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New Pyridine-anchoring Dyes for p-Type Dye-sensitized Solar Cells

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Two new pyridine-anchoring "push–pull" dyes **I** and **II** with a triphenylamine donor and different acceptors have been synthesized for p-type dye-sensitized solar cells (DSSCs), in which an overall conversion efficiency with dye **II** reached 0.14% under standard global AM 1.5 solar conditions.

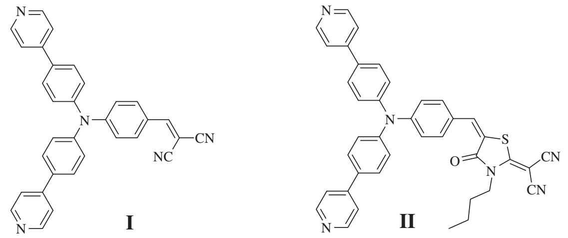
It is known that the theoretical upper limit of the overall conversion efficiency for the tandem dye-sensitized solar cell (pn-DSSC), which consists of a photoactive anode (dye-sensitized TiO_2 photoanode) and a photoactive cathode (dye-sensitized NiO photocathode), is close to 43%, which is much higher than that of DSSCs (about 30%).[1] However, the poor performance of p-type NiO-based DSSCs mainly limits the photovoltaic performance of pn-DSSCs. Therefore, it is imperative and of significant importance to develop p-type sensitizers.

Since Lindquist first reported p-type DSSCs sensitized with tetrakis(4-carboxyphenyl)porphyrin,[2] many sensitizers such as perylene monoimide[3] and coumarin[4] have been synthesized. Some groups such as Sun's,[5] Wu's,[6] and Lin's[7] groups have made great contributions in terms of "push–pull" dyes, which use triphenylamine as the electron donor. Bach and co-workers reported that dyes with triphenylamine donor and perylene monoimide acceptor exhibited long-lived charge-separated states,[8] and the overall conversion efficiency (η) of p-type DSSCs based on the dye reached 1.3% with cobalt(II)/(III) electrolytes,[9] which is the highest performance so far reported in p-type DSSCs. The majority of the dyes use carboxylic acid as their anchoring group.

Recently, the Harima group demonstrated that dyes with a pyridine ring could be used as the electron-withdrawing anchoring group for n-DSSCs.[10] However, to the best of our knowledge, there have been no reports on pyridine-anchoring dyes for p-DSSCs. Here, we have designed and synthesized two new pyridine-anchoring "push–pull" sensitizers **I** and **II** for p-type DSSCs, in which pyridine groups are used as the anchoring group and triphenylamine as an electron donor, with two different acceptors: malononitrile and 2-(3-butyl-4-oxothiazolidin-2-ylidene)malononitrile (BOMN) **I** and **II**, shown in Scheme 1.

The synthetic routes to **I** and **II** are shown in the Supporting Information (Scheme S1).[11] First, the pyridine-anchoring groups were incorporated to the triphenylamine moiety through a Suzuki coupling reaction. In the next step, the target products were prepared via the Knoevenagel condensation of the aldehyde with malononitrile and BOMN in the presence of ammonium acetate and acetic acid, respectively. Their structures were characterized by standard spectroscopic methods (ESI).[11]

The optical and electrochemical properties of **I** and **II** in CH_2Cl_2 solution are presented in Table 1. **I** and **II** displayed two absorption bands, appearing at 346, 450 nm and 345, 485 nm (Figure S1),[11] respectively, which are due to intramolecular charge transfer from triphenylamine to pyridine, dicyanovinyl and BOMN moieties, respectively (see TDDFT calculations, Table S4).[11] Their maximum extinction coefficients (ε) were 3.54×10^4 and $4.72 \times 10^4\,M^{-1}\,cm^{-1}$, respectively. Compared with **I**, the absorption band of **II** presented a bathochromic shift of 35 nm and a larger ε value, manifesting the effect of the BOMN unit in increasing the conjugation. The absorption spectra of **I** and **II** attached to a NiO film (ca. 1.4 µm) after 1.5 h adsorption were similar to those in CH_2Cl_2, indicating that they are unlikely to aggregate, which is beneficial for charge injection.



Scheme 1. Molecular structures of dyes **I** and **II**.

Table 1. Optical and electrochemical properties of dyes

Dye	$\lambda_{max}{}^a$/nm ($\varepsilon \times 10^4\,M^{-1}\,cm^{-1}$)	$\lambda_{max}{}^b$ /nm	HOMO^c/V (vs. NHE)	$E_{0-0}{}^d$ /eV	LUMO^e/V (vs. NHE)
I	346 (1.82), 450 (3.54)	450	1.66	2.44	−0.78
II	345 (3.58), 485 (4.72)	481	1.60	2.22	−0.62

[a]Absorption maximum in CH_2Cl_2 solution (1×10^{-5} M). [b]Absorption maximum on NiO film. [c]HOMO was internally calibrated with ferrocene (0.4 V vs. NHE) in CH_2Cl_2. [d]E_{0-0} was derived from the wavelength at absorption thresholds from the intersection of absorption spectra and fluorescence spectra. [e]LUMO is calculated by subtracting E_{0-0} to HOMO.

The HOMO levels of **I** and **II** corresponding to their first redox potentials were 1.66 and 1.60 V versus NHE, respectively. These values are both much more positive than the valence band (VB) edge of NiO (0.54 V vs. NHE), which can ensure efficient hole injection from the dye to the semiconductor NiO. The band-gap energies (E_{0-0}) of **I** and **II** were 2.44 and 2.22 eV, respectively, which were estimated from the intercept of the normalized absorption and emission spectra. Computed from the HOMOs and E_{0-0} values, the LUMO levels of **I** and **II** were −0.78 and −0.62 V versus NHE, respectively, which are higher than the redox potential of the $I^-/I_3{}^-$ redox couple (ca. 0.4 V vs. NHE), and there is sufficient driving force for the regeneration of **I** and **II** by $I_3{}^-$.

Since the adsorbing time makes a great difference to the photovoltaic performance of n-DSSCs sensitized with pyridine-

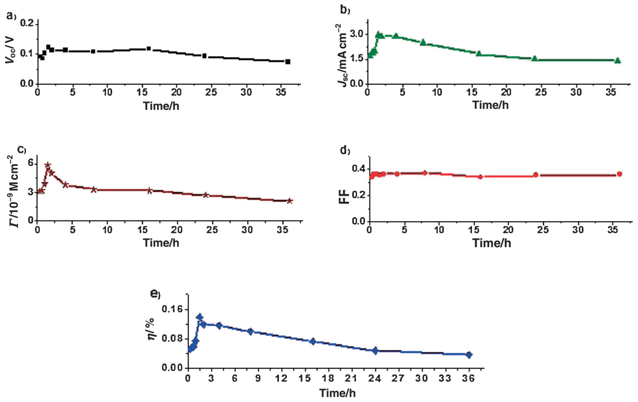


Figure 1. The relationship between photovoltaic parameters of p-type DSSCs based on dye **II** and adsorbing time.

anchoring dyes,[12] we also studied the relationship between the adsorbing time and photovoltaic performance of dye **II**-based p-type DSSCs. The results are shown in Figure 1. With increasing adsorbing time (0.3–36 h), the open-circuit voltage (V_{oc}) and fill factor (FF) of **II** changed little, but the short-circuit current density (J_{sc}) and photovoltaic conversion efficiency (η) had a positive correlation relationship with that of J_{sc}. Both J_{sc} and η showed a great increase in 0.3–1.5 h, in which J_{sc} increased from 1.71 to 2.97 mA cm^{-2}, and η increased from 0.05 to 0.14%. However, there was a gradual decrease in J_{sc} from 2.97 to 1.41 mA cm^{-2} and η fell from 0.14 to 0.04% in 1.5–36 h, which may be due to the change in adsorption capacity (Table S1).[11]

The current–voltage characteristics and incident photon-to-current conversion efficiency (IPCE) of p-type DSSCs sensitized by dyes **I** and **II** in an adsorption time of 1.5 h under standard global AM 1.5 solar light conditions are presented in Figure 2. The IPCE of **II** exceeded 22% in the spectral range 350–550 nm. It reached its maximum value of almost 30% at 490 nm, while the IPCE value of **I** was just around 20% in the spectral range 350–500 nm. The threshold wavelengths of the IPCE spectra for **I** and **II** were located at about 560 and 610 nm, respectively, consistent with the threshold wavelength of absorption spectra for adsorption onto NiO films.

Electrochemical impedance spectroscopy (EIS) was employed to study the electron recombination in p-type DSSCs based on **I** and **II** under a bias applied voltage of −0.12 V in the dark. The Nyquist plot, Bode plot, and equivalent circuit of p-type DSSCs based on dyes **I** and **II** are shown in Figure S5.[11] In the Nyquist plot, there are two semicircles. The small one belongs to the charge-transfer process between the counter electrode and electrolyte, while the other larger one is assigned to the hole recombination at the NiO/dye/electrolyte interface. Some important parameters were obtained by fitting the EIS spectra with an equivalent circuit by using the software ZSimpWin (Table S3).[11] R_S, R_{rec}, and R_{CE} represent series electrolyte interface and counter electrode (CE). The results show that radius of the larger semicircle increases in the order **I** < **II**, corresponding to the R_{rec} data. The hole lifetimes (τ_h) calculated from the Bode plot were 174 and 207 ms for **I** and **II**, respectively. These results suggest that the longer hole lifetime for dye **II** contributes to the improvement in the J_{sc} value rather than the V_{oc} value.

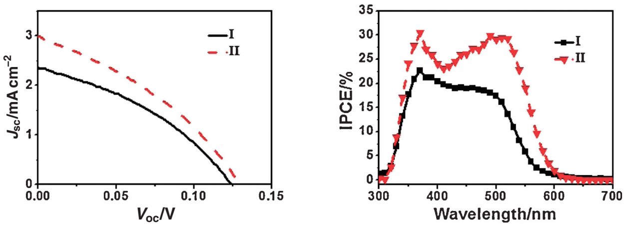


Figure 2. The *I–V* and IPCE spectra for p-type DSSCs based on **I** and **II**.

In conclusion, we have designed and synthesized two new pyridine-anchoring "push–pull" sensitizers **I** and **II** for p-type DSSCs, and studied the relationship between the photovoltaic performance and adsorbing time. The results indicated that the best adsorbing time for dye **II** for p-type DSSCs was 1.5 h, and η of **II**-based p-type DSSCs reached 0.14% ($J_{sc} = 2.97$ mA cm^{-2}, $V_{oc} = 130$ mV, FF = 0.35) under simulated AM 1.5 solar light irradiation (100 mW cm^{-2}). This work provides some valuable information for the further design and synthesis of new sensitizers for p-type DSSCs.

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