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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. 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. 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. 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%.

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. To overcome this drawback, the employment of directly linked porphyrin dimers would be an effective method to improve the optical, photophysical, and electrochemical properties. Another limitation of monomeric porphyrin-based dyes is the strong tendency to aggregate on the TiO₂ surface due to π-interactions between the macrocycle discs. The resultant intermolecular aggregation can cause self-quenching of excited states and subsequently reduce the charge injection efficiency.

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. Another alternative approach is the bridging of two chromophores into a spiro configuration similar to Ru-sensitizers.

Recently, anchoring organic dyes have gained increasing attentions because of the potential for strengthening the binding of dyes onto the TiO₂ and hence promoting the performance of solar cells. Strong binding of the dyes on the TiO₂ will not only increase their adsorption amount but also induce efficient charge injection. 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.

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 exotic 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 middle-visible 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 TiO₂ 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 TiO₂ surface.

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. That indicates JY07 has better light-harvesting ability than the single D-π-A dye JY06. On TiO₂ 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$_2$.\textsuperscript{60}

![Absorption spectra of JY06 and JY07 in THF (a) and on films (b).](Image)

**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 | $\lambda_{\text{max}}$ (nm) | $E_{\text{ox}}$ (V) | $E_{\text{red}}$ (V) |
| JY06 | 425 (5.43), 559 (0.31) | 0.80 | / |
| JY07 | 422 (2.08), 464 (2.25) | 0.85 | 1.99 |

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

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 ($E_{\text{ox}}$) 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$_3$/I$_2$; 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 were measured to be 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).

![Schematic energy-level diagram of JY06 and JY07.](Image)

**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\textsuperscript{1}). 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 Abbott et al.\textsuperscript{14}

The photovoltaic characteristics of the DSSCs based on dyes JY06 and JY07 have been investigated (see ESI\textsuperscript{1}). 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 $J_{\text{sc}}$ of 11.18 mA cm$^{-2}$, an $V_{\text{oc}}$ of 0.63 V, and a FF of 0.61. Under the same condition, JY07-based DSSC offered a $J_{\text{sc}}$ of 13.20 mA cm$^{-2}$, an $V_{\text{oc}}$ of 0.65 V, and a FF of 0.62, corresponding to an overall PCE value of 5.33%. The $J_{\text{sc}}$ is improved by 2.02 mA cm$^{-2}$; $V_{\text{oc}}$ is lifted by 0.02 V, and the $\eta$ is improved by 24% from JY06 to JY07. For comparison, the ruthenium dye N719 gave an overall PCE of 7.95%, with a $J_{\text{sc}}$ of 17.40 mA cm$^{-2}$, an $V_{\text{oc}}$ of 0.73 V, and a FF of 0.63. The porphyrin densities ($\Gamma$) adsorbed on TiO$_2$ were measured to be 75 and 62 nmol cm$^{-2}$ for JY06 and JY07,\textsuperscript{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\textsuperscript{1}). In addition, dye JY07 with two anchoring groups shows a significant photostability improvement (Fig. S5 in ESI).

![Current density-voltage curves for DSSCs sensitized by JY06 and JY07; (b) IPCE spectra of DSSCs based on JY06 and JY07.](Image)

**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 $J_{\text{sc}}$ for JY07 is consistent with its higher and broader IPCE spectrum compared with that for JY06, which can be understood from the effective excitonic coupling of the two porphyrin macrocycles in the dimer,\textsuperscript{16} whereas such a character was absent in the single D$_4$-A-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.\textsuperscript{17}

![Front and side views of geometry-optimized structures of JY06 and JY07.](Image)

**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.\textsuperscript{18} 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. Consequently, much higher $V_{oc}$ are observed for JY07 than that for JY06.

Furthermore, electrochemical impedance spectroscopy (EIS) in the dark (Fig. S6a 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 ($R_{sc}$) 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 $R_{sc}$ and slower electron recombination. In addition, the electron lifetime ($\tau_e$) could be extracted from the peak frequency ($f$) at a lower frequency region in EIS Bode plots using $\tau_e = 1/(2\pi f)$. The electron lifetimes for the DSSCs based on JY06 and JY07 were evaluated to be 31.4 and 47.0 ms, respectively. Both the $R_{sc}$ and electron lifetimes coincided well with $V_{oc}$. The enlarged $R_{sc}$ 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 $V_{oc}$.

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 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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9. 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.
10. Geometry optimization were carried out at the B3LYP/6-31G(d) level. The molecules were simplified by replacing pentaethoxyl chains with methoxyl groups to reduce the number of basis functions.