Tuning of phenoxazine chromophores for efficient organic dye-sensitized solar cells†

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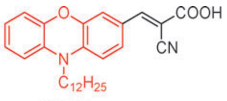
Through introducing an energy antenna system into a simple phenoxazine dye (TH301), a novel and efficient dye TH305 was designed and synthesized for application in a dye sensitized solar cell with prominent overall conversion efficiency of 7.7%.

Dye-sensitized solar cells (DSCs)[1] acting as promising solar energy-to-electricity conversion devices have been developed widely from many aspects, such as semiconductors, electrolytes, counter electrodes, as well as photosensitizers. Due to the cost and environmental consideration, organic sensitizers are deemed as good alternatives to replacing noble ruthenium metal complexes[2,3] and have been studied intensely. In recent years, many types of organic dyes, such as, coumarin,[4] indoline,[5] fluorine,[6] triphenylamine,[7] carbazole,[8] heteranthracene,[9] and tetrahydroquinoline dyes[10] have been reported to work satisfactorily in DSCs. However, to design more efficient organic dyes is still a challenge. In our recent work, we demonstrated that the intramolecular energy transfer (E_nT) and charge transfer (ICT) processes in dyes have a positive effect on improving the DSCs performance.[11] Also, Haque and co-workers have reported the antenna group of hole transport materials (HTM) can indeed slow the recombination between the photoinjected electrons and oxidized HTM through separating the holes spatially away from the electrons in the semiconductor, and thus improve the efficiency of DSCs.[12] Based on these studies, a novel organic dye (**TH305**) has been designed and synthesized through the modification of a simple phenoxazine dye (**TH301**) with triphenylamine energy antenna. The molecular structures of the two dyes are shown in Fig. 1.

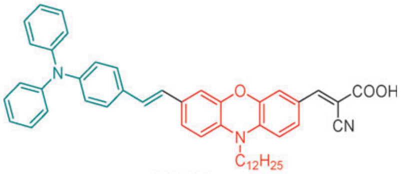
Through selecting different electron donating groups, we found that the phenoxazine (POZ) unit exhibits promising photovoltaic properties. With a simple molecular structure, the **TH301** dye can achieve a relatively high solar energy-to-electricity conversion efficiency (η) of 6.2% under AM 1.5, 100 mW cm^{-2} radiation. As a consequence, **TH301** as a core structure was employed to develop more advanced organic dyes. To further modify the molecular structure, the triphenylamine (**TPA**) group as an appropriate energy antenna was chosen and introduced into the **TH301** dye to construct the **TH305** dye.

The UV-Vis absorption spectra of the two dyes are shown in Fig. 2. **TH301** has an absorption peak (λ_{abs}) at 492 nm, which is ascribed to the HOMO → LUMO transition. An additional peak was observed at 390 nm in the absorption spectra of **TH305**, which is considered as the absorption of the energy antenna subunit. The absorption band with a peak at 517 nm of **TH305** is red-shifted in comparison to that of **TH301** due to the introduction of the TPA unit. On TiO_2 films, the absorption maxima of the two dyes are blue-shifted by 45 and 49 nm for **TH301** and **TH305**, respectively, in comparison to those in solution. The result suggests that the chenodeoxycholic acid (CDCA) should be employed to suppress the dye aggregation through co-adsorption with the photosensitizers.

The HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energy levels are usually employed to estimate the possibilities of electron injection from the excited state dye to the conduction band (CB) of the semiconductor and dye regeneration. Cyclic voltammetry (CV) measurement of these dyes were performed in CH_2Cl_2 to measure the first oxidation potentials (E_{ox}) corresponding to the HOMO levels of the dyes which are summarized in Table 1. The HOMO level of **TH305** is more negative than that of **TH301** due to the introduction of the TPA unit. The HOMO levels of **TH301** and **TH305** dyes are at 1.07 and 0.87 V, respectively, which are positive enough comparing with that of iodine–iodide (0.4 V),[13] indicating that



TH301



TH305

Fig. 1 The structure of the POZ dyes.

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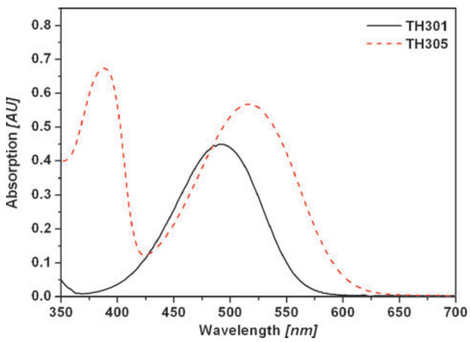

Fig. 2 The absorption spectra of the POZ dyes in CH_2Cl_2.

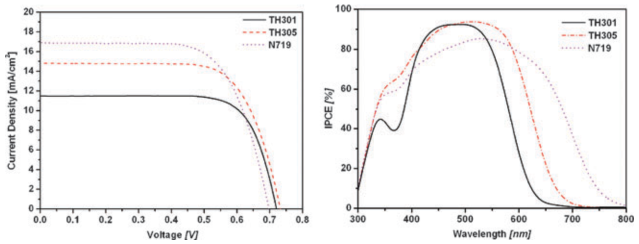

Fig. 3 The J–V curves (left) and IPCE spectra (right) of POZ dyes and **N719** dye.

the oxidized dyes could be regenerated by redox electrolyte effectively.

LUMO levels of the dyes can be obtained from the HOMO level and zeroth–zeroth energy ($E_{0\text{-}0}$) estimated from the intersection between the absorption and emission spectra, namely, $E_{ox} - E_{0\text{–}0}$. To effectively inject the electron into the CB of TiO_2, the LUMO levels of the dyes must be sufficiently negative relative to the CB energy level of TiO_2, −0.5 V (*vs.* NHE).[13] From the LUMO values, we can find the two dyes can achieve the electron injection. The relatively large energy gaps between the LUMO of the dyes and CB energy level of the semiconductor allow for the treatment the 4-*tert*-butylpyridine (TBP) to the electrolyte, which can shift the E_{cb} of the TiO_2 negatively and improve the open-circuit voltage and overall conversion efficiency consequently.[14]

In the process of DSCs fabrication, the POZ dyes showed a relatively fast adsorption rate on TiO_2. The optimized time for electrode sensitization based on **TH301** and **TH305** is 2 h. Under the optimized fabrication conditions, **TH305** achieves a prominent overall conversion efficiency of 7.7%, with short-circuit photocurrent density (J_{sc}) = 14.7 mA cm^{-2}, open-circuit photovoltage (V_{oc}) = 733 mV and fill factor (ff) = 0.71; **TH301** dye gives 6.2% efficiency (J_{sc} = 11.5 mA cm^{-2}, V_{oc} = 722 mV, ff = 0.75). From the incident photon-to-current conversion efficiency (IPCE) spectra (see Fig. 3) of these dyes, we find that **TH305** shows a broader solar light response range (300–720 nm) with values exceeding 80% from 420 to 580 nm, resulting in a high photocurrent. Interestingly, the IPCE values of **TH305** between 320 and 420 nm are much higher than that of **TH301** dye, probably due to the intense absorption of the energy antenna and an effective E_nT process. Under similar test conditions, **N719** dye obtains a referenced efficiency, 8.0% (J_{sc} = 16.9 mA cm^{-2}, V_{oc} = 700 mV, ff = 0.68), with an IPCE spectrum, extending from 300 to 800 nm. Noticeably, the IPCE values of **TH305** are obviously superior to that of the **N719** dye between 340 and 620 nm. Also, one observes that the IPCE spectra of these two dyes are more broadened compared to their absorption spectra on TiO_2 as well as in solution. This is because Li^+ ions in the electrolyte can extend the steady-state absorption spectra of the dyes through interacting with the dye molecules.[15,16]

Density functional theory (DFT) calculations[17] were performed at a B3LYP/6-31G level for the geometry optimization to observe frontier molecular orbitals (MOs) of the HOMO and LUMO. The frontier MOs of **TH305** reveals that HOMO → LUMO excitation moves the electron density distribution from TPA and POZ moieties to the cyanoacrylic acid (see Fig. 4). The result indicates that the **TH305** dye can complete the fast electron injection from the LUMO to TiO_2 and the TPA energy antenna in **TH305** dye further improves the electron donating ability.

In conclusion, two pure organic phenoxazine (POZ) dyes were designed and synthesized for application in dye sensitized solar cells. Based on an intramolecular energy transfer (E_nT) process, the **TH305** dye is obtained by introducing an energy antenna unit into the simple **TH301** dye, resulting in a prominent overall conversion efficiency (η) of 7.7%. Under similar test conditions, the **N719** dye gives a referenced η value of 8.0%. The result suggests that the energy antenna indeed plays a crucial role in improving the photovoltaic properties of DSCs and paves the road for developing more efficient organic dyes for DSCs in the future.

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Table 1 Absorption, emission and electrochemical properties of POZ dyes

	Absorption[a]			Emission	Oxidation potential[c]		
Dye	λ_{abs}/nm	ε (at λ_{abs})/M^{-1} cm^{-1}	λ_{abs} on TiO_2[b]/nm	λ_{em}/nm	HOMO/V[d]	$E_{0\text{–}0}$ (Abs/Em)[e]/V	LUMO[d]/V
TH301	491	22 000	446	610	1.07	2.24	−1.17
TH305	390	33 000	468	645	0.87	2.15	−1.28
	517	28 000		640			

[a] Absorption and emission spectra were measured in CH_2Cl_2 solution (2×10^{-5} M) at room temperature. [b] Absorption spectra on TiO_2 were obtained through measuring the dye adsorbed on TiO_2 film in CH_2Cl_2. [c] The oxidation potential of the dyes were measured in CH_2Cl_2 with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as electrolyte (working electrode: glassy carbon; reference electrode: Ag/Ag$^+$; calibrated with ferrocene/ferrocenium (Fc/Fc$^+$) as an internal reference and converted to NHE by addition of 630 mV.[7a] counter electrode: Pt). [d] *vs.* NHE. [e] $E_{0\text{–}0}$ was estimated from the intersection between the absorption and emission spectra.

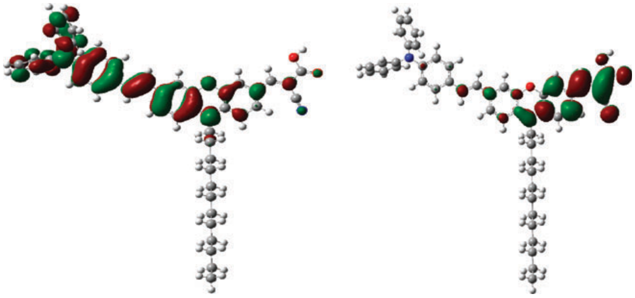

Fig. 4 The frontier molecular orbitals (MOs) of the HOMO (left) and LUMO (right) of the **TH305** dye.

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