Highly Efficient Organic Photosensitizer with Dinaphthylphenylamine Unit as a Donor for DSSCs

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Recently, dye-sensitized solar cells (DSSCs) have attracted great attention because they have advantages in converting solar energy to electrical energy at low cost. One of the key issues in high performance DSSCs is the rational design of the photosensitizers, which can exhibit high solar-to-energy conversion efficiency. The Ru complex photosensitizers such as N3, N719 and Black dye exhibit efficiencies about 11% under AM 1.5G irradiation.1

The performance of organic dyes for use as a photosensitizer has remarkably been improved showing high efficiencies over 9%.2 Organic dyes can provide structural diversity for tuning the photophysical properties such as absorption wavelength, molar extinction coefficient, and HOMO-LUMO energy level.3 Efficient organic dyes include coumarin,4 indoline,5 squaraine,6 polyene,7 hemicyanine,8 oligothiophene,9 perylene,10 porphyrin,11 merocyanine12 and cyanine13 as the characteristic structural units. In particular, π-conjugated molecules with electron donor-acceptor moieties for effective intramolecular charge transfer showed high efficiencies for DSSC.14

We recently reported that the organic dyes with phenylenevinylene or methoxy-substituted oligo-phenylenevinylene unit as π-conjugated spacer in donor-acceptor skeleton exhibited overall solar-to-electric energy conversion efficiencies higher than 9%.2,15 Therefore, we reasoned that a systematic investigation of the effect of the structural moiety of the donor-acceptor dyes on the DSSC performance would provide an opportunity for the development of highly efficient and stable organic dyes for DSSC. For that purpose, in this work, the donor moiety was modified with dinaphthyl moiety.

As summarized in Scheme 1, we prepared the organic dye, Di-Naph-DM-CA, which consists of dinaphthyl amino moiety as an electron donor and cyanoacrylic acid unit as an electron acceptor with dimethoxy-substituted phenylenevinylene spacer, to investigate the effect of the dinaphthyl amino moiety on the electrochemical and photovoltaic properties of the organic dye. The synthesis begins with preparation of 1 by the Ullmann condensation reaction of 2,2’-dinaphthylamine with 4-iodobenzaldehyde. Compound 2 was prepared from 1 by Wittig reaction. Compound 3 was prepared by Heck coupling of 2 with 4-iodo-2,5-dimethoxybenzaldehyde. Di-Naph-DM-CA was obtained by condensation of 3 with cyanoacetic acid.

The UV-vis absorption spectrum of Di-Naph-DM-CA in Figure 1 showed an absorption maximum at 433 nm in ethanol (ε = 48300 M⁻¹ cm⁻¹).

As shown in Figure 2, the HOMO value of the sensitizer was determined by using the cyclic voltammetry. The measurement was carried out using a saturated calomel electrode (SCE), glassy carbon electrode and platinum wire as reference, working and counter electrode, respectively, in DMF solution containing 0.1 M tetrabutylammonium tetrafluoroborate as a supporting electrolyte. A standard ferrocene/ferrocenium (Fe/Fe⁺) system was used to calibrate the redox peak. The HOMO value of Di-Naph-DM-CA was −5.33 eV and the optical bandgap estimated from the absorption edge of the absorption spectrum was 2.50 eV.

![Scheme 1](image)

![Figure 1](image)
The calculated LUMO value was $-2.83$ eV (Table 1), which is in the range of favorable energy matching for efficient electron transfer from the LUMO level of the dye to the conduction band of TiO$_2$.

The efficient electron transfer to the acceptor moiety in the excited state of the dye is expected by the investigation of the frontier molecular orbitals of the dye as shown in Figure 3. At the HOMO state, the electron density is well distributed along the dimethoxy-substituted phenylenevinylene linker and the electron donor moiety of the dinaphthylamino unit. At the LUMO state, due to the intramolecular charge transfer along the $\pi$-conjugated molecules, the excited electrons are transferred from the electron donor to the electron acceptor moiety of the dye. Therefore, the excited electrons can be effectively injected into the conduction band of TiO$_2$ through the carboxyl group adjacent to the electron accepting cyano group.

Figure 4 shows the photocurrent density-photovoltage (I-V) curve without mask (a) and with mask (b) in the cell. An apertured black mask on the cell was known to reduce the effect of scattered light from the edge of the glass electrodes on the TiO$_2$ layer.$^{17}$ The short circuit current density ($J_{sc}$) and open circuit voltage ($V_{oc}$) of Di-Naph-DM-CA without mask were 17.97 mA/cm$^2$ and 728 mV with a fill factor (ff) of 0.612. The overall conversion efficiency ($\eta$) for Di-Naph-DM-CA was 8.00% in which condition the efficiency of N719 was 9.41%. When the mask is used, the overall conversion efficiency of the cells with the organic dye decreased by ~30% while that of N719 decreased by ~20% as summarized in Table 2.$^{15}$

Figure 5 shows the incident photon to current conversion efficiency (IPCE) data for the organic dye and N719 as a reference. The IPCE value of Di-Naph-DM-CA reached

Table 1. Electrochemical and photophysical properties of organic dye

<table>
<thead>
<tr>
<th>Dyes</th>
<th>$E_{\text{HOMO}}$ (eV)$^a$</th>
<th>$E_{\text{bandgap}}$ (eV)$^b$</th>
<th>$E_{\text{LUMO}}$ (eV)$^c$</th>
<th>$\lambda_{\text{max}}$$^e$ (nm)</th>
<th>$\epsilon$$^e$ (M$^{-1}$cm$^{-1}$)</th>
<th>$\lambda_{\text{max}}$$^e$ (nm)</th>
<th>$\epsilon$$^e$ (M$^{-1}$cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Di-Naph-DM-CA</td>
<td>-5.33</td>
<td>2.50</td>
<td>-2.83</td>
<td>320</td>
<td>34,600</td>
<td>433</td>
<td>48,300</td>
</tr>
<tr>
<td>N719</td>
<td>-5.6$^d$</td>
<td>2.6$^d$</td>
<td>-3.0$^d$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$Estimated from the oxidation potential determined by cyclic voltammetry. $^b$Estimated from the edge of absorption spectrum. $^c$Calculated from the bandgap and HOMO value. $^d$See ref 16. $^e$Absorption spectrum in ethanol.

Table 2. Photovoltaic performance of the organic dyes

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Without mask</th>
<th>With mask</th>
</tr>
</thead>
<tbody>
<tr>
<td>J$sc$ (mA/cm$^2$)</td>
<td>V$oc$ (mV)</td>
<td>ff (%)</td>
</tr>
<tr>
<td>Di-Naph-DM-CA</td>
<td>17.97</td>
<td>728</td>
</tr>
<tr>
<td>N719</td>
<td>19.71</td>
<td>747</td>
</tr>
</tbody>
</table>
around 80% from 420 nm to 530 nm, which is higher than that of N719.

We expect that additional structural optimization for the absorption of longer wavelength would provide an opportunity for the organic dyes to show similar efficiency with Ru complexes.

**Experimental**

**General Methods.** All the reactions were carried out under nitrogen atmosphere. THF was used after distillation under sodium and benzophenone. Spectroscopic-grade solvents from Aldrich were used for spectral measurements. All other reagents were used as received and purchased from Aldrich. Water was used after purification from a Millipore Nanopure water system. All the reactions were carried out under nitrogen atmosphere. THF was used after distillation under sodium and benzophenone. Spectroscopic-grade solvents from Aldrich were used for spectral measurements. All other reagents were used as received and purchased from Aldrich. Water was used after purification from a Millipore Nanopure water system. A THF solution (50 mL) of compound 1 (2.094 g, 5.607 mmol) was added to a THF solution of potassium tert-butoxide (8.411 mL, 8.411 mmol) and methyl triphenyl phosphonium iodide (2.72 g, 6.729 mmol). The solution was then stirred at room temperature for 8 h under nitrogen. The solution was poured into a mixture of methylene chloride and distilled water. The product mixture extracted in the organic layer was purified by column chromatography on silica gel using methylene chloride and n-hexane (1:1, v/v) as an eluent. The product 2 was obtained as a white yellow solid. Yield (1.33 g, 64%). 1H NMR (400 MHz, DMSO-d6) δ 5.18 (d, J = 2.4 Hz, 1H, -(4-vinylphenyl)naphthalen-2-yl), 7.85 (m, 4H, -N=C=O-Ph); 13C NMR (100.64 MHz, DMSO-d6) δ 112.92, 120.32, 123.68, 124.22, 124.84, 126.49, 126.95, 127.43, 127.50, 129.28, 129.89, 130.12, 130.47, 131.43, 132.03, 134.07, 136.02, 144.70, 146.84.


**4-(Dinaphthalen-2-ylamino)benzaldehyde (1):** A DMAC solution (80 mL) of 4-iodobenzaldehyde (3.125 g, 12.93 mmol), 2,2'-diphenylhydrazine (4 g, 14.223 mmol) and copper(I) oxide (2.289 g, 15.516 mmol) was stirred at 190 °C for 3 days. After cooling to room temperature, the product mixture was washed with methylene chloride and water. After removal of the organic solvent, the residue was purified by column chromatography on silica gel using methylene chloride and n-hexane (1:1, v/v) as an eluent. The product 1 was obtained as a light green oil. Yield (2.094 g, 43%). 1H NMR (400 MHz, DMSO-d6) δ 7.11 (d, J = 8.4 Hz, 2H, -Ph-N=N-C=O-Ph), 7.40 (dd, J = 2.4, 2.4 Hz, 2H, -Ph-N=N-C=O-Ph), 7.50 (q, J = 3.2 Hz, 4H, -N=CH=CH-N=C=O-Ph), 7.74 (s, 2H, -N=CH=CH-N=C=O-Ph), 7.82 (m, 4H, -N=CH=CH-N=C=O-Ph), 7.96 (m, 4H, -N=CH=CH-N=C=O-Ph), 7.96 (m, 4H, -N=CH=CH-N=C=O-Ph), 9.84 (s, 1H, CHO-Ph), 13C NMR (100.64 MHz, DMSO-d6) δ 120.32, 123.97, 125.85, 126.39, 127.32, 128.02, 128.26, 130.02, 130.47, 131.43, 132.03, 134.07, 136.02, 144.70, 146.84.

**N-(Naphthalen-2-yl)-N-(4-vinylphenyl)naphthalen-2-amine (2):** A THF solution (50 mL) of compound 1 (2.094 g, 5.607 mmol) was added to a THF solution of potassium tert-butoxide (8.411 mL, 8.411 mmol) and methyl triphenyl phosphonium iodide (2.72 g, 6.729 mmol). The solution was then stirred at room temperature for 8 h under nitrogen. The solution was poured into a mixture of methylene chloride and distilled water. The product mixture extracted in the organic layer was purified by column chromatography on silica gel using methylene chloride and n-hexane (1:1, v/v) as an eluent. The product 2 was obtained as a white yellow solid. Yield (1.33 g, 64%). mp 148-152 °C. 1H NMR (400 MHz, DMSO-d6) δ 7.06 (d, J = 8.4 Hz, 2H, -N=CH=CH-N=C=O-Ph), 7.27 (dd, J = 2.4, 2.4 Hz, 2H, -Ph-CH=CH-N=C=O-Ph), 7.43 (m, 8H, -N=CH=CH-N=C=O-Ph), 7.50 (q, J = 3.2 Hz, 4H, -N=CH=CH-N=C=O-Ph), 7.74 (s, 2H, -N=CH=CH-N=C=O-Ph), 7.82 (m, 4H, -N=CH=CH-N=C=O-Ph), 7.96 (m, 4H, -N=CH=CH-N=C=O-Ph), 9.84 (s, 1H, CHO-Ph), 13C NMR (100.64 MHz, DMSO-d6) δ 112.92, 120.32, 123.97, 125.85, 126.39, 127.32, 128.02, 128.26, 130.02, 130.47, 131.43, 132.03, 134.07, 136.02, 144.70, 146.84.
chloride and n-hexane (1:2, v/v) as an eluent. Yield (1.039 g, 61%). mp 241-245 °C. 1H NMR (400 MHz, DMSO-d6) δ 3.85 (s, 3H, -Ph-OCH3), 3.96 (s, 3H, -Ph-OCH3) 7.11 (d, J = 8.8 Hz, 2H, -Ph-N=N-Ph), 7.24 (s, 1H, -Ph-CH=CH-Ph), 7.33 (m, 3H, -Ph-CH=CH-Ph), 7.42 (m, 4H, -Ph-N=N-Ph), 7.55 (m, 6H, -Ph-N=N-Ph), 7.74 (d, 2H, -Ph-N=N-Ph), 7.88 (m, 4H, -Ph-N=N-Ph), 10.31 (s, 1H, CHO-Ph). 13C NMR (100.64 MHz, DMSO-d6) δ 55.96, 56.44, 108.73, 110.04, 120.12, 120.89, 123.01, 123.22, 124.46, 125.02, 126.54, 127.04, 127.54, 128.24, 129.39, 130.07, 131.41, 132.45, 134.01, 134.08, 144.50, 147.33, 150.53, 156.30, 188.01.

(E)-2-Cyano-3-(4-(4-(diphenylthio)styryl)-2,5-dimethoxyphenyl)acrylic acid (Di-Naph-DM-CA):

Piperidine (4.154 mL, 42.054 mmol) was added into an anhydrous solution of compound 3 (1.00 g, 2.103 mmol) and cyanoacetic acid (3.577 g, 42.045 mmol). The solution was stirred at 90 °C for 24 h. After removal of the solvent, the reaction mixture was washed with methylene chloride and aqueous phosphoric acid (2.0 M in water). After removal of the solvent from the organic layer, the product mixture was purified by column chromatography on silica gel using methylene chloride and methanol (20:1, v/v) as an eluent. Yield (0.406 g, 32%). mp 276-279 °C. 1H NMR (400 MHz, DMSO-d6) δ 3.84 (s, 3H, -Ph-OCH3), 3.94 (s, 3H, -Ph-OCH3), 7.10 (d, J = 8.8 Hz, 2H, -Ph-N=N-Ph), 7.30 (d, J = 2 Hz, 1H, -Ph-CH=CH-Ph), 7.32 (d, J = 2 Hz, 1H, -Ph-CH=CH=), 7.37 (s, 1H, -Ph-CH=CH-), 7.41 (m, 4H, -Ph-N=N-Ph), 7.46 (s, 1H, -Ph-CH=CH-Ph), 7.56 (m, 5H, -Ph-N=N-Ph), 7.74 (d, J = 7.2 Hz, 2H, -Ph-N=N-Ph), 7.88 (m, 5H, -Ph-N=N-Ph), 8.49 (s, 1H, -Ph-CH=CH-), 13.5 (s, 3H, -Ph-OCH3). 13C NMR (100.64 MHz, THF-d8) δ 56.42, 56.64, 102.05, 109.36, 111.27, 117.35, 120.65, 121.72, 122.26, 124.51, 125.53, 125.67, 127.20, 127.94, 128.42, 128.93, 130.02, 131.72, 132.75, 133.09, 134.60, 135.74, 146.10, 147.94, 148.97, 151.95, 155.24, 164.32; MS (MALDI-TOF): 602.50 [M]+. Anal. Calc. for C25H19N3O6: C, 72.72; H, 5.02; N, 4.65; O, 10.62. Found: C, 72.95; H, 5.05; N, 4.68; O, 11.04.

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References