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Synthesis and investigation of triphenylamine-based double branched organic dyes for p-type dye-sensitized solar cells

Le Quoc Bao, Ho Phuong, Chau Thi Thanh Thuy, Ji Won Lee, Jae Hong Kim, and Suresh Thogiti

Department of Chemical Engineering, Yeungnam University, Gyeongsan, Gyeongbuk, Republic of Korea

ABSTRACT
Two double branched organic dyes (T1I and T2I) were synthesized, characterized, and employed as photosensitizers in *p*-type dye-sensitized solar cells (*p*-DSSC); we have compared with corresponding single branched dye (TC1) and reference dye P1. The absorbance of the dyes in solution was red shifted and the oxidation potential gradually decreased with increasing the donating ability. It was found that modification from single branched (TC1) to double branched (T1I and T2I) system resulted in increased photocurrent density leading to the higher photovoltaic performances. The charge transporting ability is increased with the introduction of double branching, as evidenced from electrochemical impedance analysis.

KEYWORDS
p-type dye-sensitized solar cells; double branched; hemicyanine; charge transfer

1. Introduction

Dye-sensitized solar cells (DSSCs), developed by Gratzel and co-workers in 1990s, are a fascinating renewable energy source and considered as a developmental low-cost alternative to the conventional silicon-based solar cells [1–4]. Two kinds of photo-electrode DSSCs devices exist; Devices using n-type semiconductors (such as TiO_2 or ZnO as a photo-anode i.e. n-DSSC) [5], and their inverse model, p-DSSC using a p-type semiconductor (usually NiO as photocathode) [6]. Numerous n-DSSCs have been studied and achieved higher conversion efficiencies [4,7–11], whereas p-DSSCs have rarely been studied and their conversion efficiencies are much lower than that of n-DSSCs [12–16]. Despite this, the conversion efficiencies of n-DSSCs still lag behind that of conventional silicon-based solar cells, which will inhibit their large-scale application. Therefore, investigating the p-DSSCs for the fabrication of inexpensive and efficient tandem-DSSCs is a feasible strategy for further increasing the power conversion efficiencies [6,13].

In p-DSSCs, dye loaded on the photocathode absorbs photons of a specific wavelength and creates electrons and holes, followed by hole-transport from the acceptor to the donor, then injecting by an anchoring (COOH) group into the valence band of the working semiconductor. Because the dye molecule is a very crucial component in DSSCs working mechanism, it is important to develop new dye sensitizers and elaborate on the molecular engineering rules to design more efficient dye sensitizers. It was firstly reported by Qin et al. the sensitizer

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CONTACT Suresh Thogiti ✉ sureshyu@ynu.ac.kr Department of Chemical Engineering, Yeungnam University, 214-1, Dae-hakro 280, Gyeongsan, Gyeongbuk, Republic of Korea.

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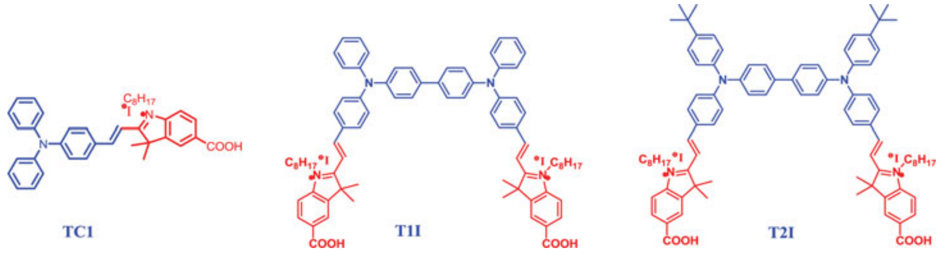


Figure 1. Chemical structures of synthesized dyes T1I, T2I and reference dye TC1.

P1 synthesized for p-type DSSCs using triphenylamine as donor and thiophene as π-linker which can impressively lift the quantum efficiency as high as 18% and 0.052% of efficiency [17]. Warnan et al. reported the use of squaraine (SQ) on NiO based DSSC, which showed considerable results of 0.034% of efficiency [18]. With the aim of developing new dyes for p-DSSCs, this study examined the potential of well-known hemicyanine. Hemicyanine exhibits a strong absorption band in the visible to the near IR region and present particularly high photostabilty [19–22]. Recently, we have reported triphenylamine dyes with different number of hemicyanine anchoring groups on NiO-based p-DSSCs, which showed satisfactory results of 0.01 to 0.02 of conversion efficiencies [22]. Also, we have studied the effect of donor in hemicyanine-based sensitizers for p-DSSC and achieved a considerable 0.02% conversion efficiency with carabazole-based donor [19].

In this study, we designed and synthesized new dibranched hemicyanince dyes (T1I and T2I; Figure 1) with a substituted triphenylamine as donor and carboxylic acid as anchoring group and compared with single branched congener (Figure 1) and their optical and electrochemical were studied. In addition, these dyes were applied to NiO-based DSSCs and compared with the reference coumarine dye C343 under similar fabrication and measurement conditions. The optical, electrochemical, current-voltage characteristics, and impedance analysis were studied to discuss their structure property relationships.

2. Experimental

2.1. Instruments and measurements

All ^{1}H NMR spectra were recorded on a Varian Mercury NMR 300 MHz spectrometer using $CDCl_3$ and DMSO-d_6, which were both purchased from Alfa Aesar Company. The chemical shifts were referenced to TMS. The absorption spectra were recorded on an Agilent 8453 UV-Vis spectrophotometer. The redox properties of three dyes were examined by using cyclic voltammetry (Model: CV-BAS-Epsilon). The electrolyte solution used was 0.10 M tetrabutylammonium hexafluorophosphate ($TBABF_6$) in freshly dried acetonitrile. The Ag/AgCl and Pt wire (0.5 mm in diameter) electrodes were used as reference and counter electrodes, respectively. The scan rate was 30 mV/s. Electrochemical impedance spectroscopy (EIS) was performed using an electronic-chemical analyzer (Iviumstat Tec.). The photovoltaic I-V characteristics of the prepared DSSCs were measured under 1 sunlight intensity (100 mW cm^{-2}, AM1.5), which was verified with an AIST-calibrated Si-solar cell (PEC-L11, Peccell Technologies, Inc., City, State, Country). The incident monochromatic photon-to-current efficiencies (IPCEs) were plotted as a function of the light wavelength using an IPCE measurement instrument (PEC-S20, Peccell Technologies, Inc.).

2.2. Synthesis of sensitizers

The starting compounds, i.e., 1-bromohexane, 1-iodooctane, pyridine, methanol are products of Sigma Aldrich, the others ones such as carbazole, *N,N*- dimethylformamide (DMF), 4-hydrazinobenzoic acid, 3-methyl-2-butanone, 2-(tri-n-butylstannyl)thiophene, trans-dichlorobis(triphenylphosphine)palladium(II) ($PdCl_2(PPh_3)_2$) are purchased from Alfa Aesar. Phosphorus oxychloride ($POCl_3$) is a product of Dea Jung and all the others solvents and components are bought from Duksan the local company.

N4,N4,N4′,N4′-tetraphenyl-[1,1′-biphenyl]-4,4′-diamine (1): N,N’-Diphenylbenzidine (2 g, 5.9 mmol), bromobenzene (3.74 g, 23.8 mmol), potassium tert-butoxide (2 g, 17.8 mmol) and Palladium (II) acetate (0.133 g, 0.59 mmol) were added to 50 ml of o-xylene and stirred under nitrogen atmosphere. After 0.5 ml of tri-tert-butylphosphine solution (1.0 M in toluene) was added slowly, the reaction was kept at 110°C in 24 hours. After regulated time, the mixture was cooled to room temperature followed by filtering. The filtrated solution was evaporated and purified via silica gel column using hexane:MC (1:1) as elute solvent. The obtained product is 2.4 (4.9 mmol) g of white solid (82.62%). ^{1}H NMR (Acetone-d_6, 300 MHz) δ 7.596 (d, J = 8.4 Hz, 4 H), 7.343 (t, J = 8.4 Hz, 8 H), 7.109–7.033 (m, 16 H).

N4,N4′-bis(4-(tert-butyl)phenyl)-N4,N4′-diphenyl-[1,1′-biphenyl]-4,4′-diamine (2): N,N’-Diphenylbenzidine (2 g, 5.9 mmol), 1-bromo-4-tert-butylbenzene (5.07 g, 23.8 mmol), potassium tert-butoxide (2 g, 17.8 mmol) and Palladium (II) acetate (0.133 g, 0.59 mmol) were added to 50 ml of o-xylene and stirred under nitrogen atmosphere. After 0.5 ml of tri-tert-butylphosphine solution (1.0 M in toluene) was added slowly, the reaction was conducted by the same process of reaction of **(1)**. The final product was 2.54 (4.22 mmol) g of white solid (71.11%). ^{1}H NMR (Acetone-d_6, 300 MHz) δ 7.576 (d, J = 8.7 Hz, 4 H), 7.393 (d, J = 8.4 Hz, 4 H), 7.327 (t, J = 8.4 Hz, 4 H), 7.086–7.032 (m, 14 H), 1.325 (s, 18 H).

4,4′-([1,1′-biphenyl]-4,4′-diylbis(phenylazanediyl))dibenzaldehyde (3): 1 g (2mmol) of **(1)** was dissolved in DMF and stirred with 0°C of ambient temperature under nitrogen condition. $POCl_3$ (3.067, 20 mmol) was add slowly to the solution. After 1h stirred, the mixture was heated up to 80°C and kept for 8 h before it was quenched by being cooled and slow addition of 2M NaOH. The mixture was extracted with DCM, then the received organic layer was dried with anhydrous $CaCl_2$ and filtered. The residue received after all solvent was evaporated was purified with silica gel column with 90% Hexane:EA used as elute solvent. The obtain product was 0.46 g (0.845 mmol) of yellow solid (41.26%). ^{1}H NMR (Acetone-d_6, 300 MHz) δ 9.858 (s, 2 H), 7.785 (t, J = 8.7 Hz, 8 H), 7.471 (t, J = 7.5 Hz, 4 H), 7.301 (t, J = 7.5 Hz, 10 H), 7.078 (d, J = 8.4 Hz, 4 H).

4,4′-([1,1′-biphenyl]-4,4′-diylbis((4-(tert-butyl)phenyl)azanediyl))dibenzaldehyde (4): 1.2 g (2 mmol) of **(3)** was dissolved in DMF and stirred with 0°C of ambient temperature under nitrogen condition. $POCl_3$ (3.067, 20 mmol) was add slowly to the solution. The reaction was conducted by the same process of reaction of **(4)**. The obtain product was 0.42 g (0.698 mmol) of yellow solid (31.96%). ^{1}H NMR (Acetone-d_6, 300 MHz) δ 9.840 (s, 2 H), 7.765 (t, J = 8.7 Hz, 8 H), 7.507 (d, J = 8.4 Hz, 4 H), 7.292 (d, J = 8.4 Hz, 4 H), 7.209 (d, J = 8.7 Hz, 4 H), 7.042 (d, J = 8.4 Hz, 4 H), 1.349 (s, 18 H).

2,2′-((1E,1′E)-(([1,1′-biphenyl]-4,4′-diylbis(phenylazanediyl))bis(4,1-phenylene))bis(ethene-2,1-diyl))bis(5-carboxy-3,3-dimethyl-1-octyl-3H-indol-1-ium) iodide (T1I): 0.1 g (0.18 mmol) of **(4)**, and 5-Carboxy-2,3,3-trimethyl-1-octyl-3H-indolium iodide (0.19 g, 0.43 mmol, 2.4 equiv) were dissolved in $CHCl_3$:MeOH (1:1) and refluxed for 6 hours. After regulated time, the mixture was cooled down to room temperature then the solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2 and recrystallized by adding Et_2O. The precipitate was washed several times with Et_2OH, hexane, ethyl acetate and finally with the mixture of 50% acetone/ether to afford the final product (0.21 g) as dark purple solid (83.61%). ^1H NMR (DMSO, 300 MHz) δ 8.49 (d, J = 17.1Hz, 2 H), 8.343 (s, 2 H), 8.129 (d, J = 7.8 Hz, 4 H), 7.894 (s, 2 H), 7.779 (d, J = 7.8 Hz, 4 H), 7.481 (m, 4 H), 7.320 (m, 10 H), 7.076 (s, 2H), 6.963 (d, J = 7.5 Hz, 4 H). 4.577(t, J = 6.8 Hz, 4 H), 1.796 (s, 14 H), 1.380–1.190 (m, 24 H), 0.781 (s, 6 H).

2,2′-((1E,1′E)-(([1,1′-biphenyl]-4,4′-diylbis((4-(tert-butyl)phenyl)azanediyl))bis(4,1-phenylene))bis(ethene-2,1-diyl))bis(5-carboxy-3,3-dimethyl-1-octyl-3H-indol-1-ium) iodide (T2I Reaction was conducted according to condition of **T1I** while compound **(5)** (0.1 g, 0.152 mmol) was used instead of **(4)**. The obtain product was 0.177 g (0.128 mmol) of dark purple solid (77.09%). ^1H NMR (DMSO, 300 MHz) δ 8.491 (d, J = 13.2 Hz, 2 H), 8.359 (s, 2 H), 8.110 (m, 4 H), 7.901 (d, J = 7.8 Hz, 2 H), 7.777–7.705 (m, 4 H), 7.513 (d, J = 7.8 Hz, 4 H), 7.423–7.297 (m, 6 H), 7.223 (d, J = 6.9 Hz, 4 H), 7.036–6.908 (m, 6 H), 4.561 (t, J = 6.9 Hz, 4 H), 1.796 (s, 12 H) 1.305–1.217 (m, 38 H), 0.784 (s, 6 H)

2.3. Assembly and characterization of DSSCs

The conducting glass substrates (FTO) were cleaned sequentially with soapy water, ethanol and acetone using an ultrasonic bath for 20 minutes. The compact NiO blocking layer was deposited on cleaned FTO glass by spin-coating of 0.5 M Nickel acetate tetrahydrate in ethanol at 3000 rpm for 30 seconds. This process was conducted 3 times. These layers were sintered at 450°C for 30 minutes. The NiO paste was prepared by blending a slurry of 6 g of NiO nanopowder in ethanol with 20 mL of 10 wt. % ethanolic ethyl cellulose solution and 40 mL α-terpineol. Then ethanol was removed via evaporation. The mesoporous NiO layer was deposited using the doctor-blade technique, on the top of bare FTO and compact NiO blocking layer already coated on FTO. Sequentially, the films were dried at 70°C for 45 minutes in air followed by sintering at 450°C for 30 minutes. Then resulting films were immersed in a 0.3 mM solution of dyes in DMF/EtOH (1:1) for 48 hours at 25°C for dye absorption. The active cell area was 0.24 cm2 (0.4 cm × 0.6 cm).

H_2PtCl_6 in an isopropanol solution was deposited on clean FTO glass and followed by thermal decomposition by annealing at 450°C for 30 minutes to make the counter electrodes. The complete device was assembled by placing face-to-face a platinum-coated FTO substrate

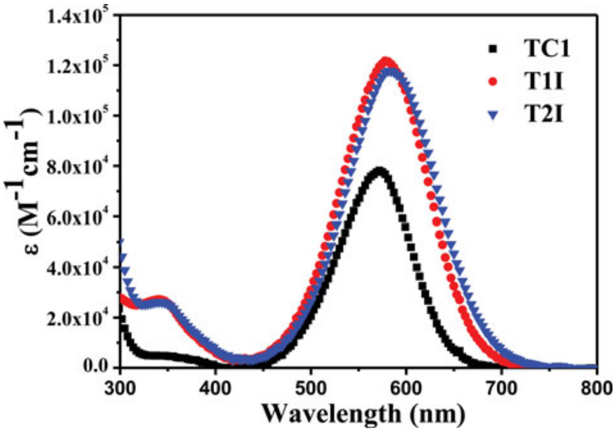


Figure 2. Absorption spectra of T1I, and T2I in a mixture of dichloromethane and methanol solvent and comparison with reference TC1.

Table 1. Optical and electrochemical parameter of the organic new sensitizers.

Dye	$\varepsilon \times 10^{-4}(M^{-1}cm^{-1})$	λ_{max} ^{a}(nm)	E_{0-0} (-eV)^{b}(abs)	E_{OX}^{c}(V vs NHE)	E_{OX}-E_{0-0}^{d}(V vs NHE)
TC1	7.81	572	—	—	—
T1I	12.17	578	1.84	0.69	– 1.15
T2I	10.93	582	1.80	0.67	– 1.13

and a dyed NiO working electrode using a 60 μm thick Surlyn (Dupont 1702). The device was heated at 120°C for 1 minute to seal them. The I^-/I_3^- based electrolyte M, contaning I_2 and 0.5 M LiI in propylene carbonate, was introduced through a pre-drilled hole on the counter electrode.

3. Results and discussion

Figure 2 show the UV-vis absorption spectra of synthesized dyes (T1I and T2I) in a mixture of chloroform: methanol solution and Table 1 lists the corresponding results. As shown in Figure 2, two major absorption bands in the range of 300–700 nm were observed for the synthesized dyes. The first band (~350 nm) comes from the spacer and the donor group, whereas the second band (~575 nm) is attributed to the π–$\pi*$ electron transition of acceptor [19]. Whereas, the single branched dye TC1 has a maximum absorption wavelength of 572 nm. When double branching introduced in T1I, the absorption maximum red-shifted to 578 nm, which shifted further to 585 nm when an additional *tert*-butyl donor group was added in T2I. The absorption differences can be attributed to increased conjugation through double branching and the donating ability of the donor moiety in the organic dye. This is due to the large oscillator strength of the charge transfer transition, according to Franck-Condon principle [23]. On the other hand, the molar extinction coefficients (ε) of T1I and T2I dyes were higher than those of single branched TC1 dye, indicating that more photons harvested.

The ground-state oxidation and reduction potentials of the dyes were measured by cyclic voltammetry (CV) in dry DMF solvent containing 0.1 M TBA(BF4) with 30 mV/s scan rate (Figure 3). The ground-state oxidation potentials E_{OX} of T1I and T2I dyes, corresponding to the highest occupied molecular orbital (HOMO) level of dyes, are 0.67 and 0.69 V vs.

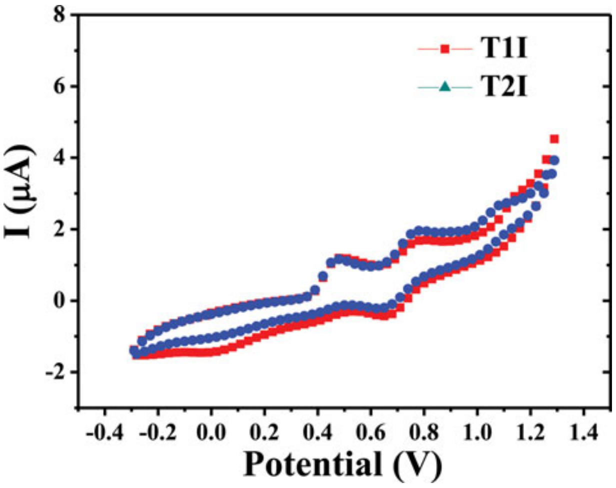


Figure 3. Cyclic voltammetry spectra of T1I and T2I in DMF solvent.

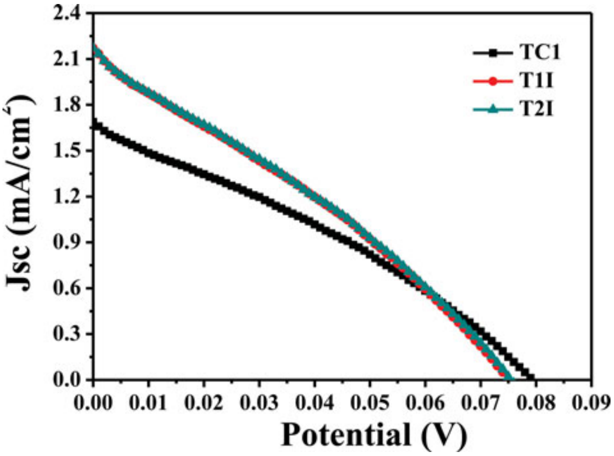


Figure 4. $J-V$ characteristic spectra of *p*-type DSSCs used T1I and T2I sensitizers and compared with reference TC1 sensitizer.

NHE; the dyes are easier to oxidize with increasing the donating ability through *tert*-butyl introduction. These values are all much more positive than the valence band of NiO (~0.5 V vs. NHE),[24] so there should be a substantial driving force for hole injection from the dye to the semiconductor. The E_{0-0} gap for these dyes estimated from the onset absorption spectra. The data was then used to obtain the LUMO (LUMO = HOMO− E_{0-0}) energy levels (Table 1). The LUMO levels (Table 1) of the dyes are higher than that of the iodide/triiodide redox system, suggesting that the reduced dyes can efficiently reduce the oxidized electrolyte.

The TC1, T1I, and T2I sensitized *p*-type DSSCs were fabricated with iodide/triiodide as a redox couple. The typical current density-voltage ($J-V$) curves of the devices are shown in Figure 4 and the photovoltaic parameters are summarized in Table 2. The fill factor (FF) and open circuit voltages (V_{OC}) values of T1I and T2I-based cells were quite similar to each other; whereas the short-circuit current densities (J_{SC}) were different. Changing from single branching to double branching in these sensitizers is reflected in the increased short circuit current density (J_{SC}) by approximately 28% compared to the single branched dye TC1. The absorption data (Fig. 2), also, indicated the increased light-harvesting properties of these dyes. This improvement in current density is due likely to the increased charge transfer, which will be discussed in the following section. The devices based double branching dyes exhibited the higher power conversion efficiency of 0.05% with a high J_{SC} of 2.17 mA cm^{-2} and V_{OC} of 75.5 mV, which is 25% higher than the single branched dye TC1 (0.04%).

Electrochemical impedance analysis (EIS) was performed under light conditions to study the effects of charge transport processes in these devices. Figure 5 shows the Nyquist plots of DSSCs and Table 3 lists the results. The EIS is a useful technique for the analysis of charge transport processes in an electrochemical device including *p*-type DSSCs [25]. Upon illumination of 1000 W m^{-2} light under open circuit conditions, the radius of the intermediate

Table 2. Photovoltaic performance of DSSCs composed of organic *p*-type sensitizers.

Dye	Jsc (mA/cm^2)	Voc (mV)	FF (%)	η (%)
Ref P1	4.379	103.4	32.57	0.14
TC1	1.688	79.9	31.92	0.04
T1I	2.171	75.5	30.54	0.05
T2I	2.171	76.2	30.29	0.05

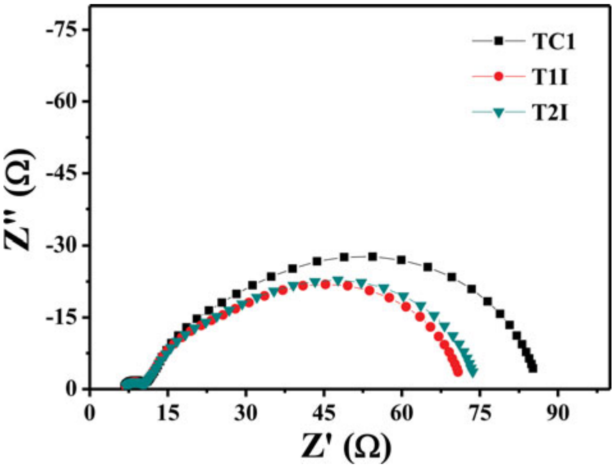
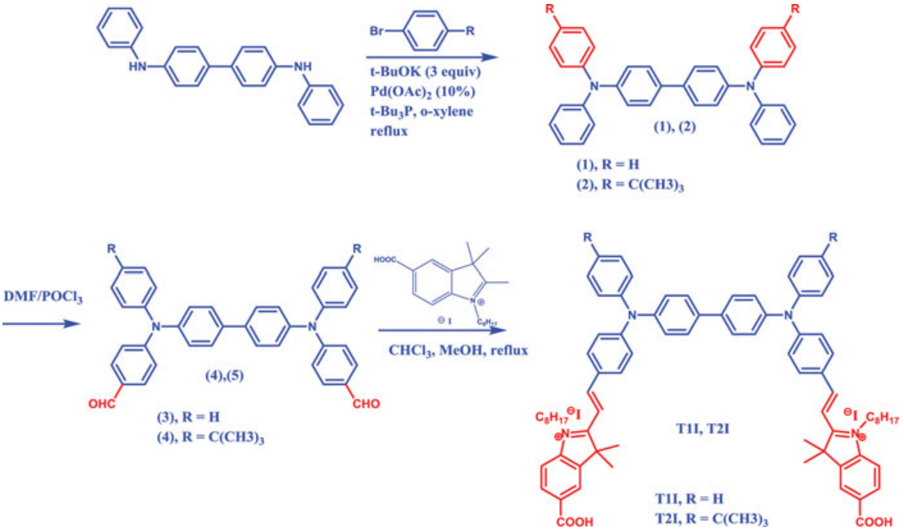


Figure 5. Electrochemical impedance analysis of DSSCs used T1I and T2I sensitizers and reference TC1 sensitizer.

Table 3. Impedance analysis of *p*-type DSSCs of organic sensitizers.

Dye	R1 (Ω)	R2(Ω)	R3(Ω)
TC1	6.689	3.833	65.95
T1I	6.993	3.161	55.35
T2I	7.062	3.344	57.83

frequency semicircle in the Nyquist plot shows the electron transport resistance. *R*1 is FTO Interface resistance. *R*2 is due to the resistance at the interface between the counter electrode and the electrolyte. *R*3 possibly originated from the backward charge transfer from NiO to the electrolyte and electron conduction in porous NiO film. It was found the charge transfer (*R3*) values for the DSSCs using T1I and T2I (55.35 and 55.21 Ω) were indeed smaller than that using TC1 (65.95 Ω) due to the enhanced charge transfer ability. The photocurrent improvement is more likely resulted from the enhanced charge transfer ability.



Scheme 1. Synthesis route for new dye-sensitizers T1I and T2I.

4. Conclusions

We have synthesized and characterized two new double branched organic sensitizers for p-type dye-sensitized solar cells and obtained some insight into their structure property relationships. The absorption spectrum red shifts and the first oxidation potential decreases with introduction of additional donor group. These double branched dyes can increase the charge transfer and increase J_{SC} of DSSCs, giving the higher power conversion efficiency of 0.05%. The DSSC based on single branched dye TC1 shows the lower photovoltaic performance compare to the double branched dye. Our work may give a useful guidance for the molecular design of the organic dyes used in *p*-type dye-sensitized solar cells.

Acknowledgements

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