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New Pyridinium Ylide Dyes for Dye Sensitized Solar Cell Applications

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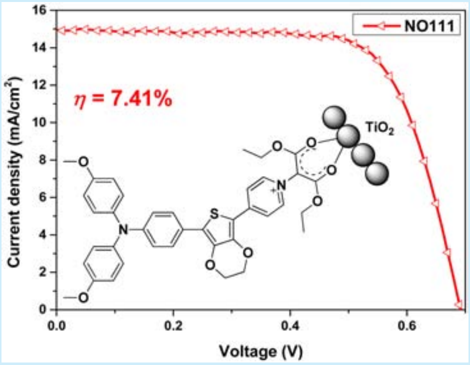
S *Supporting Information*

ABSTRACT: Novel organic pyridinium ylide sensitizers (NO109−111) consisting of various anchoring groups were synthesized and characterized for applications in dye sensitized solar cells. Compared with the pyridine-*N*-oxide dye (NO108), the ylide sensitizers with strong electron-withdrawing acceptors exhibited dominant ultraviolet absorption properties and efficient binding abilities to the TiO_2 surface. Among these dyes, the pyridinium ylide NO111 sensitized solar cell showed the highest efficiency (5.15%), which was improved to 7.41% by employing coadsorbent chenodeoxycholic acid.



Ever-increasing energy demands, rapidly depleting fossil fuel reserves, and aggravating environmental pollution have triggered the extensive research for clean and renewable energy resources. Among various energy generating tools, dye sensitized solar cells (DSSCs) have been considered one of the promising technologies for their economic cost of production and excellent power conversion efficiency.[1] The dye molecule is responsible for light absorption, excitation, and charge separation followed by injection of the excited photoelectron into the conduction band (CB) of TiO_2, which thus plays a prominent role in the device performance. Metal-free organic sensitizers with versatility, tunable molecular design, and a high molar extinction coefficient (ε) have drawn much attention to the pursuit of improved light harvesting capacities.[2]

Generally, sensitizers based on donor−π−acceptor (D−π−A) frameworks exhibit the superior intramolecular charge transfer (ICT) from the donor to the acceptor of the molecule, ensuring efficient electron transfer from the excited dye into the CB of TiO_2. Studies utilizing this reliable template afforded many sensitizers with high efficiencies.[3] Among the D−π−A dyes, numerous types of donor groups such as triphenylamine, tetrahydroquinoline, phenothiazine, phenoxazine, cyanine, merocyanine, and indoline have been investigated.[4] But only a few classes of anchoring moieties were reported. Most research related to the development of acceptors is focused on dyes constituted with anchoring groups such as carboxylic acid,[5] cyanoacrylic acid,[6] or rodanine-3-acetic acid.[7] Moreover, there were some studies in which pyridine,[8] pyridine-*N*-oxide,[9] or *N*-(carboxymethyl)-pyridinium[10] was employed as an acceptor. These studies suggest that the acceptor should be sufficiently electron-withdrawing and able to chelate efficiently with TiO_2 sites.

In order to expand the scope of the research, further exploration of new acceptors to enhance the binding strength of the dyes is necessary. Herein, we report the synthesis and characterization of novel organic pyridinium ylide dyes NO109−111 as shown in Figure 1. The donor part of each sensitizer consisted of a 4-(bis(4-methoxyphenyl)amino)phenyl group for the favorable spectral red shift. The stabilized pyirdinium ylides with various carbonyl groups (hexafluoropentanedione, squaric acid, and diethylmalonate, respectively) are served as acceptors to facilitate electron transfer from the donor moiety of dye into the CB of TiO_2 via an efficient binding between the anchoring group in the acceptor and titania thin film. To achieve a high extinction coefficient and

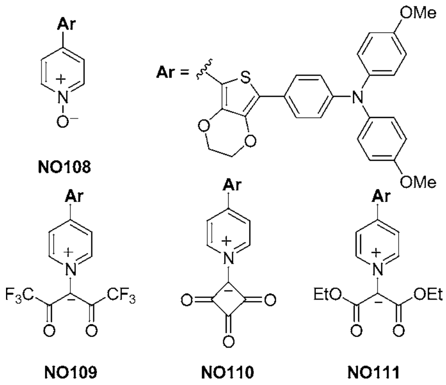


Figure 1. Chemical structures of NO108 and pyridinium ylide dyes NO109−111.

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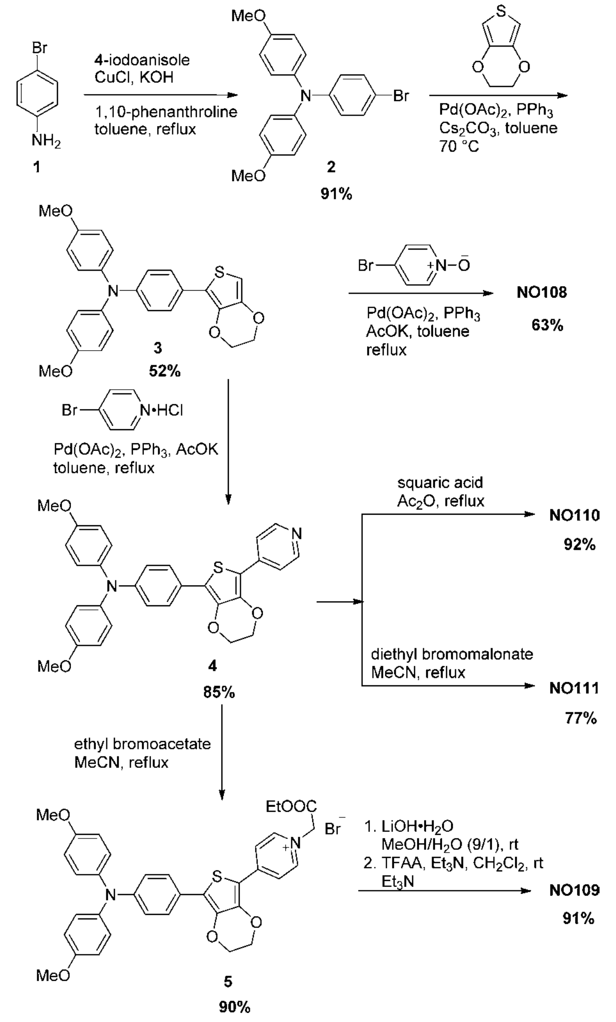
excellent absorption profile, the donor and the acceptor of each dye are bridged with the 3,4-ethylenedioxythiophene (EDOT). To evaluate the effect of new pyridinium ylides, we also prepared NO108 (Figure 1) composed of the same donor moiety and the bridge unit but of a different acceptor, pyridine-*N*-oxide.

Synthesis of the dyes NO108−111 were accomplished by simple and convenient methods as shown in Scheme 1. The Ullmann reaction of 4-bromoaniline and 4-iodoanisole gave the compound **2** which was reacted with EDOT by direct C−H bond arylation[11] to obtain the desired product **3**. Further direct C−H bond arylation of the compound **3** with 4-bromopyridine-*N*-oxide afforded NO108. Apart, the reaction between compound **3** and 4-bromopyridine hydrochloride yielded the pyridine derivative **4** which was treated with squaric acid and diethyl bromomelonate to produce NO110 and NO111, respectively. On the other side, the N-alkylation of compound **4** with ethyl bromoacetate yielded pyridinium salt **5** which was hydrolyzed with LiOH in MeOH/H_2O followed by reaction with trifluoroacetic anhydride (TFAA) and Et_3N to afford NO109. Detailed synthetic procedures and characteristic data for all the compounds are provided in the Supporting Information (SI).

Scheme 1. Synthesis Protocol of Dyes NO108−111



Ultraviolet (UV)−visible absorption spectra of dyes in DMF and on TiO_2 films are presented in Figure 2, and their corresponding data are summarized in Table 1. The UV absorption spectra of these sensitizers in solutions showed a strong absorption band in the range 400−600 nm. Owing to their carbonyl group substitution effect which might have favored the ICT excitation, the absorption bands of the sensitizers NO109−111 are highly red-shifted (particularly dye NO110) and have high molar extinction coefficients compared to that of the dye NO108. On TiO_2 films, UV spectra of these pyridinium ylides showed strong and broad absorption bands in the range 400−500 nm. In comparison with those in solution, the maxima of dyes NO109−111 are blue-shifted by 26, 78, and 15 nm, respectively and such a blue shift can be resulted from the aggregation of sensitizers on TiO_2.[12] Specifically, the dye NO110 has experienced a huge blue shift (78 nm) which might be due to an undesired direction of electron flow.[13] It is expected that the impressive absorption profile of the pyridinium ylide NO111 might fetch the light harvesting property and efficiency.

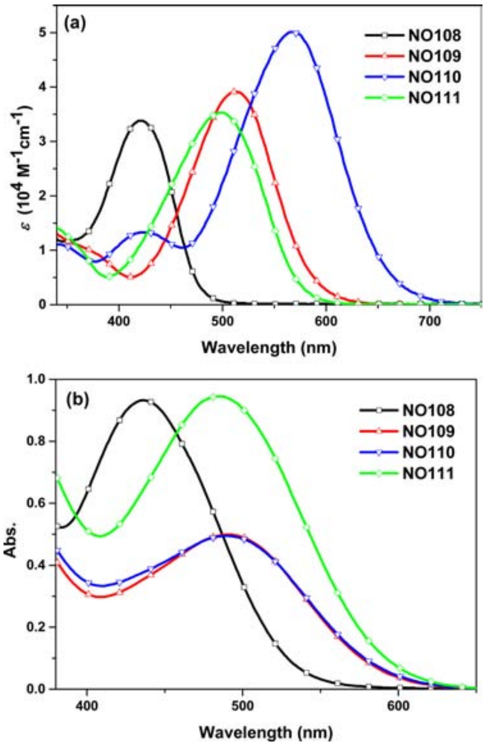


Figure 2. UV−visible absorption spectra of dyes NO108−111 in DMF (a) and on TiO_2 films (b).

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels are important parameters of the sensitizer to estimate the efficiency of the dye regeneration and possibility of the electron transfer process in DSSCs.[14] The HOMO energy level should be sufficiently negative for regeneration of the photo-oxidized dye, and the LUMO should well match the TiO_2 conduction band edge for efficient electron injection. To check the feasibility of dye regeneration by the electrolyte and electron injection into CB of the TiO_2, the HOMO and LUMO energy levels of all the dyes were calculated by their cyclic voltammograms (Figure. S1) and UV−vis absorption spectra. From Table 1, the HOMO energy levels of these dyes are sufficiently lower than that of the I^-/I_3^- (−4.8 eV) redox potential. Also, the LUMO energy levels of the NO108−111 dyes are suitable for electron injection into the TiO_2 conduction band edge. Compared to

Table 1. Optical and Electrochemical Properties Data and Performance Parameters of NO108−111 Sensitized Cells

							cell performance			
dyes	$\lambda_{max}[\varepsilon]$[a] (nm) $[10^4\ M^{-1}\ cm^{-1}]$	λ_{max}[b] (nm)	E_{OX}[c] (V vs F_c/F_c^+)	E_{HOMO}[d] (eV)	E_{LUMO}[e] (eV)	E_{0-0}[f] (eV)	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF	η (%)
NO108	419 [3.4]	437	0.64	5.04	3.02	2.02	4.52	600	0.69	1.87
NO109	515 [3.9]	489	0.71	5.11	3.20	1.91	10.35	680	0.69	4.80
NO110	569 [5.0]	491	0.72	5.12	3.22	1.90	6.76	570	0.70	2.70
NO111	501 [3.5]	486	0.71	5.11	3.21	1.90	12.16	610	0.70	5.15
NO111[g]	–	–	–	–	–	–	14.97	690	0.72	7.41

[a] Measured in DMF. [b] Absorption maxima on TiO_2 film. [c] The $Ag/AgNO_3$ reference electrode was calibrated with a ferrocene/ferrocinium (Fc/Fc^+) redox couple. [d] $E_{HOMO} = E_{OX} - E_{Fc/Fc^+} + 4.8$ eV. [e] $E_{LUMO} = E_{HOMO} - E_{0-0}$. [f] The band gap, E_{0-0}, was estimated from the onset of absorption spectrum measured in DMF. [g] Dye with addition of 1 equiv of CDCA.

the NO108 dye, the narrower band gaps and the lower LUMO energy levels of these ylides suggest that the newly designed sensitizers are advantageous for a smooth electron transfer. To further understand the distribution of HOMO and LUMO energy levels of the sensitizers NO109−111, frontier molecular orbital calculations were performed (Figure S2). The HOMO orbital densities of these dyes were localized mostly on the donor part and stretched partially to the acceptor moiety through a π-bridge. Whereas the LUMO orbitals of the ylides are populated from the acceptor extending to the π-bridge. These results evidence that the synthesized ylides are competent through favorable electron charge transfer from the donor to the acceptor.

The photovoltaic performance of DSSCs sensitized with dyes NO108−111 were studied under the simulated AM 1.5 solar light conditions. The photocurrent density−voltage (J−V) curves and incident photon to current conversion efficiency (IPCE) spectra of solar cells comprised of dyes NO108−111 are presented in Figure 3, and their corresponding open-circuit voltages (V_{oc}), short-circuit photocurrent densities (J_{sc}), fill factors (FF), and overall cell efficiencies (η) are compiled in Table 1. The overall efficiencies of the DSSCs sensitized by new pyridinium ylides NO109−111 were superior to that of the device constructed by the pyridine-*N*-oxide NO108. The cell anchored with NO109 showed the best V_{oc} among the devices based on all the dyes, which can be attributed to the strong insulating capacity of the CF_3 substituents, which might have reduced the charge recombination at the TiO_2 interface.[15] The electron-withdrawing CF_3 groups could also be responsible for the low charge injection into the TiO_2 band edge corresponding to a low J_{sc} value of the NO109 device. The ylide NO110 based cell exhibited lower J_{sc} and V_{oc} but similar FF corresponding to the overall lower efficiency (η) of 2.70% compared to those of the DSSCs sensitized by NO109 and NO111. The device with NO111 delivered the values of J_{sc} = 12.16 mA/cm^2, V_{oc} = 610 mV, and FF = 70 equiv to an overall η = 5.15%. With its excellent absorption profile on the film and feasible electronic properties, the dye NO111 resulted in an unexpected cell efficiency which is presumably due to the aggregation of dye on the TiO_2 surface. To address this problem, the coadsorption technique utilizing chenodeoxycholic acid (CDCA) was employed. The DSSC sensitized by a 1:1 ratio of NO111 and CDCA achieved the best η of 7.41% with J_{sc} = 14.97 mA/cm^2, V_{oc} = 690 mV, and FF = 72. The IPCE spectra of the DSSCs sensitized with all the dyes were covered in the region 300−700 nm except the dye NO108 and were consistent with the J−V curves. The DSSCs of NO109 and NO111 showed higher IPCE maxima (62% at 515 nm and 61% at 475 nm, respectively) than that of the NO110 device (53% at 475 nm). The IPCE of the cell based on NO111 with CDCA (1:1) is broad and has a maximum of 73.6% at 490 nm, corresponding to the highest J_{sc} among the cells of interest.

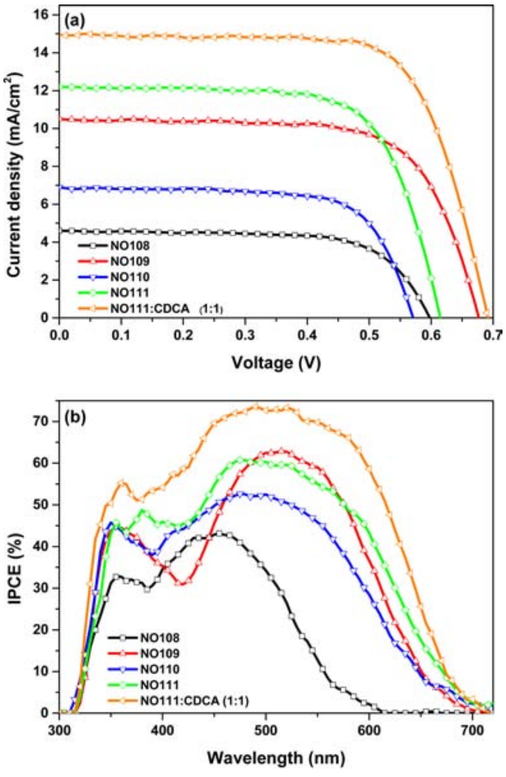


Figure 3. (a) J−V curves and (b) IPCE spectra of cells composed of dyes NO108−111 and NO111:CDCA (1:1).

Furthermore, to reveal the reasons for the V_{oc} and J_{sc} trends, electrochemical impedance spectroscopy (EIS) studies under illumination (Figure 4) as well as in the dark (Figure S3 and Table S1) conditions were employed. As shown in Figure 4, the increasing order of the electron transport resistance (R_{tr}) is NO111:CDCA (1:1) (12.86Ω) < NO111 (14.66Ω) < NO109 (19.24Ω) < NO110 (24.39Ω) < NO108 (55.17Ω), which is in accord with the obtained J_{sc} values shown in Table 1. The cell based on the sensitizer NO111:CDCA (1:1) with the least electron transport resistance value was able to inject electrons efficiently and yielded the highest J_{sc} compared to those of dyes NO108−111. The results of EIS obtained under dark conditions (Figure S2) revealed that the charge recombination resistances (R_{rec}) are consistent with the V_{oc} data observed.

In conclusion, we synthesized a set of new pyridinium ylide acceptor dyes in a short and effective synthetic route by

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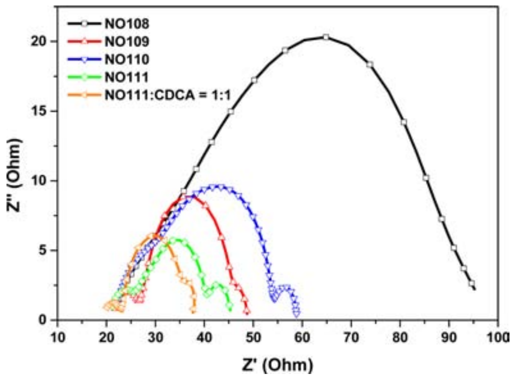

Figure 4. EIS spectra of DSSCs based on dyes NO108−111 and NO111/CDCA (1:1) under illumination.

utilizing the direct C−H bond arylation reaction. These pyridinium ylide sensitizers (NO109−111) exhibited better light harvesting efficiency than that of the pyridine-*N*-oxide NO108. Among these ylides, the NO111 dye with a strong ability for bidentate bridging with the TiO_2 surface displayed a prominent absorption profile and electronic properties, leading to the highest electron injection ability. The DSSC sensitized with the dye NO111 showed the best efficiency (5.15%) which was further improved to 7.41% by employing coadsorbent CDCA. These results suggest that use of appropriate electron-withdrawing groups in combination with an ylide provides an approach to efficient power conversion efficiency for an organic dye. Structural optimization of donor and π-bridge studies to increase the IPCE values and enhance DSSC efficiencies is a part of our future investigation and expected to allow potential for developing efficient sensitizers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01539.

Details of experimental procedures, characterization data of compounds, cyclic voltammogram, molecular orbitals, details of the DSSC fabrication (PDF)

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Notes

The authors declare no competing financial interest.

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