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Phenothiazine derivatives for efficient organic dye-sensitized solar cells†

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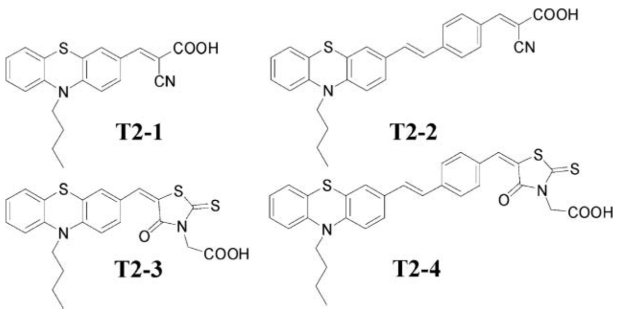
Novel organic dyes based on the phenothiazine (PTZ) chromophore were designed and synthesized for dye-sensitized solar cells, which give solar energy-to-electricity conversion efficiency (η) of up to 5.5% in comparison with the reference Ru-complex (N3 dye) with an η value of 6.2% under similar experimental conditions.

Dye-sensitized solar cells (DSSCs) have attracted much attention to researchers due to the relatively high solar energy-to-electricity conversion efficiency (η) and potentially low cost production since Grätzel and co-workers reported high efficiency in 1991.[1] Among other components, dye sensitizers have been recognized as one of the most important parts for DSSCs to get high performance. Commonly, Ru-polypyridine complexes, such as N3 dye[2,3] and black dye[4] are widely used and showed efficiencies of up to 11% at simulated AM 1.5 G irradiation.[5] In recent years, the interests in organic dyes as substitutes of noble metal complexes are increasing due to many advantages, such as diversity of molecular structures, high molar extinction coefficient, simple synthesis as well as low cost and environmental issues. Coumarin,[6,7] merocyanine,[8] indoline,[9] polyene,[10] hemicyanine,[11,12] triphenylamine,[13–15] fluorene[16–18] and tetrahydroquinoline[19] based-organic dyes have been developed and showed good performance. Here, we report a new series of organic dyes based on the phenothiazine (**PTZ**) chromophore (Scheme 1). These dyes can be easily synthesized with cheap materials and show high efficiencies for DSSCs. The **PTZ** unit in these dyes is adopted as an electron donor, cyanoacrylic acid or rhodanine-3-acetic acid as the electron acceptors (anchoring groups), and butyl carbon chains for increasing the solubility. The synthetic protocol and full characterization of these dyes are provided in the ESI.†

The absorption, emission, and electrochemical properties of this dye series **T2-1**, **T2-2**, **T2-3** and **T2-4** are listed in Table 1. Absorption spectra of these dyes in CH_2Cl_2 solutions and on TiO_2 films are shown in Fig. 1. The **T2-3** and **T2-4** dyes with rhodanine-3-acetic acid as anchoring group show red-shifts in absorption bands compared with **T2-1** and **T2-2** dyes with cynaoacrylic acid as anchoring group. Absorption maxima (λ_{abs}) of 452 and 457 nm are obtained for **T2-1** and **T2-2**, respectively, in CH_2Cl_2 solution. On TiO_2 films, the absorption maxima of these dyes are blue-shifted by 27, 41, 5 and 8 nm for **T2-1**, **T2-2**, **T2-3** and **T2-4**, respectively, in comparison to those in solution. The large blue shifts of the absorption spectra on TiO_2 of **T2-1** and **T2-2** could be ascribed to the aggregation of the dyes on the TiO_2 surface. Such a phenomenon has been also found in other organic dyes.[7,19]

The first oxidation potentials (E_{ox}) corresponding to the HOMO levels of the dyes were measured by cyclic voltammetry (CV) in CH_2Cl_2 solution, see data in Table 1. It is shown that the HOMO levels of the dyes in this series are sufficiently more positive than the iodine/iodide redox potential value, indicating that the oxidized dyes formed after electron injection into the conduction band of TiO_2 could accept electrons from I^- ions thermodynamically. The LUMO levels of these dyes (calculated by $E_{ox} - E_{0\text{–}0}$, see Table 1) are sufficiently more negative than the E_{cb} (conduction-band-edge energy level) of the TiO_2 electrode, which is -0.5 V *vs.* NHE.[20] The relatively large energy gaps between the LUMO and E_{cb} provide the possibility for the addition of 4-*tert*-butylpyridine to the electrolyte, which can shift the E_{cb} of the TiO_2 more negatively and, consequently, improve the voltage and the total efficiency.[21]

The photovoltaic properties of these dyes on DSSCs are shown in Table 2 and *J–V* curves of the dyes are shown in Fig. 2(a). Different solvents (CH_2Cl_2, THF, EtOH, MeCN and DMF) were used in the dye bath for TiO_2 film sensitization, and CH_2Cl_2 was found to show ideal η values. We have achieved an η value of 5.5% (with short-circuit photocurrent density J_{sc} = 10.9 mA cm^{-2}, open-circuit photovoltage V_{oc} = 712 mV, and fill factor *ff* = 0.71) and 4.8% (J_{sc} = 10.7 mA cm^{-2}, V_{oc} = 673 mV, and *ff* = 0.67) for DSSCs based on **T2-1** and **T2-2**, respectively. **T2-3** and **T2-4** show



Scheme 1 Molecular structure of **PTZ** dyes.

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Table 1 Absorption, emission, and electrochemical properties of **T2-1**, **T2-2**, **T2-3** and **T2-4**

	Absorption[a]			Emission	Oxidation potential data[c]		
Dye	λ_{abs}/nm	ε/M^{-1} cm^{-1} (at λ_{abs})	$\lambda_{abs}{}^{b}$/nm (on TiO$_2$)	λ_{em}/nm	E_{ox}/V (*vs.* NHE)	$E_{0\text{–}0}{}^{d}$ /V (Abs/Em)	$(E_{ox} - E_{0\text{–}0})$/V (*vs.* NHE)
T2-1	452	19400	425	592	1.10	2.37	−1.27
T2-2	457	13100	416	653	0.92	2.25	−1.33
T2-3	481	15000	476	689	1.03	2.17	−1.14
T2-4	465	27800	457	598	0.86	2.33	−1.47

[a] Absorption, 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.[15] counter electrode: Pt). [d] $E_{0\text{–}0}$ was estimated from the intersection between the absorption and emission spectra

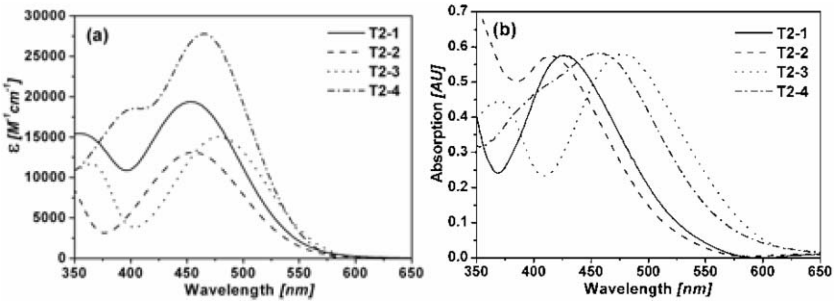

Fig. 1 Absorption spectra of **T2-1**, **T2-2**, **T2-3** and **T2-4** in CH_2Cl_2 solutions (a) and on TiO_2 films (b).

Table 2 Photovoltaic performance of DSSCs based on **T2-1**, **T2-2**, **T2-3**, **T2-4** and **N3** dye[a]

Dye	J_{SC}/mA cm^{-2}	V_{OC}/mV	Fill factor (*ff*)	η (%)
T2-1[b]	10.9	712	0.71	5.5
T2-2[b]	10.7	673	0.67	4.8
T2-3[b]	4.8	532	0.74	1.9
T2-4[b]	5.9	569	0.71	2.4
N3[c]	14.0	695	0.64	6.2

[a] Measured under irradiation of AM 1.5 G simulated solar light (100 mW cm^{-2}) at room temperature, 10 μm film thickness, 0.159 cm^2 working area. [b] The concentration of **PTZ** dye is 2×10^{-4} M in CH_2Cl_2 and 0.6 M tetrabutylammonium iodide (TBAI), 0.1 M LiI, 0.05 M I_2, 0.5 M 4-*tert*-butylpyridine (TBP) in dry acetonitrile as electrolyte. [c] The concentration of **N3** dye is 3×10^{-4} M in ethanol and 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.1 M LiI, 0.05 M I_2, 0.6 M TBP in methoxypropylnitrile (MPN) as electrolyte.

relatively low η values of 1.9% and 2.4%, respectively. Under similar conditions, the **N3** dye gives a η value of 6.2%. The incident photon-to-current conversion efficiencies (IPCEs) of these dyes in DSSCs are shown in Fig. 2(b). **T2-1** gives higher IPCE value than the other three dyes in this series, with highest value of 77% at 500 nm. The rather low IPCE values for **T2-3** and **T2-4** dyes indicate that rhodanine-3-acetic acid is a poor anchoring group in comparison to cyanoacrylic acid. We have noted that the IPCE spectrum of *e.g.* **T2-1** is significantly broadened compared to the absorption spectrum of the dye adsorbed on TiO_2 (Fig. 1). The reason for this needs further studies. It is also interesting to note that the **T2-1** dye gives a better solar cell performance than the **T2-2** dye, although its molecular structure is simpler.

To get a further insight into the big difference in performance of DSSCs based on these **PTZ** dyes, density functional theory (DFT) calculations[22] were performed at a B3LYP/6-31+G(d) level for the geometry optimization. The frontier MOs of **T2-1** and **T2-3** reveal that HOMO–LUMO excitation moves the electron density distribution from the **PTZ** moiety to the cyanoacrylic acid or rhodanine-3-acetic acid moiety (see Fig. 3). However, the LUMO electron density geometry distribution of **T2-1** is located on the cyanoacrylic group, but for **T2-3** it is mainly concentrated on the rhodanine framework, especially on the carbonyl and thiocarbonyl, and resulting in the position of LUMO isolated from the

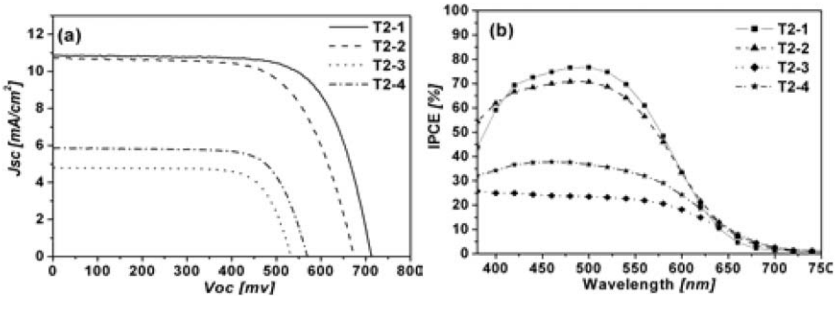

Fig. 2 (a) Photocurrent density *vs.* voltage curves for DSSCs based on **T2-1**, **T2-2**, **T2-3** and **T2-4** under irradiation of AM 1.5 G simulated solar light (100 mW cm^{-2}) and (b) the incident photon-to-current conversion efficiencies spectra for DSSCs based on **T2-1**, **T2-2**, **T2-3** and **T2-4**.

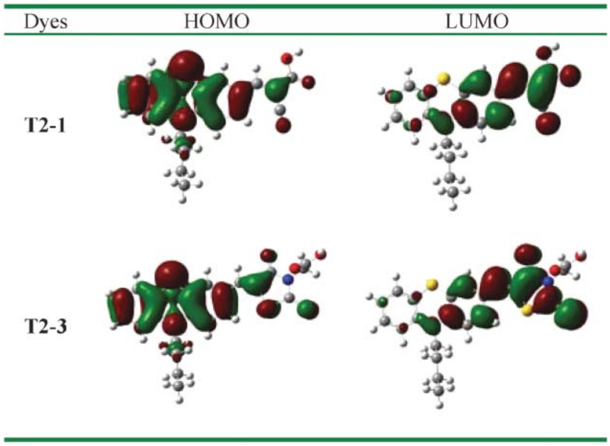

Fig. 3 The frontier molecular orbitals of the HOMO and LUMO calculated with DFT on a B3LYP/6-31+G(d) level of **T2-1** and **T2-3**.

–COOH anchoring group due to the presence of the $–CH_2–$ group. Consequently, the **T2-3** dye prevents electrons from being effectively injected into the TiO_2 conduction band *via* the carboxyl group.[23] These results indicate that the **T2-1** dye can give fast electron injection from the LUMO to TiO_2, however, the **T2-3** dye can not.

In summary, we have synthesized a novel series of **PTZ** dyes for DSSCs. A prominent solar energy-to-electricity conversion efficiency (η) of 5.5% is achieved in a DSSC based on **T2-1** dye which is simple in structure and easy to synthesize. The results also show the **PTZ** dyes containing a cyanoacrylic anchor group have much better DSSC performance than those dyes containing a rhodanine-3-acetic acid group. DFT calculation shows that the LUMO of **T2-1** dye has better orbital overlap with the TiO_2 conduction band than that of the **T2-3** dye. Further structural modification of the **T2-1** dye to get even better DSSC performance is in progress.

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