

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



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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- π -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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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

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

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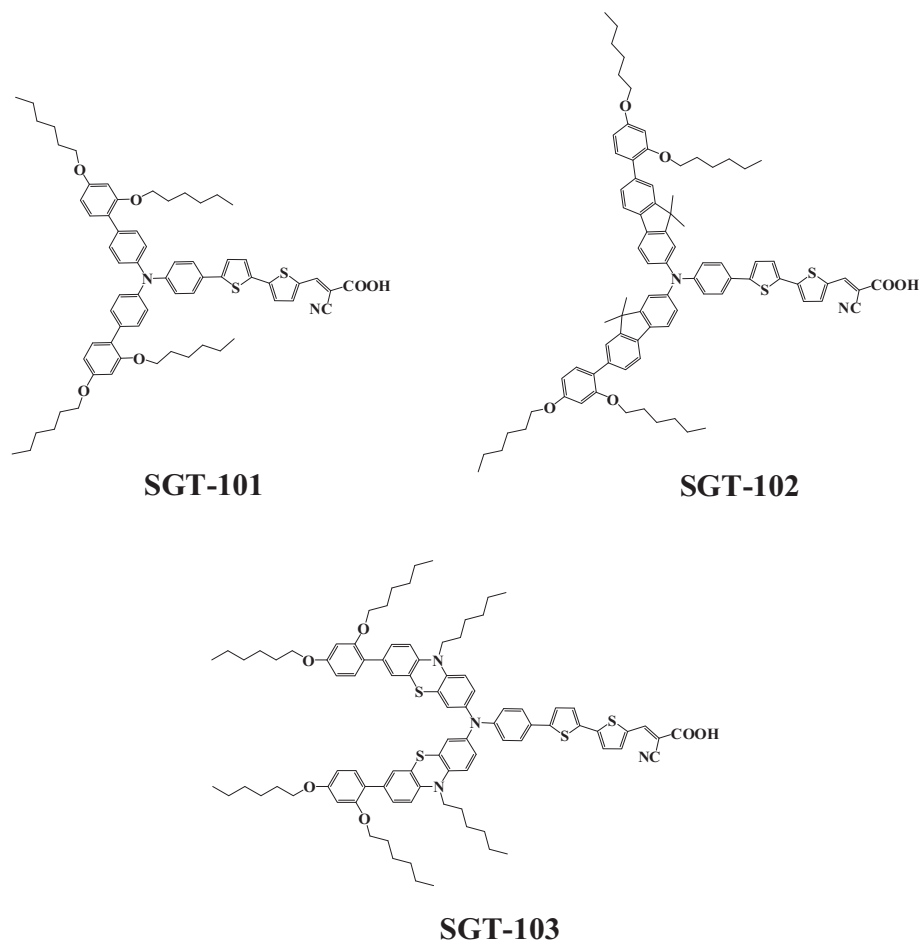


Fig. 1. Chemical structures of SGT dyes.

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

2.2. Measurements

^1H NMR and ^{13}C 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 TiO_2 was measured in CH_3CN 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 → 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 TiCl_4 at 70 °C for 30 min and then washed with water and ethanol. The first TiO_2 layer with a thickness of 5.3 μm was prepared by screen-printing TiO_2 paste (Solaronix, 13 nm anatase), and the second scattering layer containing 400 nm sized anatase particles was deposited by screen printing. The TiO_2 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 H_2PtCl_6 solution (2 mg of Pt in 1 mL of ethanol) on an FTO plate. The dye-adsorbed TiO_2 electrode and Pt counter electrode were assembled in a sealed sandwich-type cell. A drop of electrolyte solution (0.22 M $[\text{Co(II)}-(\text{bpy})_3][\text{B(CN)}_4]_2$, 0.05 M $[\text{Co(III)}(\text{bpy})_3][\text{B(CN)}_4]_3$, 0.1 M LiClO_4 , 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.

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