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Embedding an electron donor or acceptor into naphtho[2,1-b:3,4-b']dithiophene based organic sensitizers for dye-sensitized solar cells[†]

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An electron donor and acceptor, respectively, is embedded into naphtho[2,1-*b*:3,4-*b'*]dithiophene based organic sensitizers to tune their optoelectronic properties. The DSSC based on FNE52 containing an auxiliary electron acceptor displays a maximum power conversion efficiency of 8.2% and good long-term stability.

Dye-sensitized solar cells (DSSCs) have received considerable attention since the original report in 1991 by Grätzel's group.¹ Up to now, DSSCs incorporating ruthenium–polypyridine based sensitizers and a zinc–porphyrin based co-sensitizer have already achieved power conversion efficiencies (η) above 11%^{2–4} and 12%,⁵ respectively. In recent years, considerable efforts have also been made to develop metal-free organic dyes, and impressive efficiencies in the range of 8–10% have been achieved for the DSSCs with a liquid electrolyte.^{6–12}

Recently, naphtho [2,1-b:3,4-b'] dithiophene (NDT) and its derivatives have been vigorously investigated in organic photovoltaics13-15 and thin film transistors^{16,17} due to their unique properties, such as coplanarity, highly ordered π -stacked structures, high charge density and high hole carrier mobility. However, to the best of our knowledge, NDT based organic sensitizers have so far not been explored for applications in DSSCs. In this work, a NDT unit is incorporated into the spacer part of the organic dyes (Fig. 1). There are several advantages for the incorporation of the NDT unit into the π -conjugated spacer of organic sensitizers. Firstly, the large planar conjugated system can delocalize the π -electrons, which facilitates the efficient charge transfer through a NDT based bridge. Secondly, two linear alkoxyl chains can be easily introduced at the 5- and 6-positions on the NDT unit, which not only increase the solubility of the resulting organic dyes but also minimize the formation of molecular aggregates of the resulting dyes and reduce the charge recombination in the DSSCs. Thirdly, the charge transfer

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Fig. 1 Chemical structures of sensitizers FNE50, FNE51, and FNE52.

property of the organic sensitizer can be well tuned by simple incorporation of an auxiliary electron-donating group, such as 3,4-ethylenedioxythiophene (EDOT), or an electron-withdrawing group, such as benzothiadiazole. Herein, we report the synthesis and characterization of three **NDT** based organic sensitizers (Fig. 1). It is found that the incorporation of an electron acceptor is superior to that of an electron donor with respect to broadening of the absorption spectrum and improvement of the DSSC performance. As a result, the η value significantly increases from 5.2% for **FNE50** based DSSC to 8.2% for **FNE52** based DSSC with a liquid electrolyte. Most importantly, the DSSC based on **FNE52** with a quasi-solid-state electrolyte displays an η of 7.1% which remains 98% of the initial value after continuous light soaking for 1000 h.

The synthetic route to sensitizers **FNE50**, **FNE51**, and **FNE52** is depicted in Scheme S1 (ESI[†]), which starts from 5,6-dioctyloxynaphtho[2,1-*b*:3,4-*b'*]dithiophene.¹⁴ Details of the synthetic route towards the resulting sensitizers are provided in the ESI.[†] All the target compounds were characterized using ¹H NMR, ¹³C NMR spectroscopy, and mass-spectrometry, and were found to be consistent with the proposed structures.

The UV-vis absorption spectra of the resulting sensitizers in THF solutions (*ca.* 10^{-5} M) are shown in Fig. 2, and their

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⁺ Electronic supplementary information (ESI) available: Synthesis and characterization details for the resulting sensitizers. See DOI: 10.1039/c3cc44258f



Fig. 2 Absorption spectra of sensitizers **FNE50**, **FNE51**, and **FNE52** in THF solutions The absorption spectra of dye-loaded TiO₂ films are shown as the inset.

absorption data are summarized in Table S1 (ESI⁺). As shown in Fig. 2, FNE50 displays the maximum absorption wavelength at 471 nm. Upon incorporation of an EDOT unit, an electrondonating group, in the π -conjugated spacer of the FNE50 dye, a significant bathochromic shift of 24 nm, as well as increased absorption intensity can be observed for sensitizer FNE51 due to the extended π -conjugation. After introducing an electron withdrawing group, benzothiadiazole, into the organic dye skeleton, a further bathochromically shifted maximum (526 nm) along with an increased absorption coefficient $(4.03 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1})$ can be found for the maximum absorption band of sensitizer FNE52. Compared with the absorption maxima of sensitizer FNE50, the degree of the bathochromic shift and the increased absorption intensity for sensitizer FNE52 are both larger than those for sensitizer FNE51. This is obviously due to the strengthened intramolecular charge transfer interactions in FNE52 caused by the introduction of an extra acceptor group in addition to the conjugation extension. The UV-vis absorption spectra of the dye-loaded TiO₂ films ($\sim 2 \mu m$) are shown in the inset of Fig. 2, which display the same trend for the absorption maxima as those for the absorption spectra in solutions. Moreover, as compared with the maximum absorption band in solution, FNE50 displays a hypsochromically shifted absorption maxima (11 nm) for the TiO₂ film. This phenomenon has been observed for most of the organic sensitizers and is due to the deprotonation of the cyanoacrylic acid group. However, upon adsorption to the nanocrystalline TiO₂ surface, almost no shift in the absorption maximum but a broadened spectrum can be observed for sensitizers FNE51 and FNE52, respectively, which is beneficial to light-harvesting and short-circuit current enhancement.

Suitable highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the sensitizer are required to match the redox potential of the redox couple in the electrolyte and the conduction band edge of the nanocrystalline TiO₂ for efficient sensitizer regeneration and electron injection.¹⁸ As revealed by the cyclic voltammetry spectra of the dye-loaded TiO₂ films (Fig. S1, ESI[†]), the HOMO level corresponding to the first half-wave potential is determined to be 0.87, 0.79, and 0.92 V (ν s. NHE, the same below) for sensitizers **FNE50**, **FNE51**, and **FNE52**, respectively. It is clear

that all the HOMO values are more positive than I⁻/I₃⁻ redox couples (~ 0.4 V), indicating that the reduction of the oxidized dyes with I⁻ ions is thermodynamically feasible. Correspondingly, from HOMO levels and the optical band gap derived from the wavelength at 10% maximum absorption intensity for the dyeloaded TiO₂ film,⁷ the LUMO levels for sensitizers FNE50, FNE51, and FNE52 are calculated to be -1.24, -1.16, and -1.00 V, respectively, indicating enough driving force of the electron injection from the excited states of all the sensitizers. As shown in Fig. S2 (ESI⁺), it should be noted that the embedding of EDOT into the spacer part lifts up the HOMO level of the FNE51 dye relative to that of the FNE50 dye. This can be attributed to the contribution of the increased electron density, which results in a more delocalized HOMO. Upon introducing benzothiadiazole into the sensitizer's bridge, both HOMO and LUMO levels are positively shifted through a contributing inductive effect,¹⁹ but the degree of shift of the HOMO level is smaller than that of the LUMO level. Consequently, the band gap of FNE52 decreases compared with that of FNE50.

The DSSCs based on the resulting sensitizers with coadsorption of deoxycholic acid were fabricated using a liquid electrolyte containing 0.6 M 1,2-dimethyl-3-n-propylimidazolium iodide (DMPImI), 0.1 M LiI, 0.05 M I₂, and 0.5 M tert-butylpyridine (TBP) in acetonitrile. The solar-to-electricity conversion efficiencies of DSSCs were evaluated by recording the photocurrent densitvvoltage (I-V) characteristics at 100 mW cm⁻² simulated AM1.5G solar light. As shown in Fig. 3, the short-circuit photocurrent density (J_{sc}) , open-circuit photovoltage (V_{oc}) , and fill factor (FF) of the FNE50 based DSSC are 10.59 mA cm⁻², 0.726 V, and 0.68, respectively, yielding an η of 5.2%. The DSSCs based on FNE51 and FNE52 produce η of 5.5% $(J_{\rm sc} = 13.84 \text{ mA cm}^{-2}, V_{\rm oc} = 0.615 \text{ V}, \text{ FF} = 0.65)$ and 8.2% $(J_{\rm sc} = 16.36 \text{ mA cm}^{-2}, V_{\rm oc} = 0.694 \text{ V}, \text{ FF} = 0.72)$, respectively. Under the same conditions, the standard cell fabricated with the well-known N719 dye² exhibits an efficiency of 8.5% $(J_{\rm sc} = 16.02 \text{ mA cm}^{-2}, V_{\rm oc} = 0.737 \text{ V}, \text{FF} = 0.72).$

To understand the enhancement of the J_{sc} value after incorporation of an auxiliary electron donor or acceptor in the dye molecule, action spectra of the incident photon-tocurrent conversion efficiencies (IPCE) as a function of incident



Fig. 3 J–V curves for the DSSCs based on FNE50, FNE51, and FNE52. IPCE spectra are shown as the inset.



Fig. 4 Electron lifetime as a function of electron density at the open circuit for DSSCs based on the resulted sensitizers.

wavelength are recorded. As shown in the inset of Fig. 3, the **FNE50** based DSSC displays a broad solar light response with a maximum value above 80%. As the effective conjugation length of the sensitizer molecules gets longer *via* embedding of EDOT or a benzothiadiazole unit into the molecular skeleton, the IPCE spectral response for the DSSCs based on **FNE51** and **FNE52**, respectively, gets broader compared with that for the **FNE50** based DSSC, which is in good agreement with their UV-vis absorption results (Fig. 2) and beneficial to light-harvesting and photocurrent generation. With such an extended IPCE response, the DSSCs based on **FNE51** and **FNE52** provide a higher photogenerated current, respectively, as compared with the **FNE50** based DSSC.

In contrast to the behavior of the short-circuit photocurrent, the FNE50-sensitized solar cell exhibits the highest Voc among these cells based on NDT dyes. To investigate the reason for the differences between the Voc values, electron lifetime and electron density are measured using the intensity modulated photovoltage spectroscopy (IMVS) measurement and charge extraction method.^{20,21} Fig. 4 shows the electron lifetime as a function of electron density at the open circuit for the DSSCs based on the resulting sensitizers. The lifetime increases in the order FNE51 < FNE52 < FNE50, indicating the lowest charge recombination rate in FNE50 based DSSC. The retarded charge recombination rate constant will reduce electron loss at the open circuit. When more charge is accumulated in TiO₂, the Fermi level moves upward and the Voc becomes larger. Introduction of either EDOT or benzothiadiazole into the conjugated frame of the dye may strengthen the intermoleuclar π - π stacking. As a consequence, the charge recombination rate increases, thus resulting in a lower $V_{\rm oc}$. To further design organic dyes with not only good absorption properties but also slower charge recombination for high $V_{\rm oc}$, a detailed study on the charge recombination mechanism is needed.

Long-term stability is considered as an important requirement for outdoor application of the DSSC in the future. Therefore, the resulting sensitizer based quasi-solid-state DSSCs were constructed using a quasi-solid-state gel electrolyte for the longterm stability test. As shown in Fig. S3 (ESI[†]), in accordance with DSSCs based on the liquid electrolyte, the photovoltaic parameters of **FNE52** based quasi-solid-state DSSCs show a best performance of 7.1% ($J_{sc} = 15.84 \text{ mA cm}^{-2}$, $V_{oc} = 658 \text{ mV}$, FF = 0.68). Moreover, as revealed in Fig. S4 (ESI†), the quasi-solid-state DSSC based on **FNE52** remains as 98% of the initial overall efficiency value after 1000 h of visible-light soaking, indicating that sensitizer **FNE52** is sufficiently stable for application in DSSCs.

In summary, an electron donor and an electron acceptor, respectively, is embedded into **NDT** based organic sensitizers. It is found that the incorporation of a benzothiadiazole unit is superior to that of a EDOT unit in broadening the absorption spectrum of the sensitizer. Consequently, **FNE52** based DSSCs with a liquid and a quasi-solid-state electrolyte display an η of 8.2% and 7.1%, respectively, and the η value of the latter quasi-solid-state DSSC remains as 98% of the initial value after continuous light soaking for 1000 h.

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