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Anionic benzothiadiazole containing polyfluorene and oligofluorene as organic sensitizers for dye-sensitized solar cells†

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Received (in Cambridge. UK) 26th March 2008, Accepted 8th May 2008
First published as an Advance Article on the web 23rd June 2008
DOI: 10.1039/b805060k

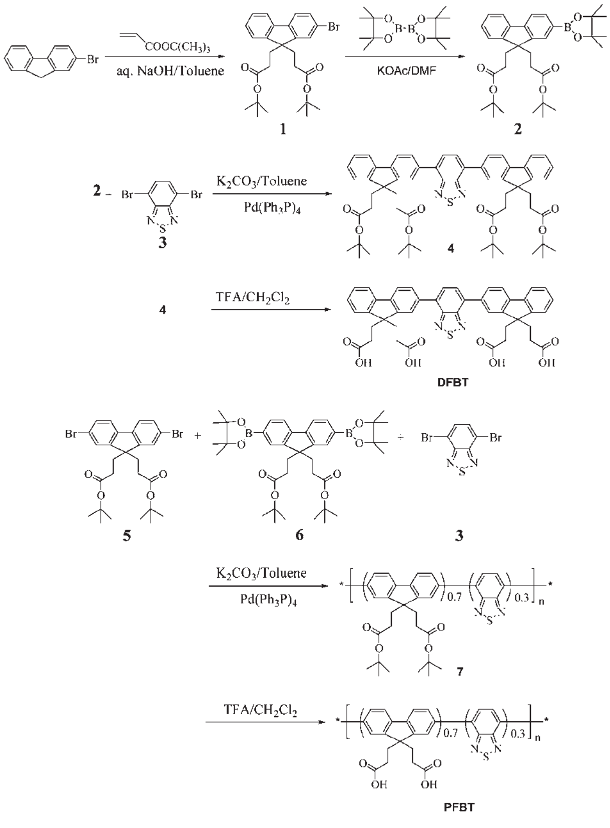
Anionic polyfluorene and oligofluorene derivatives were synthesized and utilized as organic dye sensitizers in dye sensitized solar cells to show a maximum power conversion efficiency of 1.39%.

Dye-sensitized solar cells (DSSCs) are promising photovoltaic devices with low cost and high light-to-electrical conversion efficiency.[1,2] The highest conversion efficiency for DSSCs was reported to be ~11%, which makes DSSCs potential candidates for commercial applications. One of the key elements of DSSCs is the dye sensitizer, which engages in both the light absorption process and the charge separation process. The most widely used dyes for DSSCs are Ru complexes.[3,4] However, Ru is a rare metal at high cost with a low annual yield. Therefore, great efforts have been made toward replacing Ru based dyes with pure organic dyes. The majority of the research on organic dyes is focused on π-conjugated small molecules,[5–14] and very few is on π-conjugated polymers.

Conjugated polymers are promising materials for low cost devices.[15] They have been widely used in field effect transistors,[16] light emitting diodes,[17] sensors[18] and hybrid solar cells.[19] Conjugated polymers were reported to have large absorption coefficients and tunable band gaps that span the whole visible and near-IR spectrum.[20] In addition, various strategies have been developed to fine tune the HOMO and LUMO energy levels of the polymers.[21] This property is essential for DSSCs since the high efficiency can only be achieved when the excited state charge transfer from the polymer to the photoanode is allowed and the photo-oxidized polymer can be easily reduced by the electrolyte. Recent developments in conjugated polyelectrolytes also provide the opportunity to synthesize anionic conjugated polymers with carboxylate[22] or phosphonate functionalities.[23] These functional groups are essential for firmly grafting polymers to the semiconductor oxide surface through self-assembly.

The application of conjugated polyelectrolytes as dye sensitizers in DSSCs has recently been reported.[24–26] Poly(3-thiophene acetic acid) was used as the dye for DSSCs with efficiencies varied from 0.4% to 2.4%.[24] A dual polymer system which includes a carboxylated poly(*p*-phenylene ethynylene) and a carboxylated polythiophene was also used to expand the light absorption to yield a power conversion efficiency of 0.89%.[25] Recently hyperbranched conjugated polymers with both anionic and cationic functional groups were developed for DSSCs.[26] A device efficiency of 0.62% was reported for DSSCs using self-assembled multilayer polymers.[26] The overall performance of conjugated polyelectrolyte based DSSCs is lower than DSSCs fabricated with Ru dyes, and great opportunities arise to improve the device performance through polymer design and device fabrication.

In this communication, we report the synthesis and characterization of an anionic conjugated polymer and the corresponding oligomer comprising the same ratio of fluorene and benzothiadiazole units. The application of these materials as dyes in DSSCs is studied, and the performance of the devices is compared. This work represents the first application of anionic polyfluorene derivatives as dye sensitizers in nanocrystalline TiO_2 solar cells.



Scheme 1 Synthesis and molecular structure of the polymer (**PFBT**) and the oligomer (**DFBT**).

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† Electronic supplementary information (ESI) available: Synthesis and analytical details. See DOI: 10.1039/b805060k

The synthetic entry to the polymer and the oligomer is shown in Scheme 1. The monomers 2,7-dibromo-9,9-bis(3′-(*t*-butylpropanoate))fluorene (**5**) and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(3′-(*t*-butylpropanoate)) fluorene (**6**) were synthesized according to the previous report.[22] Direct alkylation of 2-bromofluorene using *t*-butylacrylate in a mixture of toluene–aq. NaOH gave 2-bromo-9,9-bis(3′-(*t*-butylpropanoate))fluorene (**1**), in 66% yield. Conversion of **1** to the boronic ester **2** was achieved under the Miyaura reaction conditions in the presence of bis(pinacolato)diborane, Pd(dppf)$_2$Cl$_2$ and KOAc using dry dimethylformamide (DMF) as the solvent. Coupling between two equivalents of **2** and one equivalent of 4,7-dibromo-2,1,3-benzothiadiazole (**3**) under the Suzuki coupling conditions yielded the neutral oligomer **4** in 70% yield. Similarily, Suzuki polymerization between monomers **5**, **6** and **3** yielded polymer **7** in 65% yield. In the last step, the neutral polymer **7** and oligomer **4** were treated with trifluoroacetic acid (TFA) in CH_2Cl_2 (v/v = 1/1) at room temperature to yield the anionic oligomer **DFBT** and the anionic polymer **PFBT**. The structure and purity of **DFBT** and **PFBT** were confirmed with NMR spectroscopies. From the ratio of the integrated area for the signal at ~8.2 ppm for protons of benzothiadiazole units to that at 7.7–7.9 ppm for aromatic protons of fluorene segments, the content of benzothiadiazole units within **PFBT** is estimated to be ~29.5 %. Polymer **7** has a weight molecular weight of 11 000 and a polydispersity of 1.8, measured in tetrahydrofuran using polystyrene as the standard.

Fig. 1 shows the normalized UV-vis spectra of **DFBT** and **PFBT** in DMF solution. The absorption spectrum of **DFBT** is in the range of 340 to 490 nm, with the absorption maximum at 420 nm. As compared to **DFBT**, the absorption maximum for **PFBT** is red-shifted by 24 nm to 444 nm, and the spectrum covers the range of 280 to 510 nm. As compared to that for **PFBT**, the absorption spectrum for **DFBT** is narrower and closer to the UV range. Based on the fact that solar light has a continuous spectrum, and 40%–50% of solar light energy is in the visible light range (400 nm–700 nm), therefore, a smaller part of the solar light can be utilized by **DFBT**, relative to that of **PFBT**.

The electrochemical properties of **DFBT** and **PFBT** were studied using cyclic voltammetry in DMF. The results are summarized in Table 1 (ESI†) The onset oxidation potential was measured to be 1.34 V and 1.25 V (*vs.* Ag/Ag$^+$) for **DFBT** and **PFBT**, respectively. The HOMO energy levels of **DFBT** and **PFBT** were thus calculated to be −5.69 eV and −5.60 eV, respectively.[27] From the onset of the absorption spectrum, the energy gap is determined to be 2.44 eV for **PFBT** and 2.53 eV for **DFBT**, respectively. The excited state oxidation potential (E^*_{ox}, corresponding to LUMO) is calculated from the energy gap (E_{0-0}) by $E^*_{ox} = E_{ox} - E_{0-0}$ to be −1.19 V for both **PFBT** and **DFBT**. This gives the same LUMO energy for **PFBT** and **DFBT** as −3.26 eV. For both **DFBT** and **PFBT**, the LUMO energy level is energetically higher than the conduction band of TiO$_2$ (−4.2 eV), and consequently, electron injection from the single excited state of **DFBT** and **PFBT** into TiO$_2$ is energetically feasible. In addition, the oxidation potential of **DFBT** and **PFBT** is sufficiently more positive than the stantard redox potential of the iodine/iodide couple (0.335 V *vs.* Ag/AgCl), therefore, the photo-oxidized dye molecules could be efficiently reduced by the iodide ions.

Nanostructured TiO$_2$ solar cells with **PFBT** or **DFBT** as the sensitizers were fabricated. Fluorine doped SnO$_2$/glass (FTO glass, 15 ohm, Asahi) was used as the substrate. The photoanodes of DSSCs were obtained by doctorblading the commercial TiO$_2$ paste (Ti-nanoxide T/SP, Solaronix). After the TiO$_2$ layer was sintered at 450 °C, it was immersed into the **PFBT** or **DFBT** solution in DMF at 45 °C for 48 h. The dye-sensitized TiO$_2$ layer was then rinsed with DMF and dried under nitrogen. The counter electrode was FTO glass with a sputtered platinum layer. The electrolyte composed of 1.0 M LiI, 0.5 M 4-*tert*-butylpyridine and 0.05 M iodine in acetonitrile was applied to the cell.

Fig. 2 shows the incident photon to current conversion efficiency (IPCE) obtained with cells using **PFBT** or **DFBT** as the sensitizers. The maximum IPCE value (~35%) for both **PFBT** and **DFBT** based DSSCs is similar, indicating the similar electron injection efficiency for both dyes. This agrees with the same energy difference between the LUMO level of the dyes and the conductive band position of TiO$_2$. The IPCE spectrum for **PFBT** based DSSC confirms the analysis from the absorption spectra that **PFBT** has a red shifted and broadened light response as compared to that of **DFBT**. As the relatively narrow absorption peak is one of the main drawbacks for organic dyes, this result indicates that polymers could potentially be more efficient dye sensitizers for DSSCs.

The power conversion efficiency of **PFBT** or **DFBT** sensitized solar cells was evaluated under the AM1.5 100 mW cm^{-2} light illumination. The photocurrent density—photovoltage curves for the cells are shown in Fig. 3. The performance of the cells,

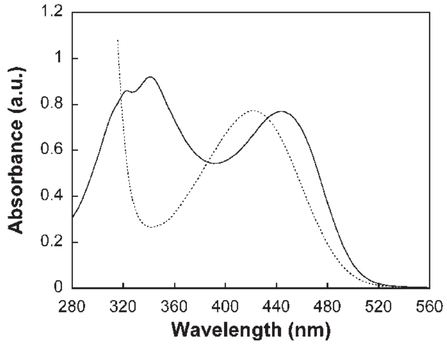

Fig. 1 Normalized absorption spectra of **PFBT** (solid line) and **DFBT** (dashed line) in DMF.

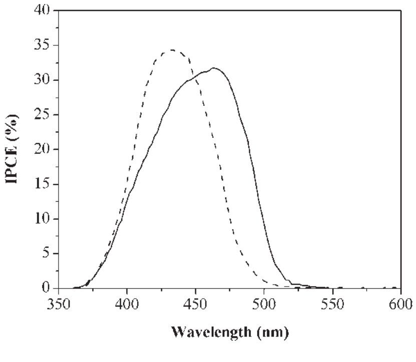

Fig. 2 IPCE spectra of **PFBT** based DSSC (solid line) and **DFBT** based DSSC (dashed line).

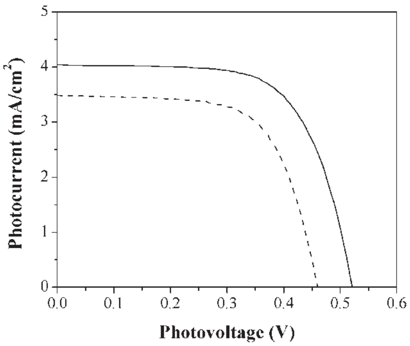

Fig. 3 Photocurrent–voltage curves of PFBT based DSSC (solid line) and DFBT based DSSC (dash line).

which includes the short circuit current density, open circuit voltage, fill factor and the power conversion efficiency is summarized in Table 1. The **PFBT** sensitized cell gave a short circuit photocurrent density of 4.03 mA cm^{-2}, an open circuit voltage of 523 mV, and a fill factor of 0.66, which yielded an efficiency of 1.39%. During the study, we found that both BT contents in the polymer and the polymer molecular weight affected the DSSC performance. A polymer of similar molecular weight to **7**, but with 50% benzothiadiazole content gave efficiencies around 1.1%–1.2%, which was potentially due to the reduced number of carboxylic acid groups that affected the dye–TiO_2 interaction. On the other hand, a polymer containing 30% BT, but with a weight molecular weight of 30 000 led to an even poorer device performance (0.8%–0.9% in efficiency). The low performance for large molecular weight polymers is generally believed to be due to the difficulty for polymer penetration into the TiO_2 porous structure. By contrast, the **DFBT** sensitized cell gave a short circuit photocurrent density of 3.47 mA cm^{-2}, an open circuit voltage of 459 mV, and a fill factor of 0.66, corresponding to an overall efficiency of 1.05%.

Based on the fact that **PFBT** and **DFBT** have a very small difference in HOMO and LUMO energy levels, and the maximum IPCE value for devices fabricated with both materials is similar, the higher short-circuit current density for **PFBT** based cells could be attributed to the broadened and red shifted light response of **PFBT**, which allows more electrons to be injected into the conductive band of TiO_2. Under the open-circuit condition, since there is no output current, the electron recombination velocity equals to the electron injection velocity.[28]

$$V_{oc} = (k_B T/\beta\cdot e)\cdot\ln(U/(n_0^{\beta}\cdot k_r)) \qquad (1)$$

Eqn (1)[29] shows the relationship between the open circuit voltage and the electron recombination velocity, where V_{oc} is the open circuit voltage, T is the temperature, β is a constant, U is the electron recombination velocity, n_0 is the electron density in the dark and k_r is the velocity constant of electron recombination. It is thus easy to understand that **PFBT** based DSSCs have a higher open circuit voltage as compared to that for **DFBT** based DSSCs.

In conclusion, we synthesized a conjugated polymer and an oligomer which are composed of fluorene and benzothiadiazole units. Both molecules were used to fabricate DSSCs, yielding an efficiency of 1.39% and 1.05% (under AM1.5 100 mW cm^{-2} light illumination), respectively, for the polymer and oligomer sensitized DSSCs. The better performance of polymer based DSSCs comes from the red-shifted and broadened absorption spectrum of the polymer relative to that of the oligomer. This result indicates that developing polymer dye sensitizers that incorporating the design strategy for organic small dyes could yield more efficient sensitizers for DSSCs. To further improve the efficiency of polymer based DSSC, new polymer dyes that could better favor electron injection are desirable.

The authors are grateful to the A-Star of Singapore (R-279-000-221-305) for financial support.

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