye JK-2 were also tested under the same experimental conditions (Table I). Their PCEs are about one-third of the best reported values, corresponding to the titania film thickness used in this study.

### 3.2 Absorption and Electrochemical Properties

As mentioned above, poor light-harvesting abilities and/or inefficient electron injection also can cause the relatively low performance of these pentacene dyes. The absorption spectra of P1–P6 solutions in THF [Fig. 4(a)] possess an intense $S_0 \rightarrow S_1$ band ($\varepsilon$ is $\sim 10^4$ M$^{-1}$ cm$^{-1}$) with fine vibronic progression in the near-IR region (between 550 and 700 nm). Figure 4(b) illustrates the absorption properties of these dyes chemisorbed onto the 3.5-$\mu$m nanocrystalline TiO$_2$ thin film.

There is no clear shift in the thin-film spectrum in comparison to the corresponding solution spectrum, indicating no obvious aggregation of dye molecules. For dyes whose photovoltaic performance in DSSCs is negatively impacted by aggregation, coadsorption of deoxycholic acid is often used to disrupt the aggregation and thus improve performance. However, TiO$_2$ nanowire array solar cells coated with a mixed monolayer of deoxycholic acid and P1–P6 were not found to exhibit any improved performance over the plain (P1–P6)–sensitized solar cells. This, together with the absence of clear shifts in the absorption data, rules out aggregation as the reason for low photocurrents. The broad absorptions extending well beyond 650 nm should yield good light harvesting for these materials.

The orbital energy levels were determined by a combination of differential pulse voltammetry (DPV) measurements and optical spectrum data (Table II). The downhill energy offset by the LUMOs of P1–P6 ($\sim -3.50$ eV versus vacuum), relative to the conduction band edge ($-4.00$ eV versus vacuum) of TiO$_2$, ensures sufficient thermodynamic driving force for electron injection. The uphill energy offset by the HOMOs ($\sim -5.00$ eV versus vacuum) with respect to that of iodide ($-4.60$ eV versus vacuum) supplies a desired negative Gibbs energy change for dye regeneration. Computational results lead to the same conclusion on the favorable energy alignment of these pentacene sensitizers.

However, the incident photon to current efficiency (IPCE) of these sensitizers reach only 5% in the near-IR absorption window of pentacene chromophore. Examples using P1 and P3 are depicted in Fig. 4(c). Although the absorption properties and orbital energies of the pentacene sensitizers are acceptable, our results point to certain electronic properties of these pentacene dyes accounting for inefficient electron injection, leading to poor IPCES and overall photocurrents.

In large conjugated systems, depending on their conformational and electronic structures, the electron-density distribution in the frontier orbitals can have a huge impact on molecular orbital mixing with the t2g/eg levels constituting the TiO$_2$ conduction band, as well as the geminate
Fig. 4 (a) Normalized absorption spectra of P1–P6 in THF. (b) Absorption spectra of P1–P6 on TiO₂ films (systematically shift along the y-axis for clarity). (c) IPCE spectra of DSSCs sensitized with P1 and P3.

charge recombination between oxidized dye molecules and photoinjected electrons in TiO₂. Therefore, the relevant photophysical process will determine the output photocurrent.

As shown in Fig. 5, an ideal example of the electron-density distribution in the HOMO and LUMO of a sensitizer is shown by the high-performance organic dye JK-2 (calculation based on reported geometry). The excited-state orbital (LUMO) populates the anchor, facilitating significant mixing with the titania conduction band and, therefore, efficient electron injection. On the contrary, P3 clearly shows a less favorable pattern. It appears that the HOMO → LUMO excitation does not significantly redistribute the electron population from the pentacene core to the carboxylic acid anchor. Although the anchoring group gains a little electron population

<table>
<thead>
<tr>
<th>Dye</th>
<th>λ_{max} (nm)</th>
<th>ε_{λ_{max}} (M⁻¹ cm⁻¹)</th>
<th>E_{0→0}^a (eV)</th>
<th>E_{HOMO}^b (eV)</th>
<th>E_{LUMO}^c (eV)</th>
<th>E_{gap}^d (eV)</th>
<th>E_{HOMO}^d (eV)</th>
<th>E_{LUMO}^d (eV)</th>
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<tbody>
<tr>
<td>P1</td>
<td>648</td>
<td>2.26 × 10⁴</td>
<td>-5.11</td>
<td>-3.36</td>
<td>1.87</td>
<td>-5.09</td>
<td>-3.22</td>
<td></td>
</tr>
<tr>
<td>P2</td>
<td>645</td>
<td>1.09 × 10⁴</td>
<td>-5.05</td>
<td>-3.28</td>
<td>1.87</td>
<td>-5.10</td>
<td>-3.23</td>
<td></td>
</tr>
<tr>
<td>P3</td>
<td>664</td>
<td>1.50 × 10⁴</td>
<td>-5.14</td>
<td>-3.50</td>
<td>1.78</td>
<td>-5.25</td>
<td>-3.46</td>
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<tr>
<td>P4</td>
<td>651</td>
<td>2.42 × 10⁴</td>
<td>-5.16</td>
<td>-3.40</td>
<td>1.84</td>
<td>-5.15</td>
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<td></td>
</tr>
<tr>
<td>P5</td>
<td>651</td>
<td>2.66 × 10⁴</td>
<td>-5.04</td>
<td>-3.27</td>
<td>1.84</td>
<td>-5.04</td>
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<tr>
<td>P6</td>
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<td>2.11 × 10⁴</td>
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<td>-3.19</td>
<td>1.85</td>
<td>-5.05</td>
<td>-3.19</td>
<td></td>
</tr>
</tbody>
</table>

^aE_{0→0} values were estimated from the onset of solution absorption spectrum.

^bE_{HOMO} versus vacuum was measured by DPV under the following conditions: Pt working electrode and Pt counter electrode; supporting electrolyte, tetrabutylammonium hexafluorophosphate, 0.1 M solution in CH₂Cl₂, scan rate 20 mV/s. For ferrocene/ferrocenium (Fc/Fc⁺) in the same conditions, E_{1/2} = -4.8 V versus vacuum.

^cE_{LUMO} versus vacuum was estimated by E_{HOMO} - E_{0→0}.

^dCalculated.
in the LUMO, most of the orbital still extends over the entire molecule. As a result, there may be less orbital mixing potentially resulting in reduced photoexcited electron injection from sensitizer into TiO$_2$. The pentacene core seems to hold delocalized electrons too strongly, even when a powerful electron-withdrawing group ($\equiv C\equiv N$) is introduced. Similar situations were observed for all the other pentacene dyes reported here. Therefore, future work involving further molecular modification to provide a system with a better distinguished ground/excited states is necessary for a highly efficient pentacene-based sensitizer. The surprisingly high efficiency of the thiophene-substituted pentacene (P6) hints that heteroacenes, with their larger, more polarizable constituents, may be more amenable for use as dyes for DSSCs.

4 Conclusions

We have demonstrated the feasibility of using acene-based dyes for DSSCs. These large aromatics show promising light-absorption profiles and have appropriate orbital energies for use in DSSCs. Enhancements in solubility allow us to dramatically increase dye loadings and device performance, and the high hole mobility of this class of materials contributes to our ultimate goal of developing oligoacene-based solid state DSSCs. Further work based on acenes and heteroacenes, such as anthradithiophene, is currently ongoing and will be reported soon.

Acknowledgments

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References


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