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N-Annulated Perylene as a Donor in Cyclopentadithiophene Based Sensitizers: The Effect of Linking Mode

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Two types of cyclopentadithiophene dyes with different linking mode with an *N*-annulated perylene (NP) donor were designed and synthesized. These new dyes were applied in Co(II)/(III) based dye-sensitized solar cells and efficiency up to 7.8% could be obtained for *peri*-NP linked CPD-1. The effect of the linking mode on the material properties and device performance was discussed.

Dye-sensitized solar cells (DSCs) have attracted extensive attention because of their high efficiencies, simple fabrication, and low production costs.¹ Considerable efforts have been devoted to improving its power-conversion efficiency (PCE). To date, PCE greater than 12% have been achieved using porphyrin-based dyes² and the efficiency has been further improved to 13% with the introduction of benzothiadiazole (BT) unit at the acceptor moiety.³ One of the key strategies to achieve highly efficient DSCs is to develop appropriate push-pull type dyes with proper energy level alignment and strong light harvesting capability. Among the various push-pull dipolar structures, arylamine based dyes are the ones that have been extensively studied.⁴ Arylamine derivatives are well-known electron-rich compounds and possess many favourable properties such as redox, ion transfer processes, photoelectrochemical behaviour as well as excellent electronic properties,⁵ which make them desirable organic sensitizers.

Our group is particularly interested in perylene and its derivatives due to their excellent photophysical properties, charge transport properties, as well as outstanding chemical, thermal, and photochemical stability.⁶ They have been successfully incorporated in both organic photovoltaics⁷ and DSCs.⁸ In particular, the *N*-annulated perylene (NP),⁹ in which the nitrogen atom is annulated at the *bay* region (Fig. 1), has emerged as a superior building block. The electron-rich nature of NP makes it an ideal electron donor that can be further functionalized.¹⁰ Our group first reported that porphyrin dyes with NP as an electron donor could give more than 10% power conversion efficiency in Co(II)/(III) based DSCs.¹¹ We also demonstrated that NP can be used as an efficient spacer for the design of push-pull type sensitizers.¹² At the same time, P. Wang¹³ and Z. Wang's¹⁴ groups also employed the same NP as building blocks for DSCs, and impressively, PCE over 12% can be achieved.^{13e} Up to now, most chemistry on the NP based dyes has been mainly focused on *peri*-positions, while the modifications at the *bay*-region has rarely been reported. Hence, it is essential to design NP-based molecules with two different modes, i.e., *peri*- and *bay* *N*-linkage (Fig. 1), and study their effects on material properties and device performance.

Fig. 1 NP functionalized cyclopentadithiophene dyes CPD-1 to CPD-4 with different linking modes.

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In this work, four NP-functionalized cyclopentadithiophene (CPDT) dyes **CPD-1** – **CPD-4** were designed and used in DSCs (Fig.1). The molecular design is based on the following considerations: (1) NP is electron-rich and thus can serve as an electron donor like aryl amines; (2) compared with normal aryl amines, NP shows strong absorption in visible range ($\lambda_{\text{abs}}^{\text{max}} = 413 \text{ nm}$) with high extinction coefficient, which will be good for light harvesting; (3) CPDT was selected as π -spacer for its rigid structure and facile introduction of alkyl chains;¹⁵ (4) cyanoacetic acid was chosen as electron-acceptor/anchoring group because they have been proved to be efficient for many metal free sensitizers;¹⁶ (5) as compared to **CPD-1** and **CPD-2**, the NP unit in **CPD-3** and **CPD-4** is linked to CPDT through the *bay* amino-site instead of the commonly studied *peri*-position. These two different linking modes will provide a good comparison and allow us to investigate their effects on the electronic structure of the dyes and consequently the device performance; (6) for **CPD-2** and **CPD-4**, an electron-deficient BT moiety was inserted between NP and CPDT unit to generate D-A- π -A structure, which is believed to facilitate intramolecular charge separation and to tailor the light-harvesting property.¹⁷

Scheme 1. Synthetic route of NP functionalized CPDT dyes **CPD-1** to **CPD-4**. Reaction condition: (a) i) $\text{Pd}(\text{PPh}_3)_4$, aq. K_2CO_3 , toluene; ii) cyanoacetic acid, piperidine, CHCl_3 ; (b) i) NBS, DMF, 0°C ; ii) $\text{Pd}(\text{PPh}_3)_4$, aq. K_2CO_3 , MeOH, toluene, 4-*tert*-butyl phenyl boronic acid; (c) Cu, 18-crown-6-ether; 1,4-dibromobenzene; (d) i) *n*-BuLi, THF; ii) *n*-Bu₃SnCl.

The synthetic route towards NP functionalized CPDT dyes **CPD-1**–**CPD-4** is shown in Scheme 1. Suzuki coupling of NP boronic ester **1**^{10b} with monobromo-CPDT **2**¹² followed by

Knoevenagel condensation with cyanoacetic acid afforded **CPD-1** in 55% yield. **CPD-2** was synthesized through similar two-step reactions in 23% yield, except that the first step would be a one-pot three-component Suzuki coupling reaction of monobromo- NP **3**^{10b} with BT diboronic ester **4** and monobromo-CPDT **2**. Synthesis of **CPD-3** and **CPD-4** commenced with the preparation of the key intermediate **7a** and **7b**. The parent NP **5** was treated with NBS followed by Suzuki coupling to afford **6** in 68% yield. Ullmann reaction of **6** with 1,4-dibromobenzene gives **7a**, which was subsequently converted into **7b**. **CPD-3** was prepared by Stille coupling of **7b** with monobromo-CPDT **2**, followed by Knoevenagel condensation. Similar to **CPD-2**, **CPD-4** was synthesized through the two-step procedure, firstly through a one-pot three-component coupling reaction followed by condensation with cyanoacetic acid.

Fig. 2. UV-vis absorption spectra of CPDT dyes in THF (10^{-5} M).

The absorption spectra of **CPD-1** – **CPD-4** in THF (Fig.2) were measured and tabulated in Table S1 (ESI[†]). **CPD-1** and **CPD-3** exhibit strong absorption peak at 488 nm ($\epsilon = 6.4 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and 450 nm ($\epsilon = 6.7 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), respectively, which can be attributed to the intramolecular charge transfer. As compared to **CPD-1**, the absorption peak of **CPD-3** was blue shifted by about 38 nm, indicating the less conjugation of the *bay*-linked NP with the CPDT moiety. When the BT moiety was incorporated to form D-A- π -A structure, **CPD-2** and **CPD-4** show two separate absorptions at 400-700 nm. **CPD-2** exhibits strong absorptions at 524 nm ($\epsilon = 4.3 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and 450 nm ($\epsilon = 4.4 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), while **CPD-4** shows two peaks at 516 nm ($\epsilon = 4.5 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) and 449 nm ($\epsilon = 5.0 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). We also observed red shift of the UV-vis absorption with the introduction of BT group, with about 36 nm for **CPD-2** as compared to **CPD-1**, and more distinctive shift value of 66 nm for **CPD-4** as compared to **CPD-3**. This red shift demonstrates that the D-A- π -A motif, in which the auxiliary electron-withdrawing unit is incorporated into the dye molecule, is a good strategy to facilitate electron transfer from donor to acceptor.

To evaluate the energetics of our synthetic dye molecules, cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in deoxygenated THF solution were performed (Fig. 3

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and Fig. S1 in ESI†). The potential was externally calibrated by ferrocenium/ferrocene (Fc^+/Fc) couple. The HOMO and LUMO energy levels of **CPD-1** – **CPD-4** were estimated to be -5.01, -5.06, -5.07, -5.12 eV (HOMO) and -3.13, -3.25, -2.77, -3.22 eV (LUMO), respectively, from the onset of the first oxidation/reduction wave. As a result, their electrochemical energy gaps were determined to be 1.88, 1.81, 2.30, 1.90 eV. Such values are in agreement with the calculated optical energy gaps (Table S1 in ESI†). The HOMO energy levels of these dyes seem similar.

Fig. 3. Cyclic voltammograms of CPDT dyes in dry THF with TBAPF_6 as supporting electrolyte, Ag/AgCl as reference electrode, Au disk as working electrode, Pt wire as counter electrode, and scan rate at 50 mV/s.

TD DFT calculations (B3LYP/6-31G*) were then conducted to gain a better understanding of the CPDT dyes. Their frontier molecular orbital profiles and calculated energy levels are shown in Fig. 4. The HOMO of **CPD-1** is delocalized through the entire molecule, while its LUMO is mainly distributed at the CPDT and acid binding moiety. **CPD-2** shares a similar electron distribution pattern as **CPD-1**, but with its HOMO more delocalized at the NP unit due to the additional BT group. The longest-wavelength absorption maximum for **CPD-1** and **CPD-2** are calculated to be 608.0 nm (oscillator strength $f = 0.8728$) and 776.0 nm ($f = 0.6272$), (Fig. S2, S3 and Table S3, S5 in ESI†). In contrast, the *bay*-NP linked dyes **CPD-3** and **CPD-4** show well-separated orbital distribution, with their HOMO mainly delocalized at the NP unit, and their LUMO at the CPDT and acid binding moiety. Due to the little overlap of HOMO and LUMO profiles, **CPD-3** and **CPD-4** show nearly zero oscillator strength for HOMO to LUMO electronic transitions. As a result, their largest oscillator strength values come from HOMO-1 to LUMO transition, with absorption maxima at 503.3 nm ($f = 1.4112$) and 606.7 nm ($f = 1.2777$), respectively (Fig. S4, S5 and Table S7, S9 in ESI†). This also suggests that the *peri*-linked NP-CPDT dyes should have better light harvesting properties than the *bay*-N-linked dyes. Calculations also show that all these four dyes have similar HOMO energy levels (-4.81– -4.85 eV) and the introduction of BT unit decreases the LUMO energy levels. All these are in agreement with the above electrochemical measurements.

Fig. 4. Calculated HOMO and LUMO profiles and energy levels of **CPD-1**–**CPD-4**.

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The newly synthesized dyes **CPD-1** – **CPD-4** were studied for photovoltaic characterizations with Co(II)/(III) based electrolyte. The photocurrent density–voltage (J – V) characteristics and the corresponding IPCE spectra for **CPD-1** – **CPD-4** cells measured under standard AM1.5 irradiance are shown in Fig.5 and device characteristics are summarized in Table 1. The IPCE of **CPD-1** covers the whole visible range and reaches a maximum value of 73%, indicating efficient electron injection from excited dye into TiO_2 . As a result, **CPD-1** cell exhibited a maximum PCE of 7.16% ($J_{\text{sc}} = 13.07 \text{ mA cm}^{-2}$, $V_{\text{oc}} = 748 \text{ mV}$, FF = 0.73). Under the same condition, **CPD-2** gave a much lower PCE of 5.21% ($J_{\text{sc}} = 9.76 \text{ mA cm}^{-2}$, $V_{\text{oc}} = 746 \text{ mV}$, FF = 0.72), mainly due to the decreased J_{sc} value. The insertion of additional BT group for **CPD-2** has facilitated its intramolecular charge separation, as a result, broader IPCE spectra were observed. However, **CPD-2** also showed disjointed electronic structure due to the less conjugation of BT group with NP and CPD unit (Fig 4), which has eventually led to the less efficient electron injection process. Therefore, the maximum IPCE value for **CPD-2** decreases considerably (< 52%). For **CPD-3** and **CPD-4** dyes with the NP unit linked through *bay* position, lower PCE values were obtained. The most distinct difference is the onset of IPCE for **CPD-3** and **CPD-4** has blue shifted by 60 nm and 110 nm, respectively, as compared to their *peri*-position linked derivatives **CPD-1** and **CPD-2**. Although the V_{oc} and FF remained almost constant for **CPD-3** and **CPD-4**, the J_{sc} values were decreased to 8.75 and 9.08 mA cm^{-2} , respectively. As a result, PCE of 4.70% and 5.01% were obtained for **CPD-3** and **CPD-4**.

Fig. 5. (a) J – V characteristics of the **CPD-1**–**CPD-4**sensitized solar cells and (b) the corresponding IPCE spectra.

Table 1. Photovoltaic parameters of DSCs based on **CPD-1**–**CPD-4** with and without co-adsorbed DCA.

Dye	$J_{\text{sc}}/\text{mA cm}^{-2}$	V_{oc}/mV	FF/%	$\eta/\%$
CPD-1	13.07	748	73.3	7.16
CPD-2	9.76	746	71.6	5.21
CPD-3	8.75	733	73.4	4.70
CPD-4	9.08	743	74.2	5.01
CPD-1+DCA	14.63	739	72.3	7.82
CPD-2+DCA	10.61	727	72.9	5.62
CPD-3+DCA	7.88	737	74.8	4.31
CPD-4+DCA	8.27	734	74.7	4.53

In order to further improve the device performance, the synthetic CPD dyes were co-adsorption with deoxycholic acid (DCA) to reduce charge recombination and dye aggregation.¹⁹ The *peri*-NP linked CPD dyes showed different results from the *bay*-NP linked CPD dyes. The efficiency of **CPD-1** and **CPD-2** were further improved to 7.82% and 5.62%. In contrast, **CPD-3** and **CPD-4** showed decreased PCE value of 4.31% and 4.53%, respectively.

To further understand the dye structure–device performance relationship, electrochemical impedance measurements were conducted on the **CPD-1** – **CPD-4** cells under illumination and open-circuit states. As commonly understood, V_{oc} is intimately correlated to the conduction band (CB) position and the charge recombination rate.²⁰ Fig. 6a shows the dependence of chemical capacitance (Q) of the four cells on V_{oc} . At a fixed bias voltage, the difference in chemical capacitance indicates that the CB position of TiO_2 slightly varies among the four cells. The **CPD-3** cell presented the largest upward shift of the CB while **CPD-1** the least,²¹ but the V_{oc} difference is not so big. Fig. 6b shows the recombination resistance (R_{ct}) of the cells at different Q . At a fixed electron density, the R_{ct} values for all four cells are only slightly different from each other. The above two factors led to a quite similar V_{oc} for all cells. Thus, the superior performance of **CPD-1** is due to its better light harvesting property, which results in a higher photocurrent.

Fig. 6 (a) TiO_2 chemical capacitance (Q) versus bias voltage; (b) electron recombination resistance (R_{ct}) versus Q for CPD1 – CPD4 cells.

In summary, two types of NP functionalized CPDT dyes were prepared and tested in DSCs. As compared to the *bay*-NP linked dyes CPD-3 and CPD-4, the *peri*-NP linked CPD-1 and CPD-2 dyes gave relatively higher power conversion efficiency due to more efficient intramolecular charge transfer and good light harvesting properties. Among them, CPD-1 exhibits 7.8% PCE with DCA. Further work to improve device performance by modifying perylene-based dyes is currently underway.

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