

Investigation of Organic Compounds as Photosensitizer for Dye Sensitized Solar Cells

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Abstract

Two organic compounds (SC-23=(E)-2-Cyano-3-(2,3-dimethoxyphenyl) acrylic acid and SC-25=(E)-2-Cyano-3-(2,5-dimethoxyphenyl) acrylic acid) involving methoxy groups as the electron donor and cyanoacrylic acid group as the electron acceptor have been investigated for dye sensitized solar cells. They shows a short-circuit current density (J_{sc}) of 2.08 and 1.81 mA cm⁻², an open circuit voltage (V_{oc}) of 0.55 and 0.53 mV and a fill factor (ff) of 0.66 and 0.62, corresponding to a solar energy to electricity conversion efficiency (η) of 0.75 and 0.59%, respectively. To get further insight into the effect of molecular structure on the performance of DSSC, their geometry and energies of HOMO and LUMO orbitals were optimized by density functional theory calculation at the B3LYP/6-31G(d) level with Gaussian 03.

Keywords: Cyanoacrylic, Dye sensitized solar cells, Organic compounds, Solar energy.

Introduction

The DSSC, or the Grätzel cell, is a complex system wherein three different components to generate electric power from light [1]. The major advantages of DSSCs over *p-n* junction cells, are less sensitivity to impurities, easy fabrication, lower production costs and the applications of the cells are more flexible since they can be made of different substrates such as glass, plastics, ceramics, fabric and metal [2]. The major disadvantages associated with DSSCs are the relative low conversion efficiency and device lifetime limitations. Until now, a large number of different ruthenium based sensitizers have been investigated in order to improve the photovoltaic performance and stability of the DSSCs [3]. Amongst them, the two Ru(II) complexes K19 and K77 have shown especially interesting properties (Fig.

1) [4].

In 2007, Officer and co-workers published a series of zinc porphyrins [5], and the highest efficiency ($\eta = 7.8\%$) was obtained with methyl substituent's on the aryl groups (Fig. 2).

In recent years, the interest in metal-free organic sensitizers has grown [6-8]. In 2000 Sayama *et al.* published a merocyanine dye (Fig. 3) which gave an efficiency of 4.2%. They exhibit high molar extinction coefficients and are easily modified due to their relatively short synthetic routes [9].

In recent years, a great deal of many groups aiming at finding highly efficient, stable organic sensitizers has been performed [6-8]. A number of coumarin, indoline, and triphenylamine based organic sensitizers, have been synthesized and investigated as photosensitizer for

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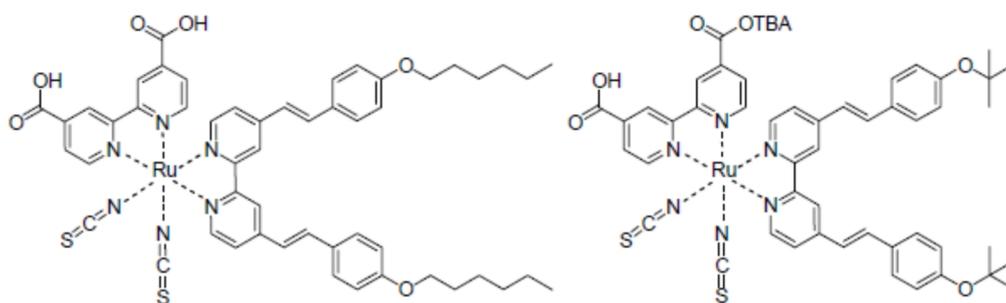


Figure 1. Novel high performing ruthenium(II) sensitizers K19 (left) and K77 (right).

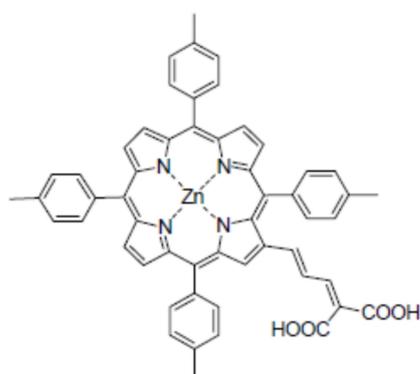


Figure 2. High performing zinc(II) porphyrin sensitizer

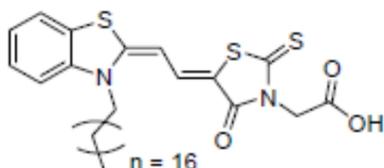


Figure 3. Merocyanine dye.

DSSCs and some of them have reached efficiencies in the range of 3-9% [10-14]. The organic dye sensitizers have three major parts; donor (D), linker (II) and acceptor (A) components. Until now, the number of combinations of different donors, linkers and acceptors is tremendous, and a trial and error strategy would be both time consuming and expensive. In this paper, we

report synthesis, characterization and theoretical studies of two organic compounds containing methoxy and acrylic acid for dye-sensitized solar cells (Scheme. 1).

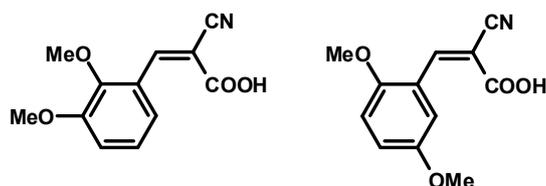
Materials and Methods

Materials and characterization

All reagents and solvents for synthesis and analysis were commercially available and used as received without further purifications. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer. UV-Vis spectra were measured with Perkin-Elmer UV-Vis spectrophotometer. $^1\text{H-NMR}$ spectra were measured on a BRUKER DRX-500 AVANCE spectrometer at 500 MHz. All chemical shifts are reported in δ units downfield from TMS.

Fabrication and characterization of DSSCs

The FTO conducting glass (FTO glass, fluorine doped tin oxide over-layer, transmission >90% in the visible, sheet resistance 8 Ω /square), titania oxide pastes of Ti nanoxide T/SP and Tinanoxide R/SP were purchased from Solaronix. A thin film of TiO_2 (16-18 nm) was coated on a 0.25 cm^2 FTO glass substrate. It was immersed in a THF solution containing 3×10^{-4} M dye sensitizers for at least 12 h, then rinsed with anhydrous acetonitrile and dried. Another piece of FTO sputtered with 100 nm thick Pt was used as a counter electrode. The active area was controlled at a dimension of 0.25 cm^2 by adhering 6 mm thick polyester tape on



Scheme 1. Molecular structures of 23-SC (left) and 25-SC (right).

the Pt electrode. The photocathode was placed on top of the counter electrode and was tightly clipped together to form a cell. Electrolyte was then injected into the seam between the two electrodes. An acetonitrile solution containing LiI (0.5 M), I₂ (0.05 M) and 4-tert-butylpyridine (TBP) (0.5 M) was used as the electrolyte 1 (E1). A solution of 3-dimethylimidazolium iodide (1.0 M), LiI (0.05 M), I₂ (0.03 M), guanidiniumthiocyanate (0.1 M), and TBP (0.5 M) in MeCN: valeronitrile (85:15, v/v) was used as electrolyte 2 (E2). Devices made of a commercial dye N719 under the same conditions (3 × 10⁻⁴ M, Solaronix S.A., Switzerland) were used as reference. The cell parameters were obtained under incident light with an intensity of 100 mW cm⁻² measured by a thermopile probe (Oriol 71964), which was generated by a 300 W (Oriol Class A Solar Simulator 91160A-1000, Newport) passing through an AM 1.5 filter (Oriol 74110). The light intensity was further calibrated by an Oriol reference solar cell (Oriol 91150) and adjusted to be 1.0 sun. The monochromatic quantum efficiency was recorded through a monochromator (Oriol 74100) under short-circuit conditions. Electrochemical impedance spectra of DSSCs were recorded by an Impedance/Gain-Phase analyzer (SI 1260, Solartron).

Theoretical study

The geometries of 23-SC and 25-SC have been optimized by using density functional method (B3LYP) with 6-31G basis set. All calculations were performed using the Gaussian 98 R-A.9 package [15].

Preparation of 23-SC and 25-SC

23-SC and 25-SC were prepared as following literature procedure [16,17].

Anal. Calc. for C₁₂H₁₁NO₄ (23-SC): C, 61.80; H, 4.75; N, 6.01%. *Found:* C, 61.75; H, 4.71; N, 5.57%. UV-Vis, λ_{max} (nm); 314 (π-π*), 379 (n-π*). ¹H-NMR (DMSO-*d*⁶, δ (ppm)): 3.81 (s, 3H, -OCH₃), 3.85 (s, 3H, -OCH₃), 7.25 (t, 1H, Ph-H), 7.33 (q, 1H, Ph-H), 7.72 (q, 1H, Ph-H), 8.47 (s, 1H, -CH=C-), 14.08 (b, 1H, -OH).

Anal. Calc. for C₁₂H₁₁NO₄ (25-SC): C, 61.80; H, 4.75; N, 6.01%. *Found:* C, 61.78; H, 4.73; N, 6.03%. UV-Vis, λ_{max} (nm); 310 (π-π*), 397 (n-π*). ¹H-NMR (DMSO-*d*⁶, δ (ppm)): 3.74 (s, 3H, -OCH₃), 3.83 (s, 3H, -OCH₃), 7.12 (d, 1H, Ph-H), 7.20 (dd, 1H, Ph-H), 7.68 (d, 1H, Ph-H), 8.49 (s, 1H, -CH=C-), 13.98 (b, 1H, -OH).

Results and Discussion

Spectroscopic characterization

The UV-Vis spectrum of 23-SC in CHCl₃ is presented in Fig. 4. The absorption spectrum of 23-SC

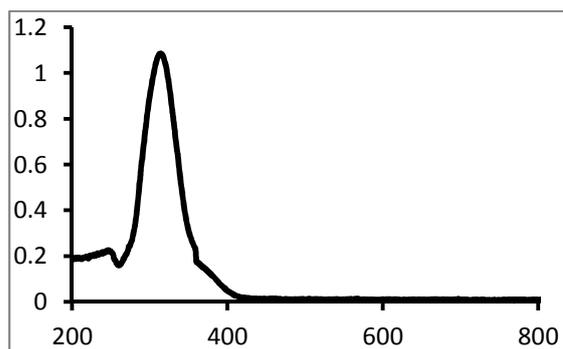


Figure 4. Absorption spectrum of 23-SC in CHCl₃.

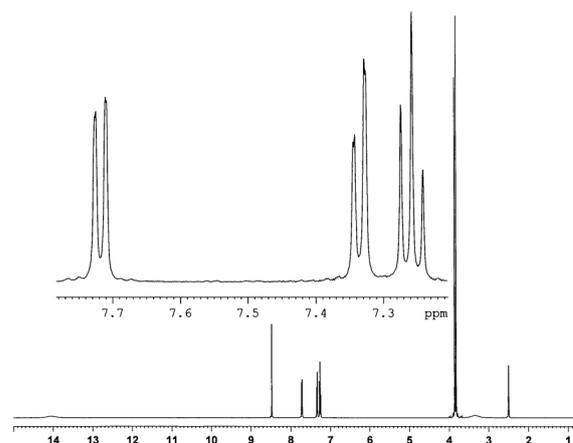


Figure 5. ¹H-NMR spectrum of 23-SC in DMSO.

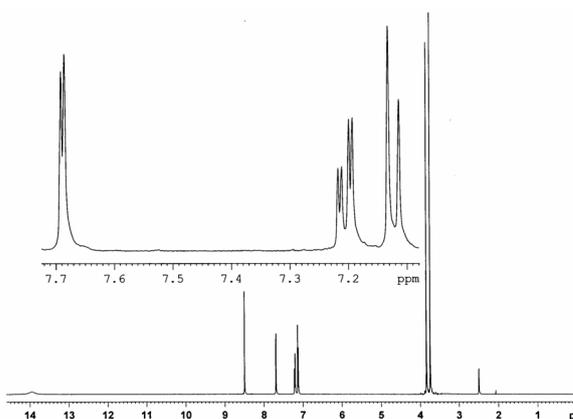


Figure 6. ¹H-NMR spectrum of 25-SC in DMSO.

exhibits two peaks with maximum at 314 nm and 379 nm, attributed to the π-π* and n-π* transitions. The π-π* transition of 25-SC is shifted to lower wavelength, 310 nm, while the n-π* transition is shifted to higher wavelength, 397 nm, relative to the 23-SC.

The $^1\text{H-NMR}$ spectra of 23-SC and 25-SC were recorded using DMSO-d^6 as the solvent and the data were summarized in the experimental section and shown in Figs. 5 and 6, respectively. The title compounds 23-SC and 25-SC have several kinds of protons. All of these kinds of protons show a distinct signal in $^1\text{H-NMR}$ spectrum. In the down field region of each spectrum, a very broad peak is appeared at 14.08 and 13.98 ppm attributed to the -OH protons of 23-SC and 25-SC, respectively. Another singlet peaks are seen about 8.47 and 8.49 ppm for each compound that correspond to the $-\text{CH}=\text{C}-$ group of 23-SC and 25-SC, respectively. The protons of aromatic ring are appeared in the region of 7.24–7.73 ppm for 23-SC and 7.11–7.69 ppm for 25-SC, as three distinct signals. The six protons of methoxy groups are appeared at two singlet signal at 3.74 ppm and 3.84 ppm for 23-SC and at 3.81 ppm and

3.85 ppm for 25-SC.

Theoretical studies

As shown in Scheme 1, 23-SC and 25-SC are cyanoacetic acid-based dyes with 2,3 or 2,5-dimethoxy benzaldehyde unit as the donor, respectively. The optimized structures of 23-SC and 25-SC were carried out using the density functional method (B3LYP) with 6-31G basis set to compare the structure differences between them (Fig. 7).

The frontier MOs of 23-SC and 25-SC reveal that HOMO–LUMO excitation moves the electron density distribution from the methoxybenzaldehyde group to the cyanoacrylic acid unit (Fig. 8). Comparing the frontier MOs of 23-SC and 25-SC at the ground state (HOMO), the electrons are dominantly distributed in the benzene ring and the methoxy groups. The LUMO electron

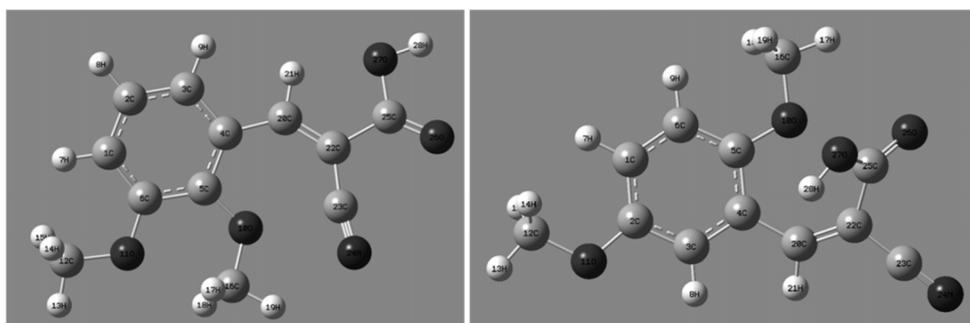


Figure 7. The optimized structures of 23-SC (left) and 25-SC (right).

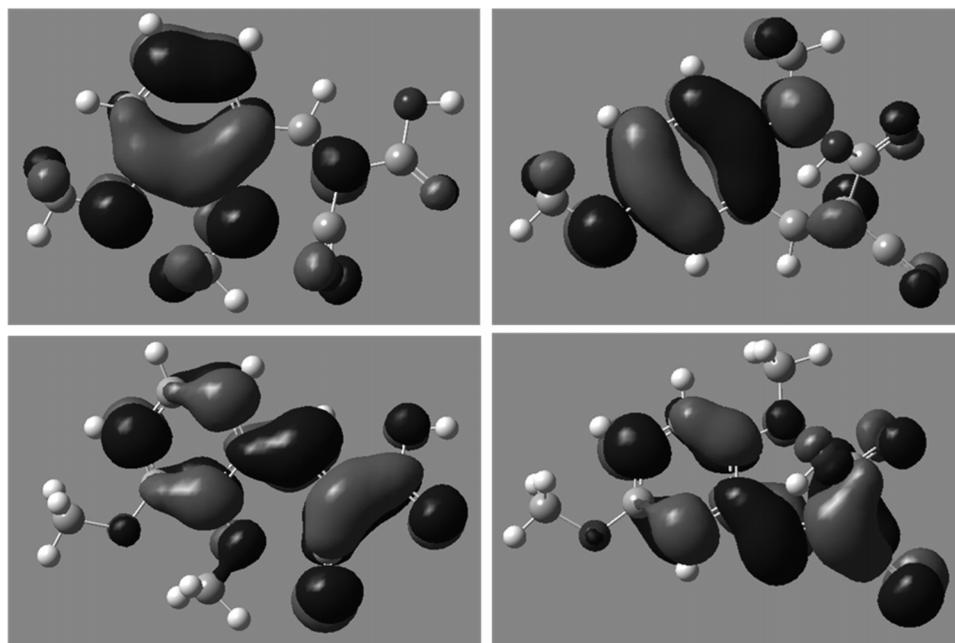


Figure 8. The frontier MOs of 23-SC (left) and 25-SC (right).

Table 1. Photovoltaic performance of DSSCs based on 23-SC and 25-SC dyes.

dye	V_{oc}/mV	$J_{sc}/mA\ cm^{-2}$	ff	$\eta(\%)$
23-SC	0.55	2.08	0.66	0.75
25-SC	0.53	1.81	0.62	0.59

density geometry distributions of 23-SC and 25-SC are located over the cyanoacrylic group through the right phenyl group and the benzene ring. The HOMO levels of 23-SC and 25-SC are -1.32 and -1.353 V and the LUMO levels of 23-SC and 25-SC are 0.094 and 0.077 V, respectively.

Photovoltaic Performance

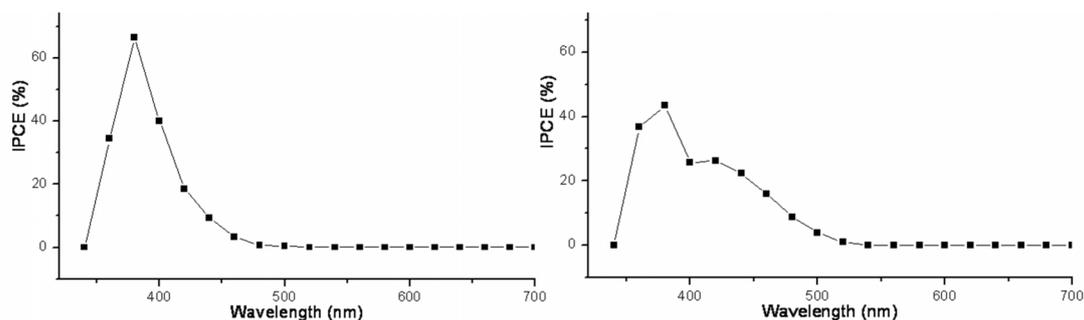
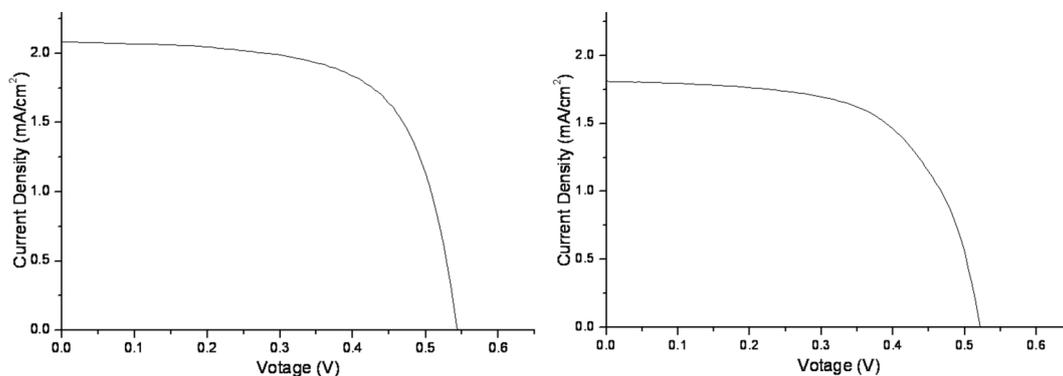
DSSCs were prepared and compared to investigate the relationships between the sensitizing behavior of 23-SC and 25-SC dyes and their structures. The incident photon-to-current conversion efficiency (IPCE) was calculated by normalizing the photocurrent densities for incident light energy and intensity according to the below Equation:

$$IPCE(\lambda) = \frac{1240(eV \cdot nm)}{\lambda(nm)} \frac{J_{sc}(mA \cdot cm^{-2})}{\phi(mW \cdot cm^{-2})}$$

where J_{sc} is the short-circuit photocurrent generated by monochromatic light, λ is the wavelength of incident monochromatic light, and ϕ is the power of the incident radiation per unit area. The detailed photovoltaic parameters are summarized in Table 1. The solar-energy-to-electricity conversion efficiency (η) of the DSSCs is calculated from short-circuit current (J_{sc}), the open-circuit photovoltage (V_{oc}), the fill factor (FF), and the intensity of the incident light (P_{in}) according to the following below Equation [18]:

$$\eta = \frac{[J_{sc}(mA \cdot cm^{-2})][V_{oc}(V)][FF]}{P_m(mW \cdot cm^{-2})}$$

Under the standard global AM 1.5 solar condition, the 23-SC cell had a short circuit photocurrent density (J_{sc}) of $2.08\ mA \cdot cm^{-2}$, an open-circuit voltage (V_{oc}) of 0.55 V, and a fill factor of 0.66, corresponding to an overall conversion efficiency of 0.75%. Under similar

**Figure 9.** The incident photon-to-current conversion efficiency spectra for DSSCs based on 23-SC and 25-SC.**Figure 10.** Current density-voltage characteristics for 23-SC and 25-SC DSSCs under illumination of simulated solar light (AM 1.5, $100\ mW \cdot cm^{-2}$).

conditions, the photovoltaic parameters (J_{sc} , V_{oc} , ff and η) of cells with the 25-SC sensitizer are $1.81 \text{ mA}\cdot\text{cm}^{-2}$, 0.53 V , 0.62 and 0.59% , respectively.

Fig. 9 shows action spectra of monochromatic incident-to current conversion efficiencies (IPCEs) for DSSCs using 23-SC and 25-SC. The IPCEs of 23-SC is more than 70% in the spectral range from 375 to 425 nm. 25-SC reaches its maximum of 40% in the spectral range from 375 to 400 nm and 40% in the spectral range from 400 to 470 nm. The decrease of the IPCE above 450 nm and 515 nm in the long wavelength region is attributed to the decrease of light harvesting for 23-SC and 25-SC, respectively. A typical photocurrent–photovoltage ($I - V$) curve for cells based on 23-SC and 25-SC is shown in Fig. 10.

Conclusion

Two new organic compounds 23-SC and 25-SC containing methoxy groups as a donor and the acrylic acid as an acceptor were characterized by various techniques. Both compounds displayed DSSCs characteristic with quantum efficiency of 0.75% for 23-SC and 0.59 for 25-SC. The density functional theory (DFT) calculations reveal that HOMO–LUMO excitation moves the electron density distribution from the donor (methoxybenzaldehyde) to the acceptor (cyanoacrylic acid).

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