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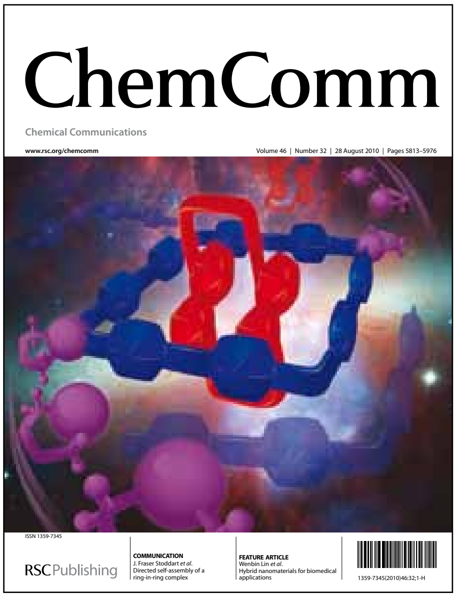

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ARTICLE TYPE

A novel D-A-π-A organic sensitizer containing diketopyrrolopyrrole unit with branched alkyl chain for highly efficient and stable dye-sensitized solar cells

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A novel D-A-π-A type organic dye (YCD01) incorporating a diketopyrrolopyrrole unit with branched alkyl chain was synthesized for dye-sensitized solar cells. YCD01 showed high conversion efficiency of 7.43 % (AM 1.5, 100 mW cm^{-2}) with a J_{sc} of 13.40 mA cm^{-2}, a V_{oc} of 0.76 V, a *FF* of 0.73 and an excellent stability.

Dye-sensitized solar cells (DSCs) have attracted considerable attention since Grätzel and co-workers published their seminal report in 1991.[1] Owing to the efforts of many researchers over the past twenty years, DSCs based on Ru(II)-polypyridyl complexes have yielded a power conversion efficiency above 11 %.[2] At the same time, the metal-free organic dyes have also been desirable due to their high extinction coefficient, ease of structure modification and low cost.[3] However, organic dyes are still limited from practical use owing to their relatively narrow absorption bands, unfavourable aggregation on semiconductors as well as weaker light stability compared to metal-based sensitizers. Recently, a D-A-π-A configuration for organic dyes was reported and received increasing attention with an additional acceptor chromophore incorporated into the common D-π-A structure.[4,5] By inserting the subordinate acceptor, which acts as an electron trap to separate charge and facilitate electron migration to the final acceptor, the sensitizer exhibits broad responsive spectra and long term stability. A high efficiency of nearly 9 % under AM 1.5 G irradiation has been achieved based on this type of sensitizers in DSCs.

Diketopyrrolopyrroles (DPPs) are a class of commercialized and easily synthesized dyes with exceptional photochemical, mechanical and thermal stability, which have aroused lots of interest in bulk heterojunction solar cells[6] and also been considered as a π-conjugated component for DSCs.[7] The efficient intermolecular charge transfer of DPP moiety allows for high absorbance and is beneficial for the sensitizer to absorb at infrared wavelength. In addition, the electron-withdrawing properties of DPP, which is suitable for constructing the D-A-π-A configuration, can assist the electron distribution and greatly stabilize the sensitizer. However, the large π-conjugated system of DPP demonstrates strong π-stacked aggregation on TiO_2,[7a] which may lead to dissipative intermolecular charge transfer and aggravate charge recombination. Recently, some researchers reported that by connecting long alkyl chains to the donor part of sensitizers, charge recombination could be successfully suppressed. However, aggregation of these modified sensitizers still occurs to a certain degree.[8] Therefore, we assumed that attaching a bulky substituent in the middle part of the sensitizer might be a more effective way to reduce π-π stacking of molecules on the TiO_2 film. Specially, owing to their bulk, branched alkyl chains effectively decrease aggregation of conjugated molecules and increase polymer solubility. With this in mind, we introduced a branched 2-ethyl-hexyl alkyl chain to the DPP moiety for the first time to further prohibit the dye aggregation. In addition, the steric hindrance of the branched chain may also block I_3^- ion from approaching the TiO_2 surface, thus reducing the charge recombination rate.

In this work, we developed a new D-A-π-A organic sensitizer, **YCD01**, bearing 2-ethyl-hexyl alkyl chain in the DPP moiety, furan as the linker, cyanoacrylic acid as the acceptor moiety and the indoline unit[9] was introduced as the donor for its powerful donor ability to further broaden the absorption spectrum and improve the efficiency. The corresponding dye **TD01** was also synthesized as a comparison (Fig. 1). Syntheses of dyes **YCD01**

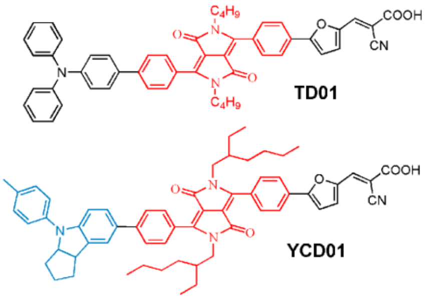

Fig. 1 Molecular structure of **YCD01** and reference dye **TD01**.

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† Electronic Supplementary Information (ESI) available: Experimental procedures for synthesis, DFT calculations, Charge Extraction and all fundamental data of DSCs. See DOI: 10.1039/b000000x/

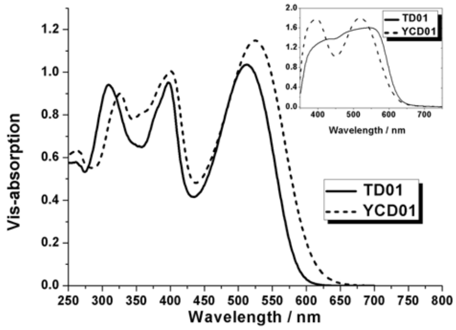

Fig. 2 Absorption spectra of **YCD01** and **TD01** in CH_2Cl_2 and anchored on a transparent TiO_2 film (inset).

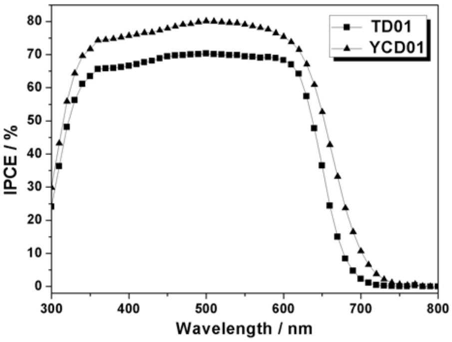

Fig. 3 IPCE spectra of DSCs based on **YCD01** and **TD01**.

and **TD01** in detail are described in the ESI (Scheme 1 and 2, ESI†).

The UV-Vis absorption spectra of the two dyes are shown in Fig. 2. Both dyes showed broad absorption spectra covering a wide range of the visible region. The maximum absorption of **YCD01** was exhibited at 526 nm with a molar extinction coefficient (ε) of 4.6×10^4 $M^{-1}cm^{-1}$, and for **TD01** was exhibited at 514 nm with ε of 4.1×10^4 $M^{-1}cm^{-1}$(Table S1, ESI†). The red-shift of the absorption band of **YCD01** in comparison to **TD01** was due to the stronger donor ability of indoline moiety than triphenylamine. When absorbed on a transparent thin TiO_2 film, **TD01** showed broader absorption bands and a ~32 nm red-shift in absorption compared to that measured in solution (Fig 2, inset). The fine absorption bands ascribed to π-π* transition and intermolecular charge transfer were vaguely visible in the spectrum. These phenomena indicate that there was a certain degree of π-π aggregation of **TD01** on the TiO_2 film. In contrast, in the spectrum of **YCD01**, fine absorption peaks were readily shown, and there was no distinct shift or extension of the absorption bands, which suggests that π-π aggregation was significantly reduced. This reduced aggregation was probably due to the presence of the branched alkyl chain, which appeared to have successfully prohibited the interaction of DPP molecules.

The energy levels of **TD01** and **YCD01** were determined by cyclic voltammetry (Table S1). The ground state oxidation potential, $S^{+/0}$, of **TD01** and **YCD01** were 1.03 and 0.78 V, respectively, which were sufficiently low compared to the redoxpotential of the iodide/triiodide couple used as an electrolyte. The $S^{+/0}$ energy level of **YCD01** was negatively shifted for 0.25 V compared to that of **TD01** due to the introduction of the indoline moiety. The estimated excited-state oxidate potential, $S^{+/*}$, for **TD01** and **YCD01**, calculated from

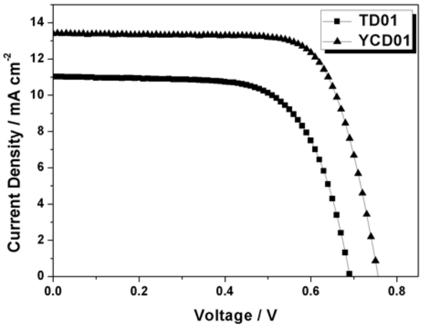

Fig.4 Photocurrent-voltage curves of DSCs sensitized by **YCD01** and **TD01**using 0.6 M MPImI, 0.1 M LiI, 0.05 M I_2 and 0.5 M TBP in the solvent of CH_3CN as the electrolyte.

$S^{+/0}$-$E_{0\text{-}0}$, were -0.91 V and -1.10 V. The $S^{+/*}$ potential of both the two dyes were more negative than the conduction-band edge of TiO_2 (-0.5 V vs. NHE), ensuring an efficient electron injection process from the excited state into the conduction band of TiO_2.

To obtain an insight into the electron distribution of **TD01** and **YCD01**, we calculated the optimized molecular structures and frontier orbitals of the two dyes by using the density functional theory computational method.[10] At the ground state (HOMO) of these dyes, electrons are distributed on the D-A system and the excited state (LUMO) is delocalized across the entire A-π-A system(Fig. S2, ESI†), which suggests an inductive or electron-withdrawing tendency from the donor unit to the cyanoacetic acid unit.

DSCs were fabricated according to the literature procedure.[11] The incident photon-to-current conversion efficiency (IPCE) spectra of the DSCs based on **TD01** and **YCD01** are shown in Fig. 3. **YCD01** showed excellent solar light response from 350 to 625 nm with a maximum value of 80 % in the plateau region. Taking into account the reflection and absorption losses by the conducting glass, the IPCE in this range exceeded 90 %. The photovoltaic performance was measured under AM 1.5 G simulated solar light at a light intensity of 100 mW cm^{-2} with a metal mask of 0.25 cm^2. Under optimized conditions, with the addition of 0.5 M *tert*-butylpyridine (TBP) in the electrolyte, the **YCD01**-sensitized solar cell achieved a prominent overall conversion efficiency of 7.43%, with a short-circuit photocurrent density (J_{sc}) of 13.40 mA cm^{-2}, an open-circuit voltage (V_{oc}) of 0.76 V and a fill factor (*FF*) of 0.73. Under the same conditions, **TD01** showed 5.18 % efficiency (J_{sc} = 11.05 mA cm^{-2}, V_{oc} = 0.69 V, *FF* = 0.68) (Fig. 4, Table S2, ESI†). **YCD01** showed a higher J_{sc} than **TD01**, which is because the introduction of indoline donor favors light harvesting in DSCs with better absorption spectra. In addition, the weak π-π aggregation of **YCD01** on the TiO_2 film also improved the electron injection efficiency of the cells.

The V_{oc} value of **YCD01** was 70 mV higher than that of **TD01**, which could be attributed to the introduction of branched 2-ethyl-hexyl chain to the DPP core. The generation of V_{oc} is related to the energy level of the TiO_2 conduction band (E_{CB}) and the charge recombination rate in DSCs. To clarify the effect of the branched alkyl chain on V_{oc}, we first measured E_{CB} with the charge extraction method (CEM)[12] (Fig. S3, ESI†) and found that E_{CB} was almost unaffected for two cases. Therefore, the improvement of V_{oc} from **TD01** to **YCD01** based DSCs should be

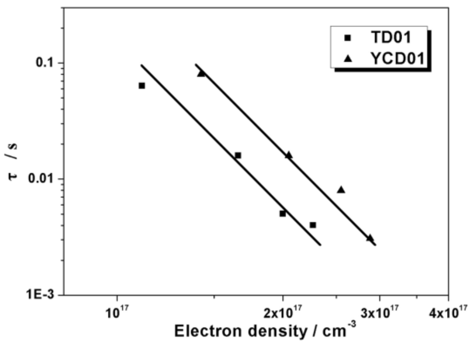

Fig.5 Lifetime (τ) of electrons versus electron density. The τ in DSCs sensitized by **TD01** and **YCD01** were derived by using intensity-modulated photovoltage spectroscopy.

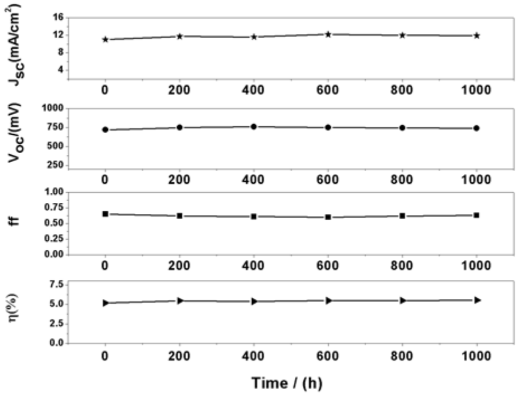

Fig.6 Variations of photovoltaic parameters with aging time for the DSCs devices sensitized by **YCD01** using the 3-methoxy-propylnitrile (MPN) as electrolyte solvent.

attributed to the suppression of charge recombination, which is related to electron lifetime (τ). We derived τ as a function of electron density by means of intensity-modulated photovoltage spectroscopy (IMVS) (Fig. 5).[13] The electron lifetime decreased with increasing electron density in a manner consistent with a power law relationship. At a fixed electron density, the electron lifetime for the DSCs based on **YCD01** was larger than that of **TD01**, which suggests that the branched 2-ethyl-hexyl chain was more effective than the single butyl chain for blocking I_3^- ions approaching the TiO_2 surface for charge recombination, and thus showed an improvement in V_{oc}.

Finally, in order to test the stability of **YCD01**, we made cells using 3-methoxy-propylnitrile (MPN) as an electrolyte solvent. The **YCD01**-sensitized solar cell showed an initial overall conversion efficiency of 5.19 % with a J_{sc} of 11.04 mA cm^{-2}, V_{oc} of 0.72 V and *FF* of 0.65. The performance of the cell improved during the first 100 h and retained almost the same after 1000 h of accelerated tests under full sunlight soaking at 60 °C (Fig. 6). This demonstrates that the amount of dye on the TiO_2 surface remained intact after long time soaking.

In conclusion, we designed and synthesized a new D-A-π-A sensitizer, **YCD01**, with indoline as the electron donor, diketopyrrolopyrrole as the additional acceptor, furan as the linker and cyanoacrylic acid as the acceptor moiety. Attaching the 2-ethyl-hexyl chain in the middle of DPP unit proved to be an effective means for reducing the π-π aggregation of the dyes on TiO_2. Moreover, the steric hindrance of the branched chain successfully suppressed charge recombination and improved the open-circuit voltage. As a result, **YCD01**-sensitized DSCs achieved a high overall conversion efficiency of 7.43% with broad IPCE response, high V_{oc} and long-term stability. A systematic study of the effect of bulky alkyl group attached to the DPP unit on the device performance and further broadening the absorption spectra to the infrared region is under process.

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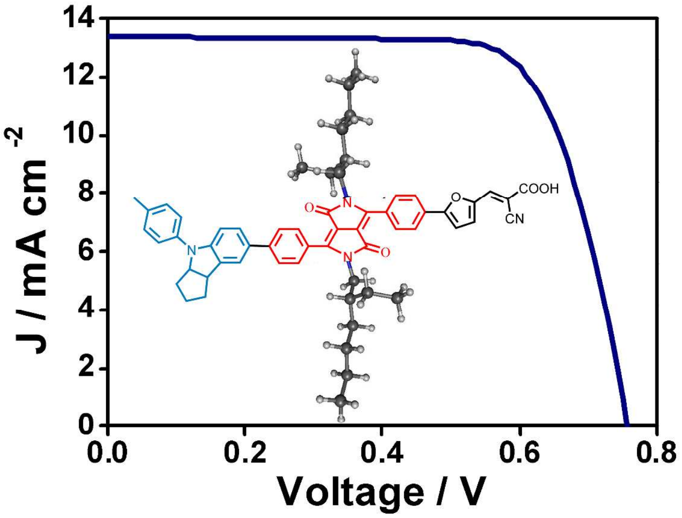

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