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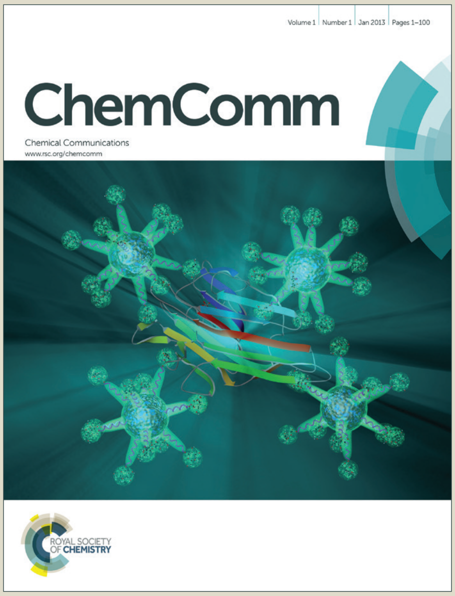

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ARTICLE TYPE

A *meso-meso* directly linked porphyrin dimer-based double D-π-A sensitizer for efficient dye-sensitized solar cells

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A novel double D-π-A branched dye (JY07) was synthesized and applied as sensitizer for DSSCs. JY07 exhibited broader and stronger light absorption capability than the single D-π-A dye (JY06). In the meantime, the orthogonal conformation of JY07 was found to be favorable for impeding intermolecular aggregation. Consequently, a power conversion efficiency of 5.33% was achieved under AM 1.5G conditions.

Dye-sensitized solar cells (DSSCs) have attracted both scientific and industrial interest over the past several decades due to their high efficiency and low cost.[1] As a key component of DSSCs, sensitizers play a crucial role in light harvesting and light-to-electricity conversion; extensive effort has, therefore, been focused on developing new and superior sensitizers.[2] Porphyrins are among the most widely studied sensitizers due to their intense absorption in Soret and Q bands to harvest solar energy efficiently in a broad spectral region.[2b,3] More importantly, their optical, photophysical, and electrochemical properties can be modulated with peripheral modifications or inner metal coordinations. Several porphyrin monomers have been used in DSSCs with good performance reaching efficiencies of over 12%.[4]

However, several limitations might hamper the further improvement of monomeric porphyrins in DSSCs. One is the absorption trough between the Soret and Q bands, and relatively weak light-harvesting ability in the green and red regions of the solar spectrum.[2b,5] To overcome this drawback, the employment of directly linked porphyrin dimers would be an effective method to improve the optical, photophysical, and electrochemical properties.[6] Another limitation of monomeric porphyrin-based dyes is the strong tendency to aggregate on the TiO_2 surface due to π-interactions between the macrocycle discs. The resultant intermolecular aggregation can cause self-quenching of exciting states and subsequently reduce the charge injection efficiency.[3a,7] To control the π-stacked aggregation and related charge recombination process, one effective strategy is the introduction of carboxylate groups into axial ligands or bulky groups into the donor part.[8] Another alternative approach is the bridging of two chromophores into a spiro configuration similar to Ru-sensitizers.[9]

Recently, dianchoring organic dyes have gained increasing attentions because of the potential for strengthening the binding of dyes onto the TiO_2 and hence promoting the performance of solar cells.[9,10] Strong binding of the dyes on the TiO_2 will not only increase their adsorption amount but also induce efficient charge injection.[11] Several organic sensitizers containing double/multi electron acceptors have been reported, in comparison to those with single acceptor, to give better cell performance with an improved photoresponse, photocurrent and stability.[10a,12]

Keeping in mind the requirement of broad absorption, strong binding ability, and reduced tendency towards aggregation, we designed and synthesized a *meso-meso* directly linked porphyrin dimer-based double D-π-A sensitizer **JY07** (Fig. 1). Owing to the strong excitonic coupling between the neighboring porphyrin moieties, the Soret band of **JY07** becomes broader by splitting into two bands and the absorption spectra is extended into the midvisible region of the solar spectrum. Unlike the *meso-meso* directly linked porphyrin dimer in literature, two strong electron-donating triarylamine units and two carboxylic acid anchoring groups are introduced into porphyrin dimer to form a double D-π-A scaffold, which can result in more paths for efficient electron extraction. The presence of two anchoring groups will further increase the binding strength of the dyes on the TiO_2 film and subsequently improve their photostability. Notably, the nearly orthogonal conformation and bulky molecular structure of **JY07** would minimize its aggregation and reduce the charge recombination on the TiO_2 surface.

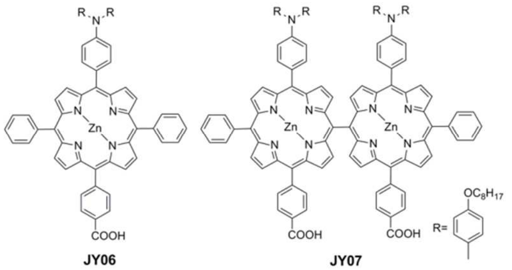

Fig. 1 Chemical structures of **JY06** and **JY07**.

The absorption spectra of both dyes are presented in Fig. 2, and their corresponding data are summarized in Table 1. In THF solution, **JY06** exhibits a typical absorption of monomeric metalloporphyrin, with one Soret band maxima at 425 nm and two Q-bands maxima at 559 and 601 nm, respectively. Compared to **JY06**, **JY07** shows broader and split Soret bands in the 360–525 nm region, and obvious red-shifted and intensity-enhanced Q bands ranging from 530 to 650 nm due to the strong interporphyrin excitonic coupling.[13] That indicates **JY07** has better light-harvesting ability than the single D-π-A dye **JY06**. On TiO_2 films, the Soret band of **JY06** is red-shifted and considerably broadened relative to the solution spectra. No such shift is observed between the film and solution spectra of **JY07**. However, its intensity of the high-energy Soret band becomes stronger than that of the low-energy Soret band. Those changes in the spectral features on TiO_2 could be attributed to the slightly distorted geometry on TiO_2.[6b]

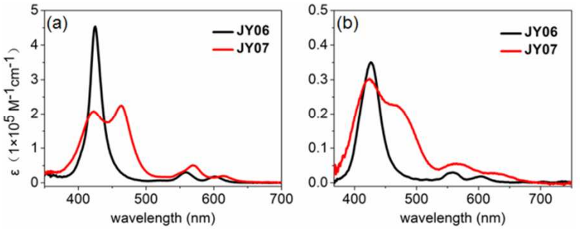

Fig. 2 Absorption spectra of **JY06** and **JY07** in THF (a) and on films (b).

Table 1 Photophysical and electrochemical data for **JY06** and **JY07**

Dye	$\lambda_{max}{}^{a}$/nm ($\varepsilon \times 10^5$ M^{-1} cm^{-1})	$E_{ox}{}^{b}$ /V	$E_{0\text{-}0}{}^{c}$ /V	$E_{ox*}{}^{d}$ /V
JY06	425 (4.53), 559 (0.31) 601 (0.18)	0.80	2.04	–1.24
JY07	422 (2.08), 464 (2.25) 569 (0.51), 615 (0.20)	0.85	1.99	–1.14

[a] Absorption data were measured in THF. [b] The potentials (*vs*. NHE) were calibrated with ferrocene. [c] $E_{0\text{–}0}$ values were determined from the intersection of the absorption and emission spectra in THF. [d] E_{ox*} were calculated by subtracting $E_{0\text{–}0}$ from the E_{ox}.

The energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are crucial to judge the possibilities of dye regeneration by the iodide and electron injection from the excited dye molecules to the conduction band of TiO_2. The electrochemical properties of **JY06** and **JY07** were investigated by cyclic voltammetry. As shown in Table 1, the oxidation potentials (E_{ox}) of **JY06** and **JY07** corresponding to the HOMO levels energy, were located at 0.80 and 0.85 V, respectively, *vs*. a normal hydrogen electrode (NHE). These values are more positive than the redox potential of the I^-/I_3^- redox couple (0.4 V *vs*. NHE). This will make it possible to guarantee an efficient dye regeneration. The estimated excited-state potentials corresponding to the LUMO levels, calculated from $E_{ox} - E_{0\text{-}0}$, were –1.24 and –1.14 V *vs*. NHE, respectively. The obtained LUMO values are much more negative than the Fermi level of TiO_2 (–0.5 V *vs*. NHE), ensuring an efficient electron injection process from the excited state of the dyes into the TiO_2 electrode (Fig. 3).

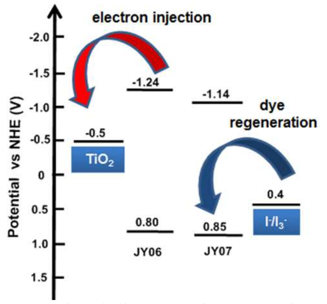

Fig. 3 Schematic energy-level diagram of **JY06** and **JY07**.

FTIR spectroscopy was performed to investigate the anchoring properties of the dyes on the TiO_2 (Fig. S3 in ESI†). Characteristic band at 1693 cm^{-1} for the carboxylic acid group of **JY06** and that at 1694 cm^{-1} for **JY07**, disappeared in the spectrum of dyes adsorbed onto TiO_2 films. This observation indicates that **JY06** and **JY07** were chemically adsorbed onto the TiO_2 surface via single- and double-anchoring modes, respectively, a result similar to the observations made by Abbotto et al.[14]

The photovoltaic characteristics of the DSSCs based on dyes **JY06** and **JY07** have been investigated (see ESI†). The current density-voltage (*J*-*V*) curves were plotted in Fig. 4a. The DSSC based on **JY06** gave an overall power conversion efficiency (PCE) of 4.30%, with a J_{sc} of 11.18 mA cm^{-2}, an V_{oc} of 0.63 V, and a FF of 0.61. Under the same condition, **JY07**-based DSSC offered a J_{sc} of 13.20 mA cm^{-2}, an V_{oc} of 0.65 V, and a FF of 0.62, corresponding to an overall PCE value of 5.33%. The J_{sc} is improved by 2.02 mA cm^{-2}, V_{oc} is lifted by 0.02 V, and the η is improved by 24% from **JY06** to **JY07**. For comparison, the ruthenium dye **N719** gave an overall PCE of 7.95%, with a J_{sc} of 17.40 mA cm^{-2}, an V_{oc} of 0.73 V, and a FF of 0.63. The porphyrin densities (Γ) adsorbed on TiO_2 were measured to be 75 and 62 nmol cm^{-2} for **JY06** and **JY07**,[15] respectively. The experiments about the photovoltaic performance of dye **JY07** with and without coadsorbent were further carried out. A 0.48% decrease of PCE was observed in the presence of chenodeoxycholic acid (CDCA), indicating dye aggregation may be negligible for **JY07** (Table S1 in ESI†). In addition, dye **JY07** with two anchoring groups shows a significant photostability improvement (Fig. S5 in ESI†).

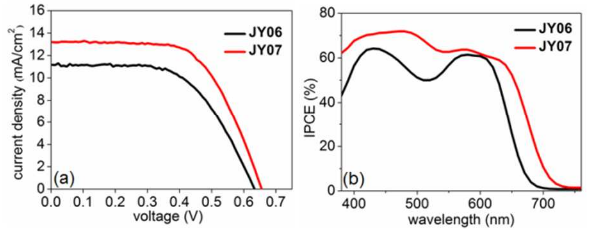

Fig. 4 (a) Current density-voltage curves for DSSCs sensitized by **JY06** and **JY07**; (b) IPCE spectra of DSSCs based on **JY06** and **JY07**.

The higher J_{sc} for **JY07** is consistent with its higher and broader IPCE spectrum compared with that for **JY06**, which can be understood to come from the effective excitonic coupling of the two porphyrin macrocycles in the dimer,[13] whereas such a character was absent in the single D-*π*-A dye **JY06**. As shown in Fig. 4b, IPCE values of over 60% ranging from 371 to 622 nm were observed for **JY07**-based DSSC, with a maximum value of 72% at 481 nm. Besides, the IPCE spectrum in the Q-band region was also intensified and extended to 750 nm, while the DSSC based on **JY06** showed a narrower IPCE spectrum with smaller IPCE values.

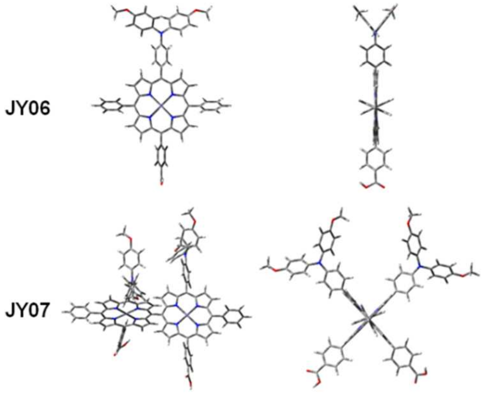

Fig. 5 Front and side views of geometry-optimized structures of **JY06** and **JY07**.

Fig. 5 shows the optimized geometrical structure of the two dyes. As shown in the figure, **JY06** has a rod shape, whereas **JY07** has an orthogonal shape.[16] As a result, after the dye molecules were adsorbed on the TiO_2 surface, the rod-shaped structure of **JY06** may cause aggregation which can aggravate charge recombination for the triiodide and can easily penetrate through the big interspaces between chromophores, while the orthogonal conformation for **JY07** can minimize aggregation and suppress the approach of I_3^- ions in the electrolyte to the TiO_2 particles for charge recombination.[15] Consequently, much higher V_{oc} are observed for **JY07** than that for **JY06**.

Furthermore, electrochemical impedance spectroscopy (EIS)[17] in the dark (Fig. S6 in ESI†) were performed to analyze the origin of improvement in V_{oc}. There were two semicircles in the Nyquist plots (Fig. S6a in ESI†), and the larger semicircle in the low-frequency region represents the charge-transfer resistance (R_{rec}) at the TiO_2/dye/electrolyte interface. In comparison to single D-π-A dye **JY06**, **JY07** containing double D-π-A branches showed a larger radius which indicated a larger R_{rec} and slower electron recombination. In addition, the electron lifetime (τ_e) could be extracted from the peak frequency (f) at a lower frequency region in EIS Bode plots using $\tau_e = 1/(2\pi f)$.[18] The electron lifetimes for the DSSCs based on **JY06** and **JY07** were evaluated to be 31.4 and 47.0 ms, respectively. Both the R_{rec} and electron lifetimes coincided well with V_{oc}. The enlarged R_{rec} and lengthened electron lifetime of **JY07** further indicated that the electron recombination between the injected electrons and the electrolyte was efficiently suppressed, leading to a higher V_{oc}.[18]

In conclusion, we have successfully designed and synthesized a novel double D-π-A sensitizer **JY07** based on a *meso-meso* directly linked porphyrin dimer. The orthogonal conformation of **JY07** can reduce intermolecular π-π interaction and suppress the approach of I_3^- ions in the electrolyte to the TiO_2 particles for charge recombination. In addition, the strong excitonic coupling between porphyrin moieties significantly broadened the absorption spectrum and enhanced the light-harvesting capability. As a result, much higher V_{oc} and J_{sc} values as well as better efficiency were achieved for double D-π-A sensitizer **JY07** compared to **JY06** based on single D-π-A structure. Further studies for *meso-meso* directly linked porphyrin dimer-based double D-π-A sensitizers with higher efficiency through molecular modifications are ongoing in our laboratory.

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Notes and references

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† Electronic Supplementary Information (ESI) available: See DOI: 10.1039/b000000x/

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15 The loading amount of **JY06** and **JY07** on TiO_2 was measured to be 75 and 62 nmol cm^{-2}, respectively. Since **JY07** has much larger molecular size than **JY06**, more compact dye layer for **JY07** are formed on the TiO_2 surface.

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