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Novel D– π –A type II organic sensitizers for dye sensitized solar cells

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ABSTRACT

Four organic donor– π –conjugated-acceptor (D– π –A) type II dyes with different thiophene linkers are reported for dye sensitized solar cells (DSSCs). For the first time, a donor (triphenylamine) was introduced in type II sensitizers, and 2-hydroxybenzonitrile as acceptor/anchoring moiety was covalently linked TiO₂ particles. The dye **LS203** in this series gives the best solar energy conversion efficiency of 3.4%, with J_{sc} = 7.4 mA cm⁻², V_{oc} = 0.67 V, *FF* = 0.69, the maximum IPCE value reaches 66.9%.

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Due to the increase in solar energy conversion efficiency and decrease in cost, dye sensitized solar cells (DSSCs) have drawn much attention during the past two decades.^{1,2} In most of traditional organic D– π –A dyes, cyanoacrylic acid group was always introduced as acceptor and anchoring group, which has limited much more excellent dyes that were developed.² It is well known that the traditional DSSCs (Type I DSSCs) are the devices in which electrons are injected from the adsorbed dyes by photoexcitation of the dyes followed by electron injection from the excited dyes to TiO₂.^{3,4} Type II DSSCs in which electrons are injected not only by electron injection from the excited states of dves to TiO₂, but also by direct one-step electron injection from the dyes to TiO₂ by photoexcitation of the dye-to-TiO₂ charge-transfer bands.⁵⁻¹³ The DSSCs employing catechol or its derivatives in the dye structures have been considered as typical examples of Type II DSSCs. An et al. reported a class of Type II thiophene-catechol sensitizers used in DSSCs.¹⁴ However, the reported solar energy-to-electricity conversion efficiencies of Type II DSSCs did not exceed 1.6%.^{5,14}

In this Letter we report four novel Type II organic dyes **LS201**, **LS202**, **LS203**, and **LS204** with Donor– π –Acceptor design in structure (Fig. 1). Triphenylamine was introduced as a donor part in Type II sensitizer, and catechol was used instead by 2-hydroxybenzonitrile as the electron acceptor/anchoring group. Compared with the traditional organic D– π –A dyes with cyanoacrylic acid system, the electron donor, π -spacer and electron acceptors were linked by C–C single bonds without the involvement of any vinyl group, which would hopefully increase the stability of DSSCs.^{15,16} This is a new strategy to design Type II sensitizers. Among the four

dyes, **LS203** gives the best solar energy conversion efficiency of 3.4%, the maximum IPCE value reaches about 66.9%.

The absorption spectra of the four dyes dissolved in CH_2Cl_2 (Fig. 2a) and adsorbed on TiO₂ (Fig. 2b) are displayed in Figure 2, and the photophysical data are collected in Table 1. In CH_2Cl_2 solution, the absorption maxima are between 351 and 376 nm. When the four dyes were absorbed on the TiO₂, the absorption maxima do not have significant changes, but the absorption peaks become much wider and the cut-off absorptions of the four dyes changed from 400 nm dissolved in CH_2Cl_2 to more than 450 nm absorbed on TiO₂. That brings about a surprising change of the colors of the dyes from the CH_2Cl_2 solutions to the TiO₂ absorbed films showed in Figure 3.

The first oxidation potentials ($E_{\rm ox}$) of the four dyes were measured by cyclic voltammetry (CV) in CH₂Cl₂ solution; the data were collected in Table 1. It shows that the HOMO levels of the four dyes were sufficiently more positive than the iodine/triiodide redox potential value (0.4 V vs NHE), indicating that the oxidized dyes formed after electron injection into the CB of TiO₂ could accept electrons from I⁻ thermodynamically.^{17,18} In addition, the LUMO levels of the four dyes were more negative than the $E_{\rm cb}$ of TiO₂ (-0.5 V vs NHE) indicating that the dyes all have enough driving force for electron injection.¹⁷

The *J*-*V* characteristic curves are shown in Figure 4a, and all data are summarized in Table 2. The best solar cell we have achieved is sensitized by **LS203** dye, which has 3.4% efficiency under AM 1.5 solar simulator illumination with a short circuit J_{sc} of 7.4 mA cm⁻² and an open circuit voltage V_{oc} of 0.67 V. The solar cells sensitized by **LS201**, **LS202**, and **LS204** have efficiencies of 2.8%, 3.1%, and 2.6%, respectively. All the dyes show better cell performance compared to the compound Cat-v-Q.⁵ From the data, it is clear to see that introducing alkyl group to the π -spacer is



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Figure 1. Molecular structures of Type II dyes LS201, LS202, LS203, and LS204.



Figure 2. The UV-vis spectra of dyes in CH_2Cl_2 (2 \times 10⁻⁵ M) (a) and on TiO₂ films (b).

beneficial for increasing the efficiency of DSSCs. The J_{sc} and V_{oc} of the devices based on LS202 and LS203 are much higher than that of LS201. The IPCE spectra of these DSSCs are shown in Figure 4b, the maximum IPCE obtained for LS203 was 66.9% at 440 nm, and the maximum IPCE values for LS201, LS202, and LS204 are 66.2%,

Table 1 Optical and electrochemical properties of LS201, LS202, LS203, and LS204

Dye	λ_{max}^{a} in CH ₂ Cl ₂ (nm)	ϵ (10 ⁴ M ⁻¹ cm ⁻¹)	λ _{max} ^b on Tio ₂ (nm)	E ₀₋ o ^d (V)	E _{ox} ^c (V) (vs NHE)	E _{ox} -E ₀₋₀ (V) (vs NHE)
LS201	376	3.85	376	2.82	0.85	-1.97
LS202	356	3.35	358	2.92	0.84	-2.08
LS203	351	2.95	356	2.92	0.88	-2.04
LS204	364	3.30	365	2.72	0.84	-1.88

^a Absorption spectra were measured in CH_2Cl_2 solution (2 \times 10⁻⁵ M) at room temperature. b Absorption spectra on TiO₂ were measured through the dye adsorbed on TiO₂

film in CH₂Cl₂.

^c The oxidation potentials of the dyes were measured in CH₂Cl₂ with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as electrolyte (working electrode: glassy carbon; reference electrode: Ag/Ag+; calibrated with ferrocene/ ferrocenium (Fc/Fc⁺) as an internal reference and converted into NHE by addition of 440 mV, counter electrode: Pt).

^d E_{0-0} was estimated from the onset point of absorption spectra on TiO₂.



Figure 3. The color change of the dyes dissolved in CH₂Cl₂ (above) and absorbed on TiO₂ (below).

68.9%, and 72.9%, respectively, at 420 nm. Although the maximum IPCE of LS203 is not the highest, the IPCE curve of LS203 is broader than the other three dyes. The integral current value of LS203 is



Figure 4. *J*-*V* characteristic curves (a) and IPCE spectra (b) of LS201, LS202, LS203, and LS204.

Table 2

Photovoltaic performances of DSSCs sensitized by LS201, LS202, LS203, $\textbf{LS204}^{\rm a},$ and Cat-v-Q^b

Dyes	$J_{\rm sc}$ (mA cm ⁻²)	$V_{\rm oc}\left({\sf V}\right)$	FF	η (%)	IPCE _{max}	Integral current (mA cm ⁻²)
LS201	6.3	0.62	0.71	2.8	66.2	6.3
LS202	6.9	0.65	0.70	3.1	68.9	7.0
LS203	7.4	0.67	0.69	3.4	66.9	7.3
LS204	6.9	0.55	0.69	2.6	72.9	7.0
Cat-v-Q ^b	4.3	0.58	0.63	1.6		

^a Irradiating light: AM 1.5 G (100 mW cm⁻²); working area: 0.159 cm²; electrolyte: 0.6 M 1,2-dimethyl-3-*n*-propylimidazolium iodide (DMPII), 0.06 M Lil, 0.04 M I₂, 0.1 M 4-tert-butylpyridine (TBP) in acetonitrile.

^b Data taken from Ref. 5.

7.3 mA cm⁻² showed in inset of Figure 4a, which match with *J*–*V* measurement.

In order to study the electron transport and recombination properties in the DSSCs based on **LS201**, **LS202**, **LS203**, and **LS204**, the electrochemical impedance spectroscopy of these DSSCs (Fig. 5) were measured at an applied bias of V_{oc} under dark condition. From the Nyquist plots (Fig. 5a) two semicircles were observed clearly, the smaller one is ascribed to the charge-transfer process at the interfaces between the redox couple and the platinized counter electrode. The bigger one is related to the transport



Figure 5. Electrochemical impedance spectra of DSSCs sensitized by LS201, LS202, LS203, and LS204.

process of the injected electrons at the interfaces between TiO₂ and the electrolyte/dye.¹⁹ It is clear to see that the device based on **LS203** has the biggest charge recombination resistance (R_{rec} = 24.1 Ohm) on the TiO₂, which can reduce the charge recombination rate. It seems reasonable to conclude that the better performance of the device based on **LS203** can be ascribed to a reduced rate of charge recombination, which led to highest value of V_{oc} (0.67 V). The similar result can be found from the Bode plots (Fig. 5b).

In summary, a new strategy to design the Type II dye sensitizers for DSSCs was developed. For the first time, a triphenylamine donor unit was introduced in Type II sensitizers. Catechol was replaced by 2-hydroxybenzonitrile and the vinyl group was avoided to increase the stability of the DSSCs. By using the strategy four novel dyes were successfully synthesized. The dye **LS203** giving the best solar energy conversion efficiency of 3.4%, with J_{sc} = 7.4 mA cm⁻², V_{oc} = 0.67 V, *FF* = 0.69, the IPCE value reaches 66.9%. Improvement of the dye structure of this type might further increase the performance of the DSSCs. Related work is in progress.

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Supplementary data

Supplementary data (details of synthesis of the dyes and the device fabrication) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet. 2012.04.049. These data include MOL files and InChiKeys of the most important compounds described in this article.

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