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Photovoltaic properties of new cyanine–naphthalimide dyads synthesized by 'Click' chemistry

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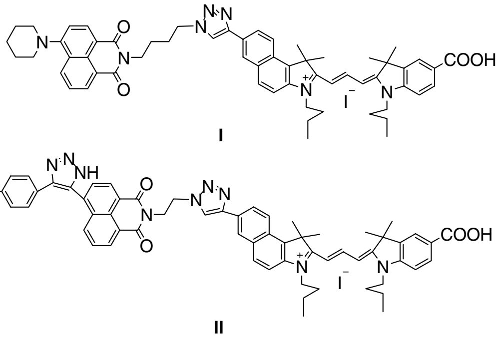
Abstract—Two novel cyanine dyads, in which a naphthalimide unit is attached to benzoindole ring of unsymmetric trimethine cyanine, have been synthesized via 'Click' reaction and characterized by ^{1}H NMR, ^{13}C NMR, and MS-ESI. Under the illumination of AM 1.5 (75 mW cm^{-2}), the power conversion efficiency of cyanine **I** reached 4.8% ($J_{sc} = 14.5$ mA cm^{-2}, $V_{oc} = 0.50$, FF = 0.49). The results show that the two cyanine dyes are promising sensitizers for nanocrystalline dye-sensitized solar cell.

Dye-sensitized solar cells (DSSC) have been actively investigated since the report of highly efficient ruthenium complex-sensitized TiO_2 solar cells by Grätzel and co-workers. Up to now, the Ru(II) polypyridyl complexes have reached highly efficient photoelectric conversion efficiencies of up to 11%.[1] However, pure organic dyes exhibit not only higher extinction coefficient, but simple preparation and purification procedure with a low cost. Recently, great progress has been made in this field and the highest overall photoelectric conversion efficiency of solar cells sensitized by organic dyes has reached 9%, indicating the promising perspective of metal-free organic dyes.[2–5]

Cyanine dyes have very high absorption extinction coefficients ($\sim 10^{5}$ M^{-1} cm^{-1}). Apparently, the sharp absorption peaks and shoulder absorption peaks in solution disable their utility as sensitizers for solar cell, but cyanine dyes adsorbed on the nanocrystalline TiO_2 film can form J- or H-aggregates, which contributed to hypochromism and bathochromism, respectively. Relative high incident photo-to-electron conversion efficiency (IPCE) values are expected over a wide region of wavelength, which will in turn enhance the conversion efficiency of light to electricity. Among a variety of cyanine dyes, structural unsymmetric ones exhibit more outstanding performance. Compared with symmetric cyanine dyes, the shift in electron density of their unsymmetrical counterparts occurs towards the indole ring which contains the carboxylic acid group used for linking the molecule to the semiconductor surface.[6] An unidirectional flow of electron distribution can result in favorable charge separation and electron injection in DSSCs. According to the advantages outlined above, the structure of unsymmetric cyanine dyes was chosen in this Letter.

Recently, we have succeeded in the synthesis of a series of hemicyanine derivatives, and we found that through reasonable design, hemicyanine dyes could perform excellent spectral sensitization.[2c,d] In order to enrich the research field of cyanine dyes for dye-sensitized and gain more information on the structure–property relationships, we synthesized the two new cyanine dyes containing naphthalimide via Cu(I) catalyzed 1,3-dipolar cycloaddition (**I–II**, Scheme 1). The 'Click' reaction



Scheme 1. Structures of the cyanine dyes (**I** and **II**).

Keywords: Cyanine dyes; Dye sensitized solar cell; Naphthalimide.

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of azides and acetylenes was widely used in organic synthesis because of its mild reaction conditions, high yield and simple purification steps.[7] To our knowledge, no organic solar cell sensitizer was reported to be synthesized by 'Click' reaction. The introduction of naphthalimide moiety whose feature absorption peak is around 410 nm aimed to broaden the absorption field of cyanine dyes. Triphenylamine moiety on **II** was expected to greatly locate the cationic charge from the TiO_2 surface and efficiently restrict recombination between conduction band electron and oxidized sensitizer.[8]

The brief synthetic route to these cyanine dyes (**I** and **II**) is depicted in Scheme 2. Two butyl chains on indole nucleus can improve the solubility and form a tightly packed insulating monolayer blocking the I_3^- or cations approaching the TiO_2. Varied reaction systems (CuI, di-*i*-propylethylamine (DIPEA), $CHCl_3$; CuI, DIPEA, THF; CuI, DIPEA, DMSO; CuI, DIPEA, DMF; CuBr, DIPEA, DMF; $Cu(PPh_3)Br$, DIPEA, DMF) have been explored to pursue the suitable 'Click' approach for cyanine dyes. Then a standard 'Click' protocol has been established using a catalystic system including CuI as the copper source, DIPEA as the ligand, including DMF as solvent. Under the similar conditions, naphthalimide moiety was introduced through 1,2,3-triazole ring via 'Click' reaction between alkyl-end aldehyde and azido derivatives.[9] Then the target products were prepared via Knoevenagel condensation. All the intermediates and cyanine dyes (**I** and **II**) were characterized by standard spectroscopic methods (see Supplementary data for details).

Different from the present synthetic route, the original steps was to finish the synthesis of cyanine dyes firstly, then clicked with naphthalimide moiety. But the separation of final dyads from pristine cyanine dyes was unexpectedly frustrating due to their similar polarity and strong adsorption on gel column. The updated plan avoided this difficulty, spared the commonly used costly purification by Prep. HPLC and proclaimed the bright commercial future of these two products.

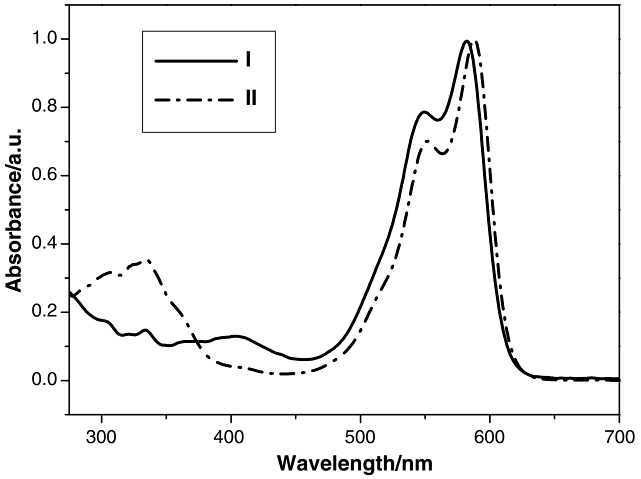


Figure 1. Absorption spectra of **I** and **II** in $CH_2Cl_2/C_2H_5OH = 1/1$ (10^{-5} M).

The absorption spectra of **I** and **II** were recorded in a dilute solution of dichloromethane/ethanol = 1/1 as shown in Figure 1. Cyanine dyes **I** and **II** showed maximum absorption at 588 and 589 nm with vibrational shoulder peaks at 555 and 562 nm because of their similar conjugation systems. Naphthalimide unit attributed to the feature absorption band of **I** at 420 nm; the existence of triphenylamine–naphthalimide dyad resulted in the wide absorption band at 350 nm. The extinction coefficient of **I** and **II** were 0.75 and $1.17 \times 10^5\ M^{-1}\ cm^{-1}$, respectively, which is very high in comparison to $0.139 \times 10^5\ M^{-1}\ cm^{-1}$ at 541 nm for *cis*-di(thiocyanato)bis(2,2′-bipyridyl)-4,4′-dicarboxylate) ruthenium(II) (N3).[3b] Figure 2 gives the absorption spectra of

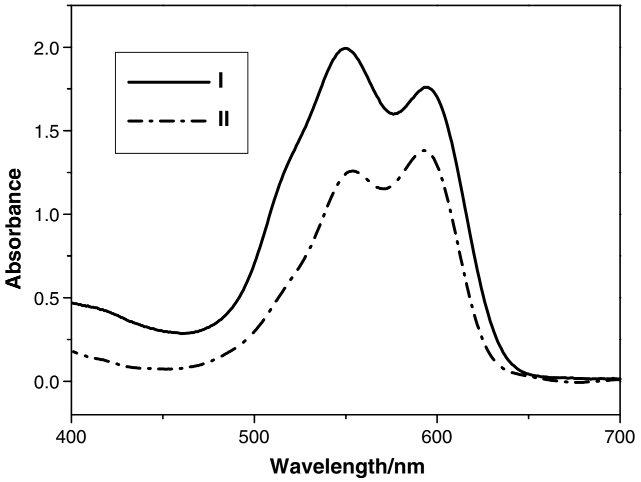
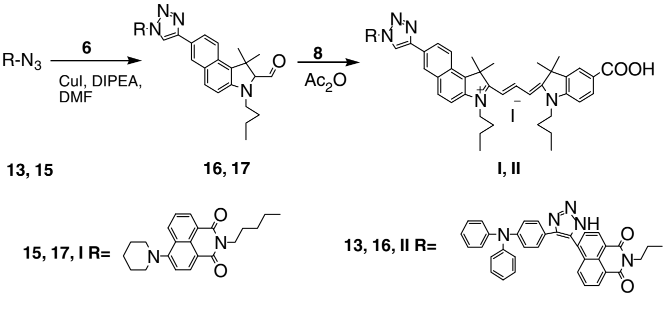


Figure 2. Absorption spectra of **I** and **II** on TiO_2 electrode after adsorption for 12 h.



Scheme 2. Synthetic route of cyanine dyes **I** and **II**.

I and **II** on TiO_2 films after 12 h adsorption. Upon adsorption on TiO_2 film the spectra were broadened compared with those in solution (cf. Fig. 1). It was found that the spectra were broadened on both sides (Fig. 2), that is, blue shifted and red shifted due to the correspondent H- and J-aggregates formed on TiO_2 film.

The amount of **I** and **II** adsorbed on a TiO_2 electrode per unit area was tested by spectroscopic measurement of the concentration change of the dye solution before and after adsorption. As shown in Table 1, dye **I** (2.33×10^{-7} mol cm^{-2}) has higher value than dye **II** (1.76×10^{-7} mol cm^{-2}). This may be explained by the size of the molecule. Large molecule occupies more space on the TiO_2 nanoparticle surface and the larger steric hindrance is unfavorable for the dye molecule diffusion into the smaller pores of TiO_2 film, so the electrode can adsorb more dyes with smaller size, which resulted in a wider region and higher intensity of absorption spectra (Fig. 2).

Two dyes display a strong fluorescence emission at room temperature. Interestingly, the fluorescence emission bands of the dyes in the visible region disappear when the dyes are adsorbed onto the nanocrystalline TiO_2 electrodes. The phenomena can be explained by the efficient electron injection from the excited singlet state of the dyes to the conduction band of TiO_2, and suggesting that products are good sensitizers for nanocrystalline TiO_2 electrodes.

To judge the possibility of electron transfer from the excited dye to the conduction band of TiO_2, the highest occupied molecular orbital (HOMO) levels of −5.93 eV for **I**, −5.94 eV for **II** were measured by cyclic voltammetry (CV) in DMF using Ag/AgCl as a reference electrode. With reference to the absorption maxima, corresponding to the gap between the HOMO and LUMO levels for **I** and **II**, the energy levels of the LUMO can be estimated to be −4.01 and −4.00 eV, respectively. Obviously, the excited-state energy levels for the products are higher than the bottom of the conduction band of TiO_2 (−4.4 eV),[2c] clarifying that the electron injection should be possible thermodynamically.

Figure 3 shows the action spectra of nanocrystalline TiO_2 solar cells sensitized with these cyanine dyes. The dye-sensitized solar cells efficiently convert visible light to photocurrent efficiently in the range from 400 to 680 nm, which corresponds well with the absorption of the electrode. The IPCE of **I** reached maximum (60%) at 540 nm; however, the highest IPCE value of **II** (44%) was obtained at 600 nm. The broader action spectra of **I** indicated that **I** sensitized TiO_2 electrode would generate a higher conversion yield.

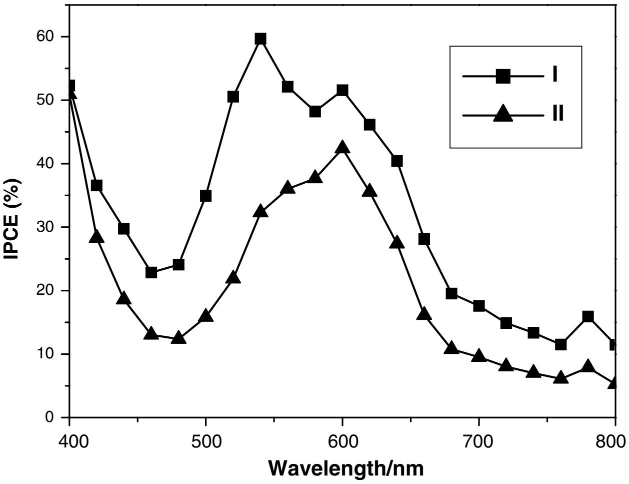


Figure 3. Photocurrent action spectra of the TiO_2 electrodes sensitized by **I** and **II**.

Under irradiation of AM 1.5 (75 mW cm^{-2}) or a Xe lamp (20 mW cm^{-2}), the photo-electrochemical properties of **I** and **II** sensitized TiO_2 electrodes are listed in Table 2, while the corresponding photocurrent–voltage curves are shown in Figure 4. The dye-coated TiO_2 film, as working electrode, was placed on top of an FTO glass as a counter electrode, on which Pt was sputtered. The redox electrolyte was introduced into the inter-electrode space by capillary force. Because the amount of **I** adsorbed on the electrode is much more than that of **II**, the short-circuit photocurrent, open-circuit photo voltage, and power conversion efficiency of **I** were also higher than **II** sensitized solar cell. Unlike the stable performance of silicon solar cell, DSSC is sensitive to variable illumination. When the irradiation intensified, the transport of I_3^-/I^- to and from the counter electrode is not fast enough to fully regenerate the oxidized dye.[10] The diffusion kinetics in the electrolyte become

Table 2. Parameters of dye-sensitized solar cells

Dye (light intensity/mW cm^{-2})	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	η (%)
I (75)	14.5	0.50	0.49	4.8
I (20)	4.34	0.54	0.49	5.8
II (75)	9.7	0.51	0.52	3.5
II (20)	3.33	0.56	0.53	5.0

Table 1. Optical properties and redox potentials of **I** and **II**

Dye	λ_{max}^{ab} [a] (nm)	ε[b] (M^{-1} cm^{-1})	Adsorption[c] (mol cm^{-2})	HOMO[d] (eV)	LUMO[d] (eV)
I	588	0.75×10^5	2.33×10^{-7}	−5.93	−4.01
II	589	1.17×10^5	1.76×10^{-7}	−5.94	−4.00

[a] Absorption maximum in $CH_2Cl_2/C_2H_5OH = 1/1$ (10^{-5} M).

[b] Molar extinction coefficient at λ_{max}^{ab}.

[c] Adsorption amount per unit area of TiO_2 film.

[d] Redox potential. Scan rate: 20 mV s^{-1}, electrolyte: tetrabutyl ammonium perchloride.

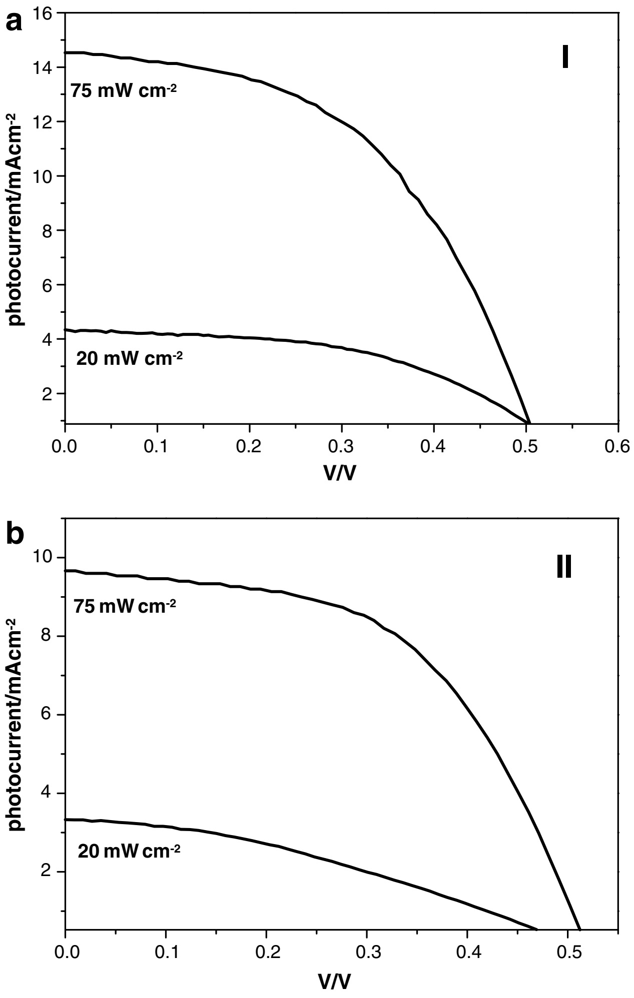


Figure 4. Photocurrent–voltage curve of **I** (a) and **II** (b) sensitized TiO_2 electrodes under different light intensities.

the limiting step in the current production, which has a dramatic influence on the efficiency of **I** and **II**, which decreases from 5.8% to 4.8%, 5.0% to 3.5%, respectively.

In conclusion, two new cyanine dyes with carboxylic acid group were synthesized via 'Click' reaction and characterized by ^{1}H NMR, ^{13}C NMR and MS-ESI. Through investigation of their absorption and photoelectrochemical properties, **I** is found to be a better sensitizer, which has a conversion yield of 4.8%, with a short-circuit photocurrent of 14.5 mA cm^{-2}, an open-circuit voltage of 0.5 V and a fill factor of 0.49 under illumination of AM 1.5 (75 mA cm^{-2}). The optimal measurement of their photovoltaic properties is in progress.

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Supplementary data

Supplementary data (experimental details, synthetic and spectroscopic data) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.02.034.

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