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$D-\pi$ -A organic dyes with various bulky amine-typed donor moieties for dye-sensitized solar cells employing the cobalt electrolyte



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1. Introduction

To date, the cell efficiencies of DSSCs with a cobalt(II/III) redox couple are reported 13.0% for zinc porphyrin dyes [1], 12.8% for metal-free organic dyes [2,3], while ruthenium dyes-based DSSCs with a cobalt(II/III) redox couple have showed conversion efficiency of about 12% [4]. Recently, Murakami et al. has found that metal-free organic sensitizers containing triphenylamine donors performed very well with cobalt-based redox shuttles because the two phenyl groups at the tip of triphenylamine donor group play a significant role in blocking the recombination reaction [5]. Also, the sensitizers containing a bulky bis-dimethylfluorenylamine donor are able to achieve a relatively high molar extinction coefficient as well as efficient charge injection and electron lifetime [6]. Recently, phenothiazine derivatives have also been used as a promising donor in the organic dyes used as sensitizers in DSSCs [7-9]. Phenothiazine is a well-known heterocyclic compound with electron-rich sulfur and nitrogen heteroatoms, and the phenothiazine ring is nonplanar with a butterfly conformation, which can impede the molecular aggregation and the formation of intermolecular excimers [10]. However, the relationship between the bis-dihexylphenothiazine amino groups and DSSC performance has not been studied.

Here, we prepared **SGT** organic dyes containing various amine-typed donors, such as triphenylamine, bis-fluorenylamine

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ABSTRACT

SGT dyes containing various amine-typed donors as triphenylamine, bis-fluorenylamine and bis-phenothiazinylamine as the electron donor and a cyanoacrylic acid moiety as electron acceptor in $D-\pi$ -A system, were developed to use in dye-sensitized solar cells (DSSCs). The **SGT-102** dye containing bis-fluorenylamine had a better prevented charge recombination than other SGT dyes; leading to improvement in V_{oc} . As a result, the conversion efficiency of 7.22% was achieved with a J_{sc} of 12.1 mA cm⁻², V_{oc} of 865 mV and a *FF* of 69.1 for the DSSC employing a dye containing the bulky bis-fluorenylamine donor unit, while the DSSC based on a dye containing the bulky bis-phenothiazinylamine donor unit showed a lower J_{sc} and V_{oc} , leading to a lower efficiency of 5.16%, due to slow charge recombination associated with differently geometric structure orientations.

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and bis-phenothiazinylamine, as shown in Fig. 1, and we investigated the structure–property relationship between the donor group and conversion efficiency in the DSSCs. The organic sensitizers based on the D– π –A structural motif compose of various amine-typed units as donor, the bithiophene group as π -bridge and cyanoacrylic acid as acceptor. The oligothiophene derivatives are intensively exploited as π -bridges [11–13]. Further extension of the π -conjugation increases the absorption but unexpected additional processes, like self-quenching or recombination processes, occurred to reduce the photocurrent and photovoltages, thus leading to the decrease of the overall efficiency of the DSSCs [14]. Also, the bulky dihexyloxyphenyl group was introduced into the donor moiety for suppression of dye aggregation and charge recombination [15].

2. Experimental

2.1. Materials and synthesis

All reactions were carried out under a nitrogen atmosphere. Solvents were distilled from appropriate reagents. All reagents were purchased from Aldrich. All reactions were carried out under a nitrogen atmosphere. Solvents were distilled from appropriate reagents. All reagents were purchased from Aldrich. 7-(2,4-bis(hexyloxy)phenyl)-N-(7-(2,4-bis(hexyloxy)phenyl)-9,9-dimethyl-9H-fluoren-2-yl)-N-(4-bromophenyl)-9,9-dimethyl-9H-fluoren-2-amine [6], (5'-(1,3-dioxolan-2-yl)-2,2'-bithiophen-5yl)-tributylstannane [16] were synthesized following procedures as





SGT-103

Fig. 1. Chemical structures of SGT dyes.

described previously. The detailed synthetic procedure and characterization are shown in the ESI.

2.2. Measurements

¹H NMR and ¹³C NMR spectra were recorded at room temperature with Varian Oxford 300 spectrometers and chemical shifts were reported in ppm units with tetramethylsilane as the internal standard. FTIR spectra were taken on a JASCO, 4200+ ATR Pro-450-S spectrophotometer. UV–visible absorption spectra were obtained in THF on a Shimadzu UV-2401PC spectrophotometer. Cyclic voltammetry was carried out with a Versa STAT3 (AMETEK). A three-electrode system was used and consisted of a reference electrode (Ag/AgCl), a working electrode, and a platinum wire electrode. The redox potential of dyes on TiO₂ was measured in CH₃CN with 0.1 M TBAPF₆ with a scan rate between 50 mV s⁻¹.

2.3. Density functional theory (DFT)/time-dependent DFT (TDDFT) calculations

Structural optimization of **SGT** dyes was done with a PBE exchange–correlation function using the Vienna *ab initio* simulation package (VASP) [17,18]. We used 400 eV as the cut-off energy, and the conjugate gradient method was employed to optimize the geometry until the force exerted on an atom was less than 0.03 eV/Å. In order to calculate the absorption spectra, we performed the TD-DFT calculations for more stable one between the two configurations. Calculations were done in the gas phase using

the 6-31G(d,p) basis set in GAUSSIAN03 program [19]. We focused on transitions occurring in the range of 350–800 nm, specifically those whose oscillation strengths were greater than 0.1. In order to treat the low wavelength excitations correctly around 350 nm, we made extensive calculations up to 100 singlet \rightarrow singlet transitions.

2.4. Fabrication and testing of DSSC

FTO glass plates (Pilkington) were cleaned in a detergent solution using an ultrasonic bath for 1 h, then rinsed with water and ethanol. The FTO glass plates were immersed in an aqueous solution of 40 mM TiCl₄ at 70 °C for 30 min and then washed with water and ethanol. The first TiO_2 layer with a thickness of 5.3 μ m was prepared by screen-printing TiO₂ paste (Solaronix, 13 nm anatase), and the second scattering layer containing 400 nm sized anatase particles was deposited by screen printing. The TiO₂ electrodes were immersed into the dye solution (0.3 mM) in THF/EtOH (2:1) with and kept at room temperature overnight. Counter-electrodes were prepared by coating with a drop of H₂PtCl₆ solution (2 mg of Pt in 1 mL of ethanol) on an FTO plate. The dye-adsorbed TiO₂ electrode and Pt counter electrode were assembled in a sealed sandwich-type cell. A drop of electrolyte solution (0.22 M [Co(II)-(bpy)₃](B(CN)₄)₂, 0.05 M [Co(III)(bpy)₃](B(CN)₄)₃, 0.1 M LiClO₄, and 0.8 M TBP in ACN) was placed on the drilled hole in the counter electrode of the assembled cell and was driven into the cell via vacuum backfilling. Finally, the hole was sealed using additional Surlyn and a cover glass.

2.5. Photoelectrochemical measurements of DSSC

Photoelectrochemical data were measured using a 1000 W xenon light source (Oriel, 91193) that was focused to give 1000 W/m², the equivalent of one sun at AM 1.5G, at the surface of the test cell. The light intensity was adjusted with a Si solar cell that was double-checked with an NREL-calibrated Si solar cell (PV Measurement Inc.). The applied potential and measured cell current were measured using a Keithley model 2400 digital source meter. The current–voltage characteristics of the cell under these conditions were determined by biasing the cell externally and measuring the generated photocurrent. This process was fully automated using Wavemetrics software.

3. Results and discussion

The absorption and emission spectra of SGT dyes are summarized in Table 1. In the UV-vis spectra (Fig. 2), the three SGT dyes exhibited two main prominent bands, appearing at 300-400 and 400–550 nm, respectively. The intense peak positioned at *ca*. 300–400 nm is attributed to the localized π – π * transition, and low energy absorption occurring at above 450 nm is attributed to the intramolecular charge transfer (ICT) transition between the donor and the cyanoacrylic acid acceptor. The SGT-101 and SGT-102 dyes showed a maximum absorption at 479 nm. Also, the molar absorption coefficient (ε) of the **SGT-102** dye was higher than **SGT-101** dye due to π -extended conjugation. Unlike expectation, the SGT-103 dye containing the bulky phenothiazine donor group showed a maximum absorption of 484 nm, which was red-shifted by 5 nm, compared to the other dyes, since it has been recently reported that the blue-shifts in solution with the number of the donor groups in the starburst 2D– π –A organic dye would be expected due to the higher ICT energy levels resulting from the increase of donor moieties [20,21]. However, increasing the number of the donor moiety improves the molar extinction coefficients of the ICT absorption peaks of the dyes. The molar absorption coefficient of the **SGT-103** dye was higher ($\varepsilon_{max} = 36,800 \text{ M}^{-1} \text{ cm}^{-1}$) than the other dyes, indicating that the SGT-103 dye has a good light-harvesting ability.

The electrochemical properties were investigated by cyclic voltammetry (CV) to obtain the HOMO and LUMO levels of the present dyes (Table 1). HOMO values (1.16, 1.10, 1.22 V vs. NHE) were more positive than the cobalt redox couple (0.5 V vs. NHE). Electron injection from the excited sensitizers to the conduction band of TiO₂ should be energetically favorable because of the more negative LUMO values (-1.15, -1.19, -1.06 vs. NHE) compared to the conduction band edge energy level of the TiO₂ electrode [22]. Structural optimization of **SGT** dyes was done with a PBE exchange–correlation function using the Vienna *ab initio* simulation package (VASP). The shapes of HOMO and LUMO levels of



Fig. 2. The UV-visible absorption (solid lines) and emission spectra (dashed lines) of **SGT-101** (red), **SGT-102** (blue) and **SGT-103** (green) in 2×10^{-5} M in THF. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the **SGT** dyes and the geometrically structural orientations with various donor groups in the **SGT** dyes are shown in Fig. 3 (see **GA**). The electrons in the ground state of all the dye was homogeneously distributed in the donor, and upon light illumination, electrons were excited to an anchoring group through the change from the HOMO to the LUMO by ICT. It indicates that photoinduced electrons are able to transfer from the dye to the TiO₂ electrode efficiently.

Fig. 4a shows the IPCE spectrum of SGT dyes-based cells. The onset wavelengths of the IPCE spectra for the DSSC based on SGT-102 appeared at 690 nm. IPCE values of higher than 60% were observed in the range of 400-550 nm with a maximum value of 70% at 500 nm for the DSSC based on SGT-102. The maximum IPCE value of the DSSC based on SGT-101 was slightly lower than the value of the DSSC based on SGT-102 due to lower molar extinction coefficient. On the other hand, the SGT-103-sensitized DSSC remarkably reduced the IPCE value compared to two other dyes. The lower IPCE value of the DSSC based on SGT-103 is probably due to its less negative HOMO level than that of two other dyes, which might lead to the relative decrease of the electron-regeneration yield [23]. The photovoltaic performance of the SGT dye-based DSSCs are summarized in Table 1 (Fig. 4b). Under the standard global AM 1.5 solar condition, SGT-101-sensitized cell gave a short circuit photocurrent density $(J_{\rm sc})$ of 11.9 mA cm⁻², an open circuit voltage $(V_{\rm oc})$ of 862 mV, and a fill factor (FF) of 69.4, corresponding to an overall conversion efficiency (η) of 7.11%. For the **SGT-102**-sensitized DSSC, compared to the SGT-101-sensitized DSSC, Jsc increased from 11.9 to

Table 1	
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Photophysical, electrochemical and photovoltaic performance	data	of SGT	dyes.
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Dye Absorption ^a λ_{max} (nm), ε (M ⁻¹ cm ⁻¹)	Absorption ^a	Emission	Potentials and energy level		$\Gamma/10^{-7}$	Photovoltaic performance ^e				
	(λ_{\max}/nm)	E _{ox} ^b /V (vs. NHE)	E_{0-0}^{c}/V	<i>E</i> _{LUMO} ^d /V (vs. NHE)	$(mol \ cm^{-2})$	J _{sc} (mA cm ⁻²)	$V_{\rm oc}\left({\sf V}\right)$	FF	η (%)	
SGT-101	337 (34,100), 479 (29,900)	588	1.16	2.31	-1.15	0.51	11.9	862	69.4	7.11
SGT-102	380 (63,100), 479 (30,700)	597	1.10	2.29	-1.19	0.38	12.1	865	69.1	7.22
SGT-103	351 (50,400), 484 (36,800)	593	1.22	2.28	-1.06	0.34	8.95	793	72.7	5.16

^a Absorption and emission spectra were measured in THF.

^b Oxidation potentials of dyes on TiO₂ were measured in CH₃CN with 0.1 M TBAPF₆ with a scan rate of 50 mV s⁻¹ (vs. NHE).

^c E_{0-0} was determined from the intersection of absorption and emission spectra in THF.

^d LUMO was calculated by $E_{\rm ox} - E_{0-0}$.

^e TiO₂ thickness 8.3 µm, (5.4 + 3), TiCl₄ cell active area 0.16 cm²; electrolyte conditions 0.22 M [Co(bpy)₃]²⁺, 0.05 M [Co(bpy)₃]³⁺, 0.8 M *tert*-butylpyridine and 0.1 M LiClO₄ in an acetonitrile solution; dye was dissolved in THF 1/EtOH 2.



Fig. 3. Isodensity plots of the HOMO and LUMO levels and the geometrically structural orientations of SGT dyes.



Fig. 4. Photon-to-current conversion efficiencies (IPCE) (a) and photocurrent-voltage characteristics (b) of representative $\rm TiO_2$ electrodes sensitized with SGT dyes.

12.2 mA cm⁻² and 7.11–7.22% of η due to high light-harvesting ability, while the DSSC based on **SGT-103** dye showed a lower J_{sc} and V_{oc} , leading to a lower efficiency of 5.16%.

To further characterize the electron transport and recombination effect on photovoltaic performance for the **SGT** dyes with

the differently geometric structure orientations, we measured the electrochemical impedance spectroscopy (EIS) under dark conditions at a forward bias of \sim 0.81 V (see Fig. S1). The fitted R_{ct} values at the TiO₂/dye/electrolyte interface corresponding to the second semicircle of the Nyquist plot were in the order of SGT-102 $(150.6 \Omega) >$ **SGT-101** $(140.2 \Omega) >$ **SGT-103** (65.92Ω) , indicating that the recombination rate is decreased in the order of SGT-103 < SGT-101 < SGT-102 in the dark. SGT-101 and SGT-102 had almost the same recombination resistance. From the EIS results, it is clear that the charge recombination rate is the rate-determining step of the DSSC in terms of device performance, since SGT-102 DSSCs decreased the charge recombination rate and resulted in an improvement of the device performance. This insulating molecular layer, associated with differently geometric structure orientations, effectively inhibits back electron transfer from the TiO₂ to cobalt electrolyte and gives a higher $V_{\rm oc}$.

4. Conclusions

We have successfully synthesized organic sensitizers containing various amine-typed donors with interesting optical and photovoltaic performance. The **SGT-102** had a better prevented charge recombination than other **SGT** dyes; leading to improvement in V_{oc} . As a result, the solar cell based on the **SGT-102** dye showed better photovoltaic performance with a J_{sc} of 12.1 mA cm⁻², a V_{oc} of 865 mV, and an *FF* of 69.1, corresponding to an overall conversion efficiency η of 7.22% under standard AM 1.5 irradiation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.orgel.2015.06. 011.

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