Anthracene based organic dipolar compounds for sensitized solar cells

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1. Introduction

In the design of organic dyes for sensitized solar cells (DSSCs), it has been established that a few key characters for an effective design of dye structures. One of them is the linear shape of molecules, which is usually a rigid rod with an electron donor (D) attached onto one terminal and an electron acceptor (A) onto the other side. During device fabrication, the dyes are absorbed on the surface of titanium oxide (TiO2) forming a densely packed monolayer that acts as a p–n junction in the circuit. Upon photoexcitation, a charge transfer (CT) transition occurs from D to A along the long axis of the molecules. In a subsequent step the negative charge is injected inside TiO2, while the positive charge is along the long axis of the molecules. In a subsequent step the excitation, a charge transfer (CT) transition occurs from D to A layer that acts as a p-conjugated chromophore with considerable rigidity, so that the dye molecules can stand vertically on the surface of TiO2. The monolayer fabricated by the dye molecules has to cover the surface of TiO2 as complete as possible to eliminate the presence of pinholes. A direct contact between TiO2 and the electrolyte at the pinholes will lead to an unwanted charge recombination, therefore reduces the quantum efficiency. A typical way of achieving the maximal coverage is to add suitable substituents onto the dye structure, such as flexible long alkyl chains or bulky groups. However, the existence of bulky substituents may also repel each other on the surface of TiO2, thus reduces the loading amount. An alternative way to achieve this goal is to enhance the ability of self-assembling of the dye molecules. A wide variety of organic dyes have been reported in the literature including the derivatives of coumarin, indoline, cyanine, perylene, dithienyl, spirobiﬂuorene, carbazole, phenothiazine, etc. In this report we examine the possibility of using anthracene as part of the spacer group to enhance the morphology of the dye. The semiconducting properties of anthracene, tetracene, and pentacene derivatives have drawn considerable attention in the researches of organic opto-electronic materials. They have been successfully applied onto a variety of devices, such as organic field effect transistors, organic light emitting diodes, and organic.

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photovoltaics. Among all acenes, anthracene possesses a size similar to the dihydrophenanthrene moiety in PA\textsuperscript{17} and the phenothiazine in PNS (Fig. 1), while both have been reported to exhibit remarkable performance in DSSCs. In our previous studies, we have also shown that by locking the central double bond of stilbene in STR, the quantum efficiency of IND could be enhanced to a degree of ca. 15%.\textsuperscript{38,39} The planar shape and higher rigidity of the central ring system in these dyes is believed to have played a critical role in their DSSC performance.

2. Results and discussion

2.1. Synthesis strategies and chemical characterization

The structures of two dyes are shown in Fig. 2. An anthracene bridge moiety is placed between the amine donor moiety and the cyanoacrylic acid acceptor of the dyes. Either a trisopropylsilylthynyl or a butyl group is substituted at the 9,10-positions of anthracene and the cyanoacrylic acid acceptor of the dyes. Either a triisopropylsilylthynyl or butyl were introduced through a reductive procedure to form 2,6-dibromoanthracene for AN-TIPS and AN-Bu, while the side groups of triisopropylsilylthynyl or butyl showed a broader bandwidth with slightly large stoke shift, revealing a larger conformational re-adjustment upon photo-excitation (Fig. S11). A higher conformational flexibility can be beneficial to the device performance, as a better surface coverage may be achieved on top of TiO\textsubscript{2} that could retard the rate of charge recombination and therefore increase the photocurrent.

2.2. Photophysical properties

The absorption spectra of dyes in dilute THF solution (3 \times 10^{-5} M) were shown in Fig. 3. They exhibit three major absorption regions appearing at 285–320 nm, 320–410 nm, and 410–550 nm. The first two regions were composed of localized aromatic $\pi-\pi^*$ transitions, and the last one was assigned to a charge-transfer (CT) transition. The CT band of AN-TIPS is slightly red-shifted with respect to that of AN-Bu, due to a $\pi$-conjugation with the TIPS substituents. The influence of $\pi$-conjugation can be shown by a comparison between AN-TIPS and AN-Bu using theoretical models, where the former exhibited a longer absorption wavelength yet a smaller extinction coefficient, i.e., $\varepsilon$=1.75 e 10$^4$ M$^{-1}$ cm$^{-1}$ and 2.50 e 10$^4$ M$^{-1}$ cm$^{-1}$, respectively (Tables 1). These values are consistent with their oscillator strengths calculated by TDDFT, i.e., 0.36 and 0.45 (Table S1). In the $\pi-\pi^*$ transition region, both AN-TIPS and AN-Bu showed a high molar extinction coefficient ($>$4.00 e 10$^4$ M$^{-1}$ cm$^{-1}$).

The dihedral angles between the planes of anthracene and the adjacent aminophenyl and thiophenyl rings were calculated to be ca. 32$^\circ$ and 23$^\circ$, respectively (Fig. 4). The absorption spectra of dyes, after they were chemisorbed onto the surface of TiO\textsubscript{2}, displayed a mild blue shift with respect to those in solutions (Fig. S10). Such a phenomenon has been observed previously, and was attributed to the reduction of electron accepting ability of the cyanoacrylate group comparing to a free carboxylic acid.\textsuperscript{45–47} The emission spectrum of AN-Bu showed a broader bandwidth with slightly large stoke shift, revealing a larger conformational re-adjustment upon photo-excitation (Fig. S11). A higher conformational flexibility can be beneficial to the device performance, as a better surface coverage may be achieved on top of TiO\textsubscript{2} that could retard the rate of charge recombination and therefore increase the photocurrent.

2.3. Electrochemical properties

The oxidation potentials ($E_{\text{onset}}$) were measured by cyclic voltammetry (CV) in THF, and the results were included in Table 1. The HOMO levels correspond to the first oxidation potentials ($E_{\text{onset}}$) of AN-TIPS and AN-Bu. The LUMO level was estimated by the values of $E_{\text{onset}}$ and the zero-zero absorption wavelength, while the latter was obtained at the intersection of absorption and emission spectra. The HOMO–LUMO energy gap of AN-TIPS (2.31) was smaller than that of AN-Bu (2.43). The estimated LUMO levels of both dyes are sufficiently higher than the conductive band level of TiO\textsubscript{2} (ca. –0.5 V vs. NHE), while their HOMO levels are sufficiently lower than that of electrolyte ion pair I$^-$/C\textsubscript{14} (ca. 0.4 V vs. NHE).\textsuperscript{49,50} It thus ensures an exothermic flow of charges through the photo-electronic conversion process (Fig. 5). The low level of HOMO (0.88 V) warrants an efficient charge regeneration after each light harvesting.

2.4. Theoretical calculation

The electronic configuration of the dyes was examined by using B3LYP/6-31G* hybrid functional implanted in a Q-Chem 3.0 software.\textsuperscript{51} For the excited states, a time-dependent density functional theory (TDDFT) with the B3LYP functional was employed. The optimized molecular geometry of AN-TIPS and AN-Bu is shown in Fig. 4. The frontier orbital plots of HOMO and LUMO were drawn by using GaussView 4.1. The HOMO/LUMO energy levels and the corresponding band gaps are listed in Fig. 5 and Table 1 (also shown in Table S1 and Fig. S13). The parameters were found to be remarkably consistent with the experimental values. The electron density of HOMO is localized mainly on the amine moiety, while the LUMO at the cyanoacrylic acid (Fig. S13). In both the ground and excited states, the distribution of electron density is heavily coupled with...
the orbitals in the central bridge linkage. The anthracene moiety therefore functions as an effective charge carrier between D and A.

The difference in Mulliken charge shift surrounding D, B, and A segments, before (S0 state) and after (S1 state) the photo-excitation, can be clearly depicted by the magnitude of bar charts (Fig. S12). Comparing with AN-TIPS, compound AN-Bu exhibits a better charge separation for more efficient electron injection. The presence of triisopropylsilyl substituents in AN-TIPS can

![Scheme 1. Synthesis route of AN-series organic dyes.](image)

![Fig. 3. Absorption spectra of the dyes in THF.](image)

![Fig. 4. Optimized molecular structure of the dyes.](image)

<table>
<thead>
<tr>
<th>Dye</th>
<th>HOMO/LUMO (eV)</th>
<th>Band gap (eV)</th>
<th>f (S1)</th>
<th>λmax (nm)</th>
<th>λmax (film)</th>
<th>λmax (nm)</th>
<th>λmax (film)</th>
<th>HOMO/LUMO (eV)</th>
<th>Eox (V)</th>
<th>E0e0 (V)</th>
<th>Ered (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN-TIPS</td>
<td>-4.99/-2.78</td>
<td>0.3580</td>
<td>2.21</td>
<td>500 (17,500)</td>
<td>492</td>
<td>611</td>
<td>-5.38/-3.07</td>
<td>0.88</td>
<td>2.31</td>
<td>-1.43</td>
<td></td>
</tr>
<tr>
<td>AN-Bu</td>
<td>-4.97/-2.67</td>
<td>0.4538</td>
<td>2.30</td>
<td>475 (25,000)</td>
<td>469</td>
<td>595</td>
<td>-5.38/-2.95</td>
<td>0.88</td>
<td>2.43</td>
<td>-1.55</td>
<td></td>
</tr>
</tbody>
</table>

f: oscillator strength for the lowest energy transition; ε: absorption coefficient; Eox: oxidation potential; E0e0: 0–0 transition energy measured at the intersection of absorption and emission spectra.

* TDDFT/B3LYP calculated values.

* Absorptions and emission were measured in THF.

* Oxidation potentials of dyes (10⁻³ M) in THF containing 0.1 M (n-C₄H₉)₄NPF₆ with a scan rate of 50 mV s⁻¹ (vs. Fc⁺/Fc).

* LUMO calculated by HOMO-E0e0.

* Ered calculated by Eox-E0e0.

* E0e0 determined from the intersection of absorption and emission in THF.

* Eox calculated by HOMO-E0e0.
stabilize both the HOMO and LUMO levels (Fig. S13). It promotes the electron donating tendency of the triphenylamine donor, yet reduced the degree of charge separation in the excited state.

2.5. DSSCs performance

The DSSCs devices made with these two dyes were fabricated according to a standard procedure. The parameters were measured under AM 1.5 solar light (100 mW cm$^{-2}$), i.e., short-circuit current ($J_{sc}$), open-circuit photovoltage ($V_{oc}$), fill factor (FF), and solar-to-electrical photocurrent density ($\eta$) are summarized in Table 2. The photocurrent—voltage ($J$–$V$) values of all devices are shown in Fig. 6. Two kinds of electrolytes were used in order to achieve the best result, i.e., system E1 was made of LiI (0.5 M), I$_2$ (0.05 M), and TBP (0.5 M) in MeCN, and system E2 was composed of 3-dimethylimidazolium iodide (DMII) (1.0 M) and guanidinium thiocyanate (0.1 M), in addition to LiI (0.05 M), I$_2$ (0.03 M), and TBP (0.5 M) in a mixed solvent of MeCN and valeronitrile (85:15, v/v). An apparent improvement of $J_{sc}$, $V_{oc}$, and FF was observed by using the new type electrolyte E2, e.g., an increase of ca. 0.05–0.07 V was obtained with respect to those using E1 (Table 2). The relative quantum efficiency of AN-Bu was higher than that of AN-TIPS, a result attributed to the higher efficiency of electron injection to the conduction band of TiO$_2$. The devices made with AN-Bu and electrolyte E2 performed quite good, with $J_{sc}$ 12.78 mA cm$^{-2}$, $V_{oc}$ 0.73 V, and FF 0.67, which summed up to an overall quantum efficiency 6.23%. The incident-photon-to-current conversion efficiency (IPCE) plots of the dyes are shown in Fig. 7. To further optimize the performance of DSSC, it is known that the alignment of dyes on the surface of TiO$_2$ is a critical factor. The organic compound needs to be planted vertically on the surface of metal oxide, and covers the surface as complete as possible. To avoid electrolyte contacting directly with TiO$_2$, the electrolyte was changed from E1 to E2. The lower concentration of LiI in E2 raised the conduction fermi level of TiO$_2$, therefore enhanced the $V_{oc}$ value. The effect is supported by the higher resistance in the electrochemical impedance spectrum (EIS). The $V_{oc}$ values of the devices using electrolyte E2 are considerably higher than those using electrolyte E1 (Table 2). The bulky side chains of both compounds also help preventing a contact between I$_3$ and the surface of TiO$_2$. The size of AN-TIPS is larger than that of AN-Bu, therefore the former is able to reduce the dark current by decreasing the rate of charge recombination better than the latter.

Electrochemical impedance spectroscopic (EIS) analysis was performed to further elucidate the photovoltaic property. The EIS for the DSSCs made with these compounds were taken under a forward bias of −0.73 V in the dark. In the Nyquist plot (Fig. 8), a major semicircle was observed in a frequency range of 20–100 Hz, which is related to the transport process of injected electrons at the interfaces between TiO$_2$ and the electrolyte/dye.

The charge recombination resistance ($R_{rec}$) can be deduced by fitting the curves using a Z-view software. It is related to the charge recombination rate at the TiO$_2$ surface of DSSC, e.g., a larger $R_{rec}$ indicates a slower charge recombination and therefore a larger $V_{oc}$ values. The radius of the semicircle was enlarged along by using

Fig. 5. Energy levels of HOMO and LUMO of dyes.

Fig. 6. $J$–$V$ curves of the dyes, with a comparison to N719.

Fig. 7. IPCE plots of the dyes, with a comparison with N719.

| Table 2 Photovoltaic parameters under AM 1.5 |
|-----------------|--------------|-------------|--------|-----------------|
| Dye            | E1/E2        | $J_{sc}$ (mA cm$^{-2}$) | $V_{oc}$ (V) | FF   | Dye Loading (%) |
| AN-TIPS        | E1           | 11.59        | 0.67       | 0.63 | 5.06            | 2.48 |
|                | E2           | 11.61        | 0.72       | 0.65 | 5.42            |       |
| AN-Bu          | E1           | 13.33        | 0.66       | 0.64 | 5.60            | 4.53 |
|                | E2           | 12.78        | 0.73       | 0.67 | 6.23            |       |
| N719           | E1           | 16.89        | 0.73       | 0.60 | 7.38            |       |
|                | E2           | 15.46        | 0.76       | 0.64 | 7.52            |       |

$J_{sc}$: short-circuit photocurrent density; $V_{oc}$: open-circuit photovoltage; FF: fill factor; $\eta$: total power conversion efficiency.

$^a$ Electrolyte 1 (E1): LiI (0.5 M), I$_2$ (0.05 M), and TBP (0.5 M) in MeCN. Electrolyte 2 (E2): 3-dimethylimidazolium iodide (1.0 M), LiI (0.05 M), I$_2$ (0.03 M), guanidinium thiocyanate (0.1 M), and TBP (0.5 M) in MeCN/valeronitrile (85:15, v/v).

$^b$ Performance of DSSC measured in a 0.25 cm$^2$ working area on an FTO (8 Ohm square) substrate.
The effect of anthracene for improving the film morphology was examined by using deoxycholic acid (DCA). For some dyes that were not able to form high quality films, the addition of DCA as a co-absorbent can effectively improve the film morphology, and consequently reduce the rate of charge recombination. However, the addition of DCA may not improve the devices whose morphology are already of sufficient quality. Upon the addition of DCA as a co-absorbent (10 mM), the open-circuit voltage was found not to be changed in a significant amount (Table 3). This is a firm evidence supporting our initial assumption that the inclusion of an anthracene unit in the structure of dyes can enhance the self-assembling ability for forming a high quality film. The FF values also stayed nearly the same in the range of 0.63–0.64. As it would be expected, the values of short-circuit current were reduced. The \( J_{sc} \) values were dropped from 11.99 to 10.66 mA cm\(^{-2}\) for AN-TIPS and from 13.33 to 11.87 mA cm\(^{-2}\) for AN-Bu. An overall reduction of quantum efficiency in 8.30–9.28% was observed (Fig. 9). The decrease of \( J_{sc} \) value can be readily explained by a lower amount of loading, because the surface of TiO\(_2\) was partly occupied by DCA (Fig. S21). The new design of including an anthracene moiety in organic dyes does provide a profound effect of improving film morphology.

### Table 3

<table>
<thead>
<tr>
<th>Dye( ^a )</th>
<th>DCA (mM)</th>
<th>( J_{sc} ) (mA cm(^{-2}))</th>
<th>( V_{oc} ) (V)</th>
<th>FF</th>
<th>( \eta ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN-TIPS</td>
<td>0</td>
<td>11.99</td>
<td>0.67</td>
<td>0.63</td>
<td>5.06</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>10.66</td>
<td>0.69</td>
<td>0.63</td>
<td>4.61</td>
</tr>
<tr>
<td>AN-Bu</td>
<td>0</td>
<td>13.33</td>
<td>0.66</td>
<td>0.64</td>
<td>5.60</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>11.87</td>
<td>0.68</td>
<td>0.63</td>
<td>5.08</td>
</tr>
<tr>
<td>AN-26( ^b )</td>
<td>0</td>
<td>16.63</td>
<td>0.71</td>
<td>0.64</td>
<td>7.52</td>
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<td></td>
<td>10</td>
<td>18.44</td>
<td>0.74</td>
<td>0.66</td>
<td>9.11</td>
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<td>AN-910A( ^c )</td>
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<td>6.00</td>
<td>0.565</td>
<td>0.648</td>
<td>2.20</td>
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<tr>
<td></td>
<td>10</td>
<td>5.39</td>
<td>0.678</td>
<td>0.797</td>
<td>2.91</td>
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<tr>
<td>AN-910B( ^d )</td>
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<td>6.00</td>
<td>0.565</td>
<td>0.648</td>
<td>2.20</td>
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<td>5.39</td>
<td>0.678</td>
<td>0.797</td>
<td>2.91</td>
</tr>
</tbody>
</table>

\( J_{sc} \): short-circuit photocurrent density; \( V_{oc} \): open-circuit photovoltage; FF: fill factor; \( \eta \): total power conversion efficiency.

\( ^a \) Concentration of dye is \( 3 \times 10^{-3} \) M in THF.

\( ^b \) Performance of DSSC measured in a 0.25 cm\(^2\) working area on an FTO (8 Ω/square) substrate with electrolyte 1 (E1) under AM 1.5 condition.

\( ^c \) Ref. 65.

\( ^d \) Ref. 36.

\( ^e \) Ref. 66.

A comparison of our results with a few recent reports involving anthracene is instructive (Fig. 10). The remarkable performance of compound AN-26, prepared by Lin and Ho, reached the highest quantum efficiency of 9.11% in the presence of DCA (Table 3). It took the advantage of high \( J_{sc} \) value induced by the 2,6-substituted anthracene unit. In another two reports of AN-910A and AN-910B, \( J_{sc} \) values of the anthracene units were substituted at the 9 and 10 positions, the quantum efficiencies were reduced to 2–3%. The \( J_{sc} \) values were substantially reduced due to the lower degree of \( \pi \)-conjugation along the main chromophore. These results strongly implies that a 2,6-disubstituted anthracene can act a highly efficient spacer group, significantly better than the 9,10-disubstituted derivative, in the design of organic dyes for DSSCs.

### 3. Conclusion

The 2,6-disubstituted anthracene derivatives, AN-TIPS and AN-Bu, were proven to be effective dyes for the application on DSSCs. The planar shape of anthracene, along with the bulky TIPS and butyl substituents, exhibited a good film-forming property on the surface of TiO\(_2\). Both dyes displayed remarkable solar-to-energy conversion efficiency. A typical device made with AN-Bu dye performed a maximal photon-to-current conversion efficiency (IPCE) 65% in the region of 350–510 nm, a short-circuit photocurrent...
4.1. General information

All reactions and manipulations were carried out under a nitrogen atmosphere. Solvents were distilled freshly according to standard procedures. $^1$H and $^{13}$C NMR spectra were recorded on Brucker (AVIII 300/AV 400/AV 500 MHz) spectrometer in CDCl$_3$, THF-d$_8$, and DMSO-d$_6$ as a solvent. Chemical shifts are reported in scale downfield from the peak for tetramethylsilane. Absorption spectra were recorded on a Jasco-550 spectrophotometer. Emission spectra were obtained from a Hitachi F-4500 spectrophuorometer. The emission spectra in solutions were measured in spectral grade solvent by a 90° angle detection. The redox potentials were measured by using cyclic voltammetry on CHI 620 analyser. The data were collected and analyzed using electrochemical analysis software. All measurements were carried out in THF solutions containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as supporting electrolyte at ambient condition after purging 10 min with N$_2$. The conventional three electrode configuration was employed, which consists of a glassy carbon working electrode, a platinum counter electrode, and a Ag/AgNO$_3$ (0.1 M) reference electrode calibrated with ferrocene/ferroenium (Fc/Fc$^+$) as an internal reference with a scan rate of 50 V s$^{-1}$. Mass spectra were recorded on a VG70-2509 mass spectrometer. The cell containing the solution of the sample (1 mM) and the supporting electrolyte was purged with nitrogen gas thoroughly before measurements. The oxidation potentials of organic dyes were estimated by averaging the anodic and cathodic peak potentials. The HOMO and LUMO values were calculated with reference to the ferrocene oxidation potential by using the following equations: HOMO = $E_{ox} + 4.8$ eV; LUMO = HOMO - $E_{eq}$, where the HOMO of ferrocene was set at 4.8 eV.

The chemicals, i.e., 2,6-diaminoanthracene-9,10-dione-copper (II) bromide, tert-butyl nitrite (t-BuONO), trisopropylsilylethynyl acetylene, tin(II) chloride dihydrate (SnCl$_2$·2H$_2$O), tetrakis(triphenylphosphine)palladium (Pd[PPh$_3$]$_4$), N-butylthiophene (1.6 M in hexane), trans-dichlorobis(triphenylphosphine)palladium (II) (PdCl$_2$(PPh$_3$)$_2$)$_2$, NN-dimethylformamide, N-bromosuccinimide (NBS), tri-n-butyl chloride, cyanoacetic acid, ammonium acetate, and acetic acid glacial, were purchased from ACROS, Alfa, Merck, Lancaster, TCI, Sigma-Aldrich, Showa, separately, and purified while necessary. Chromatographic separations were carried out by using silica gel from Merk, Kieselgel si 60 (40–63 μm). All structures were confirmed by their spectroscopic data were provided in Supplementary data.

4.1.2. 2,6-Dibromoanthracene-9,10-dione (4a). To a three-necked flask containing a mixture of 2,6-diamoanthracene-9,10-dione (5 g, 21.0 mmol), CuBr$_2$ (11.72 g, 52.5 mmol), and t-BuONO (6.3 mL, 52.5 mmol) was added acetonitrile (250 mL). The reaction mixture was stirred at 90 °C for 24 h. After cooling, the mixture was quenched by adding 20% HCl, and filtered to give brown solid in 97% yield (7.5 g, 20.5 mmol); mp 157–159 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.43 (s, 2H), 6.97 (d, 2H, J = 8.4 Hz), 7.79 (d, 2H, J = 8.4 Hz). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 137.4, 130.4, 129.1; MS (EI, 70 eV): m/z (relative intensity) 363 (M$^+$, 100); HRMS calcd for C$_{14}$H$_8$Br$_2$O$_2$: 363.8735, found 363.8744.

4.1.3. 2,6-Dibromo-9,10-dibutylanthracene (3b). A mixture of 3a (200 mg, 0.3 mmol), 4-(diphenylamino)phenylboronic acid (83 mg, 0.3 mmol), Pd(PPh$_3$)$_4$ (10.4 mg, 0.009 mmol) in 2 M K$_2$CO$_3$/THF/toluen (90 °C) in a three-necked flask under a nitrogen atmosphere. After 4 h, the reaction mixture was warmed up to room temperature and washed with brine. The mixture was extracted with CH$_2$Cl$_2$, then the organic layer was dried over anhydrous MgSO$_4$. Evaporation of the solvent gave a crude product, which was purified by silica gel column chromatography eluted with hexane. Yellow solid was obtained in 43% yield (4.1 g, 5.9 mmol). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.80 (s, 2H), 8.13 (d, 2H, J = 9.5 Hz), 7.54 (dd, 2H, J = 9.5, 1.5 Hz), 3.47 (t, 4H, J = 8.0 Hz), 1.71–1.78 (m, 4H), 1.56–1.62 (m, 4H), 1.03 (d, 6H, J = 7.5 Hz). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 133.7, 130.5, 128.8, 123.8, 127.2, 127.1, 119.9, 33.5, 27.3, 21.4, 14.0. MS (EI, 70 eV): m/z (relative intensity) 695 (M$^+$, 100); HRMS calcd for C$_{29}$H$_{16}$Br$_2$: 446.0245, found 446.0253.

4.1.4. N-(4-(2-Bromo-9,10-bis(2-(triisopropylsilyl)ethynyl)phenyl)anthracen-6-yl)(phenyl)amine (4a). A mixture of 3a (200 mg, 0.3 mmol), 4-(diphenylamino)phenylboronic acid (83 mg, 0.3 mmol), Pd(PPh$_3$)$_4$ (10.4 mg, 0.009 mmol) in 2 M K$_2$CO$_3$/THF/toluene at 90 °C for 4 h in a three-necked flask under a nitrogen atmosphere. After 4 h, the reaction mixture was warmed up to room temperature and washed with brine. The mixture was extracted with CH$_2$Cl$_2$, then the organic layer was dried over anhydrous MgSO$_4$. Evaporation of the solvent gave a crude product, which was purified by silica gel column chromatography eluted with CH$_2$Cl$_2$ hexane. Yellow solid was obtained in 61% yield (157.4 mg, 0.18 mmol); mp 141–143 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.81–8.82 (m, 2H), 8.61 (d, 1H, J = 8.9 Hz), 8.46 (d, 1H, J = 9.1 Hz), 7.90 (dd, 1H, J = 9.1, 1.6 Hz), 7.68 (d, 2H, J = 8.7 Hz), 7.63 (dd, 1H, J = 9.0, 1.9 Hz), 7.29 (t, 4H, J = 7.8 Hz), 7.16–7.19 (m, 6H), 7.05 (t, 2H, J = 7.2 Hz), 1.2–1.3 (m, 42H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 147.5, 138.8, 134.0, 133.2, 132.2, 131.81, 130.3, 130.3, 130.1, 139.3, 129.1, 128.9, 128.0, 127.8, 124.5, 124.1, 123.9, 123.7, 123.1, 122.6, 121.3, 118.8, 117.6, 105.6, 104.2, 102.7, 18.9, 18.8, 11.5. MS (FAB, 70 eV): m/z (relative intensity) 860 (M$^+$, 100); HRMS calcd for C$_{50}$H$_{30}$Br$_2$N$_6$: 860.3682, found 860.3704.

4.1.5. N-(4-(2-Bromo-9,10-dibutylanthracen-6-yl)phenyl)-N-phenylbenzenamine (4b). Compound 4b was synthesized according to the same procedure as that of 4a. Yellow solid of 4b was obtained in 33% yield. Mp 101–103 °C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.40 (s, 2H), 8.13 (d, 2H, J = 9.5 Hz), 7.54 (dd, 2H, J = 9.5, 1.5 Hz), 3.47 (t, 4H, J = 8.0 Hz), 1.71–1.78 (m, 4H), 1.56–1.62 (m, 4H), 1.03 (d, 6H, J = 7.5 Hz). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 133.7, 130.5, 128.8, 123.8, 127.2, 127.1, 119.9, 33.5, 27.3, 21.4, 14.0. MS (EI, 70 eV): m/z (relative intensity) 446 (M$^+$, 100); HRMS calcd for C$_{29}$H$_{18}$Br$_2$: 446.0245; found 446.0253.
4.1.5. 5-(2-(4-(Diphenylamino)phenyl)-9,10-bis(2-(triisopropyl-silyl)ethynyl)anthracen-6-yl)thiophene-2-carbaldehyde (6b). A mixture of 4a (500 mg, 0.6 mmol), (5-(13-dioxolan-2-yl)-thiophene-2-yl) tributylstannane (517 mg, 1.2 mmol), PdCl2(PPh3)2 (204 mg, 0.03 mmol) were dissolved in dry DMF, then heated to 90 °C with stirring. After 24 h, the reaction was cooled to room temperature, then quenched by the addition of methanol and saturated KFaq (15 mL). The mixture was extracted with CH2Cl2, while the organic layer was dried over anhydrous MgSO4. Evaporation of the solvent gave a crude product. The crude mixture was added Acetic acid/T2H/de-ionized water (40/20/10 mL) at 90 °C. After 3 h, the reaction was quenched by adding de-ionized water and brine. To mixture extracted with CH2Cl2, and the organic layer was dried over anhydrous MgSO4 and evaporated under vacuum, which was purified by silica gel column chromatography eluted by CH2Cl2/hexane (1/4). Red solid of 6a was obtained in 55% yield (285 mg, 0.3 mmol); mp 165–167 °C; 1H NMR (400 MHz, CDCl3): δ 9.94 (s, 1H), 9.00 (s, 1H), 8.85 (s, 1H), 8.66 (d, 2H, J = 8.9 Hz), 7.83–7.93 (m, 2H), 7.81 (d, 1H, J = 3.9 Hz), 7.70 (d, 2H, J = 8.5 Hz), 7.61 (d, 1H, J = 3.8 Hz), 7.30 (t, 4H, J = 7.8 Hz), 7.17–7.20 (m, 6H), 7.0 (t, 2H, J = 7.3 Hz), 1.2–1.3 (m, 42H); 13C NMR (100 MHz, CDCl3): δ 182.5, 154.0, 147.8, 147.5, 142.8, 139.0, 137.3, 133.9, 133.3, 132.4, 132.1, 131.9, 130.9, 129.3, 128.4, 128.0, 127.8, 126.9, 124.9, 124.6, 123.9, 123.6, 123.1, 119.1, 118.6, 105.9, 105.52, 103.0, 102.8, 119.1, 118.5; MS (FAB, 70 eV): m/z (relative intensity) 892 ((M+H)+, 100); HRMS calcd for C55H54NOSSi2: 892.4404, found 892.4438.

4.1.6. 5-(2-(4-(Diphenylamino)phenyl)-9,10-dibutyl-anthracen-6-yl)thiophene-2-carbaldehyde (AN-Bu). Compound AN-Bu was synthesized according to the same procedure as that of AN-TIPS. Dark red solid of AN-Bu was obtained in 70% yield; mp 159–161 °C; IR (KBr) v max 3526, 2955, 2852, 1683, 1498, 1431 cm−1; 1H NMR (400 MHz, CDCl3): δ 8.47 (s, 1H), 8.45 (s, 1H), 8.44 (d, 1H, J = 2.0 Hz), 8.42 (d, 1H, J = 2.1 Hz), 8.40 (s, 1H), 7.94 (d, 1H, J = 4.0 Hz), 7.88 (d, 1H, J = 9.2 Hz), 7.85 (d, 1H, J = 9.2 Hz), 7.78 (d, 1H, J = 3.9 Hz), 7.74 (d, 2H, J = 8.4 Hz), 7.28 (t, 4H, J = 7.7 Hz), 7.18 (d, 2H, J = 8.4 Hz), 7.13 (d, 4H, J = 7.9 Hz), 7.03 (t, 2H, J = 7.7 Hz), 3.68–3.76 (m, 4H), 1.81–1.88 (m, 4H), 1.60–1.68 (m, 4H), 1.10 (t, 3H, J = 7.3 Hz), 1.04 (t, 3H, J = 7.3 Hz); 13C NMR (100 MHz, CDCl3): δ 164.4, 148.8, 148.7, 146.3, 139.9, 138.2, 136.6, 136.0, 135.9, 135.1, 131.6, 130.6, 130.4, 130.3, 130.2, 130.1, 128.8, 127.0, 126.0, 125.7, 125.5, 124.8, 124.1, 123.8, 122.7, 116.9, 34.9, 34.8, 28.6, 28.5, 14.7, 14.6; MS (FAB, 70 eV): m/z (relative intensity) 710 ((M+H)+, 100); HRMS calcd for C49H42N2O2S: 710.2967, found 710.2991.

4.2. Fabrication of DSSCs and characterization of DSSCs

The FTO conducting glass (FTO glass, fluorine doped tin oxide over-layer, transmission >90% in the visible, sheet resistance 8 Ω square−1), titanium-oxide oxides of Ti-Nanoxide T/SP and Ti-Nanoxide R/SP were purchased from Solaronix. A thin film of TiO2 (16–18 μm thick) was coated on a 0.25 cm2 FTO glass substrate, while the thickness was measured by Veeco Dektak 150. It was immersed in a THF solution containing 3·10−3 M dye sensitizers for at least 12 h, then rinsed with anhydrous acetonitrile and dried. Another piece of FTO with sputtering 100 nm thick Pt was used as a counter electrode. The active area was controlled at a dimension of 0.25 cm2 by adhering 60 μm thick polyester tape on the Pt electrode. The photocathode was placed on top of the counter electrode and was tightly clipped together to form a cell. Electrolyte was then injected into the seam between two electrodes. Two kinds of electrolytes were used in order to achieve the best result, i.e., system E1 was made of LiI (0.5 M), I2 (0.05 M), and TBP (4-cetylpyridine) (0.5 M) in MeCN, and system E2 was composed of 3-dimethylimidazolium iodide (DMDI) (1.0 M) and guanidinium thiocyanate (0.1 M), in addition to LiI (0.05 M), I2 (0.03 M), and TBP (0.5 M) in a mixed solvent of MeCN and valeronitrile (85:15, v/v). Devices made of a commercial dye N719 under the same condition (3·10−3 M, Solaronix S.A., Switzerland) was used as a reference.

The cell parameters were obtained under an incident light with intensity 100 mW cm−2 measured by a thermopile probe (Oriel 71964), which was generated by a 300 W Xe lamp (Oriel 6258) passing through an AM 1.5 filter (Oriel 81088). The current-voltage parameters of DSSCs were recorded by a potentiotstat/galvanostat model CH650B (CH Instruments, USA). The light intensity was further calibrated by an Oriel reference solar cell (Oriel 91150) and adjusted to be 1.0 sun. The monochromatic quantum efficiency was recorded through a monochromator (Oriel 74100) at short-circuit condition. Electrochemical impedance spectra of DSSCs were recorded by an Impedance/Gain-Phase analyzer (SI 1260, Solartron).

4.3. Theoretical calculation

All organic dyes were optimized by using B3LYP/6-31G* hybrid functional. Geometry optimizations were performed to locate the minima on the potential energy surface, in order to predict the equilibrium structure of a given molecule. For the excited states,
a time-dependent density functional theory (TDDFT) with the B3LYP functional was employed. All analyses were performed under Q-Chem 3.0 software. The frontier orbital plots of HOMO and LUMO were drawn by using Gaussian 03. All calculations were performed using the Gaussian 03 suite of programs.

Acknowledgements

Financial supports from the National Science Council of Taiwan and Academia Sinica are gratefully acknowledged. (NSC 101-2113-M-035-001-MY2) Special thanks to Professor C.-P. Hsu in the Institute of Chemistry, Academia Sinica, for the assistance on Quantum chemistry computations.

Supplementary data

1H and 13C NMR spectra of all compounds, absorption spectra and emission spectra in THF solution, absorption spectra on TiO2 film, TDDFT calculated orbitals, Mulliken charges, low energy transitions, CV spectra, HOMO/LUMO level, and EIS spectra. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.11.072

References and notes