

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

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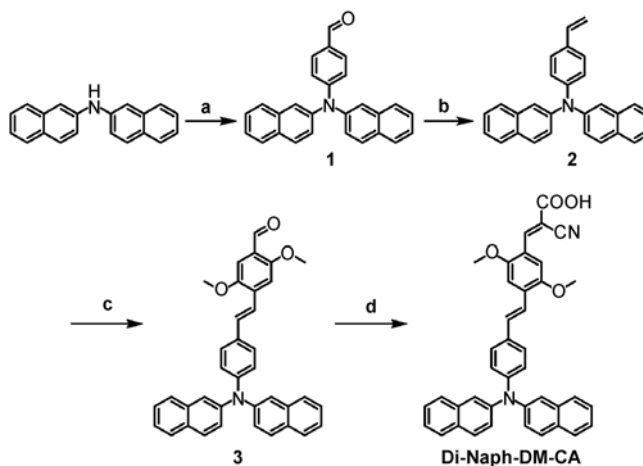
Recently, dye-sensitized solar cells (DSSCs) have attracted great attention because they have advantages in converting solar energy to electrical energy at low cost. One of the key issues in high performance DSSCs is the rational design of the photosensitizers, which can exhibit high solar-to-energy 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,^{2b,2c,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%.^{2a,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 ($\epsilon = 48300 \text{ M}^{-1} \text{ cm}^{-1}$).

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. (a) DMAc, 4-iodobenzaldehyde, Cu₂O, 190 °C, 3 days; (b) THF, KO(*t*-Bu), CH₃PPh₃I, rt, 4 h; (c) DMAc, 4-iodo-2,5-dimethoxybenzaldehyde, Na₂CO₃, Pd cat., 130 °C, 24 h; (d) Acetonitrile, cyanoacetic acid, piperidine, 90 °C, 24 h.

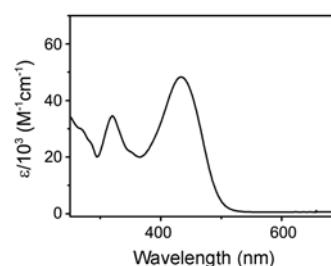


Figure 1. Absorption spectrum of **Di-Naph-DM-CA** in ethanol.

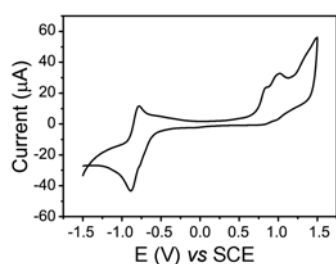


Figure 2. Cyclic Voltammogram of **Di-Naph-DM-CA** measured at a sweep rate of 100 mV sec^{-1} .

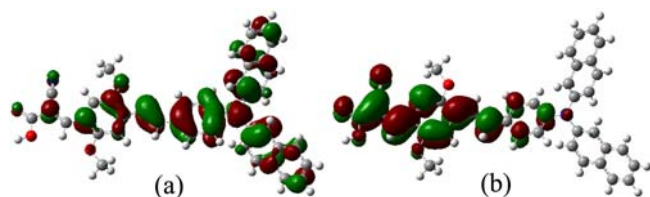


Figure 3. The frontier (a) HOMO and (b) LUMO orbitals of **Di-Naph-DM-CA** at the B3LYP/6-31G level.

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 .¹⁶

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 π -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

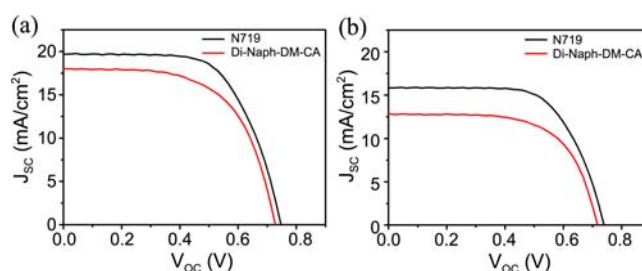


Figure 4. Photocurrent density-photovoltage curves of **Di-Naph-DM-CA** without (a) and with mask (b) under AM 1.5 G 1 sun illumination (100 mW/cm^2). Electrolyte: 0.7 M 1-propyl-3-methylimidazolium iodide, 0.2 M LiI, 0.05 M iodine, 0.5 M *tert*-butylpyridine in acetonitrile/valeronitrile (85/15).

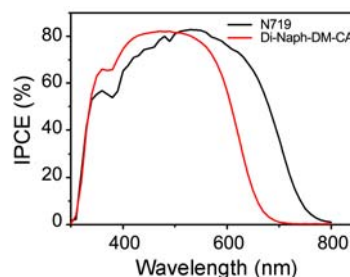


Figure 5. IPCE spectra for the DSSCs based on **Di-Naph-DM-CA** and N719.

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 (η) 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 $\sim 30\%$ while that of N719 decreased by $\sim 20\%$ 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

| Dyes | E_{HOMO} (eV) ^a | E_{bandgap} (eV) ^b | E_{LUMO} (eV) ^c | λ_{max}^e (nm) | ϵ^e ($\text{M}^{-1}\text{cm}^{-1}$) | λ_{max}^e (nm) | ϵ^e ($\text{M}^{-1}\text{cm}^{-1}$) |
|---------------|--|---|--|----------------------------------|---|----------------------------------|---|
| Di-Naph-DM-CA | -5.33 | 2.50 | -2.83 | 320 | 34,600 | 433 | 48,300 |
| N719 | -5.6 ^d | 2.6 ^d | -3.0 ^d | - | - | - | - |

^aEstimated from the oxidation potential determined by cyclic voltammetry. ^bEstimated from the edge of absorption spectrum. ^cCalculated from the bandgap and HOMO value. ^dSee ref 16. ^eAbsorption spectrum in ethanol.

Table 2. Photovoltaic performance of the organic dyes

| Dyes | Without mask | | | | With mask | | | |
|---------------|----------------------------------|------------------|-------|------------|----------------------------------|------------------|-------|------------|
| | J_{sc} (mA/cm^2) | V_{oc} (mV) | ff | η (%) | J_{sc} (mA/cm^2) | V_{oc} (mV) | ff | η (%) |
| Di-Naph-DM-CA | 17.97 | 728 | 0.612 | 8.00 | 12.83 | 718 | 0.642 | 5.91 |
| N719 | 19.71 | 747 | 0.639 | 9.41 | 15.87 | 740 | 0.656 | 7.70 |

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. ^1H and ^{13}C NMR spectra were recorded on a Varian UNITY INOVA 400 at 400 and 100 MHz, respectively. FT-IR spectra were obtained using Perkin-Elmer System 2000 FR-IR spectrophotometer. MALDI-TOF spectra were obtained using Voyager Biospectrometry time of flight mass spectrometer (Perspective Biosystem) operated at 25 kV accelerating voltage in reflector mode with positive ionization and dithranol was used as the matrix. UV-vis spectra were recorded on Hewlett-Packard 8452A spectrophotometer. Elemental analysis was recorded on a CE Instrument EA1110 analyzer.

DSSC Fabrication. FTO-coated conducting glass substrates (TEC8, Pilkington, 8 ohm/square, glass thickness of 2.3 mm) were pre-cleaned by ultrasonication in ethanol. The surface of FTO was pre-treated with 0.15 M titanium(IV) bis(ethylacetoacetato) diisopropoxide in 1-butanol solution by spin coating, which was sintered at 500 °C for 10 min. The screen printable TiO_2 paste was prepared by mixing the home-made nanocrystalline anatase TiO_2 particles (~20 nm) with ethyl cellulose (Aldrich), lauric acid (Fluka) and terpineol (Fluka). The prepared TiO_2 paste was coated on a FTO glass substrate, which was annealed at 500 °C for 30 min. A light scattering overlayer, composed of anatase TiO_2 particles (~400 nm, CCIC), was formed on the nanocrystalline TiO_2 film. The annealed TiO_2 film was treated with 0.2 M TiCl_4 at 30 °C for 16 h, which was heated at 500 °C for 30 min. The thickness of annealed nanocrystalline TiO_2 underlayer and scattering overlayer measured with Alpha-step IQ surface profiler (KLA Tencor) were 10 and 5 μm , respectively. For dye adsorption, the annealed TiO_2 films were immersed in ethanol containing 0.5 mM of **Di-Naph-DM-CA** for 24 h at ambient temperature. N719 dye ($\text{Ru}[\text{LL}'(\text{NCS})_2]$, L = 2,2'-bipyridyl-4,4'-dicarboxylic acid, L' = 2,2'-bipyridyl-4,4'-ditetrabutylammonium carboxylate) was also used for comparison. A counter electrode was prepared by dropping a 7 mM of H_2PtCl_6 solution on a FTO substrate, which was heated at 400 °C for 20 min to form the metallic Pt nanoparticles. The dye-adsorbed TiO_2 working electrode and the Pt counter electrode were sealed with a 25 μm thick surlyn (Dupont). An electrolyte solution was introduced through a drilled hole on the counter electrode, where the electrolyte solution was composed of 0.7 M 1-

propyl-3-methylimidazolium iodide (PMII), 0.05 M I_2 , 0.2 M LiI and 0.5 M 4-*tert*-butylpyridine in the mixture of acetonitrile and valeronitrile (85:15, v/v). The active area of dye coated TiO_2 film was about 0.27 cm^2 as measured by an image analysis program equipped with a digital microscope camera (Moticam 1000). A black mask with an aperture being close to the active area was put on the DSSC while measuring under 1 sun illumination.

4-(Dinaphthalen-2-ylamino)benzaldehyde (1): A DMAc solution (80 mL) of 4-iodobenzaldehyde (3.125 g, 12.93 mmol), 2,2'-dinaphthylamine (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, $\text{DMSO}-d_6$) δ 7.11 (d, $J = 8.4$ Hz, 2H, *-Ph-N-Naph*₂), 7.40 (dd, $J = 2, 2.4$ Hz, 2H, *-Ph-N-Naph*₂), 7.50 (q, $J = 3.2$ Hz, 4H, *-N-Naph*₂), 7.74 (s, 2H, *-N-Naph*₂), 7.82 (m, 4H, *-N-Naph*₂), 7.96 (m, 4H, *-N-Naph*₂), 7.96 (m, 4H, *-N-Naph*₂), 9.84 (s, 1H, *CHO-Ph*-); ^{13}C NMR (100.64 MHz, $\text{DMSO}-d_6$) δ 120.32, 123.97, 125.85, 126.39, 127.32, 128.02, 128.26, 130.02, 130.47, 131.43, 132.03, 134.63, 144.01, 153.33, 191.45.

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 (1:10, 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, $\text{DMSO}-d_6$) δ 5.18 (d, $J = 10.8$ Hz, 1H, *H-CH=CH-*), 5.73 (d, $J = 17.6$ Hz, 1H, *H-CH=CH-*), 6.70 (m, 1H, *CH₂=CH-Ph-*), 7.06 (d, $J = 8.4$ Hz, 2H, *-Ph-CH=CH₂*), 7.27 (dd, $J = 2.4, 2.4$ Hz, 2H, *-N-Naph*₂), 7.43 (m, 8H, *-N-Naph*₂), 7.71 (d, $J = 7.6$ Hz, 2H, *-Ph-CH=CH₂*), 7.85 (m, 4H, *-N-Naph*₂); ^{13}C NMR (100.64 MHz, $\text{DMSO}-d_6$) δ 112.92, 120.32, 123.68, 124.22, 124.84, 126.49, 126.95, 127.43, 127.50, 129.28, 129.89, 132.07, 134.07, 136.02, 144.70, 146.84.

(E)-4-(4-(Dinaphthalen-2-ylamino)styryl)-2,5-dimethoxybenzaldehyde (3): A DMAc solution (40 mL) of compound **2** (1.33 g, 3.58 mmol), 4-iodo-2,5-dimethoxybenzaldehyde (2.3 g, 7.876 mmol), sodium carbonate (0.949 g, 8.95 mmol), 2,6-di-*tert*-butyl-4-methylphenol (0.158 g, 0.716 mmol) and trans-di(μ -acetato)bis[*o*-(di-*o*-tolylphosphino)-benzyl] dipalladium(II) (0.034 g, 0.036 mmol) was stirred at 130 °C for 24 h. After removal of the solvent, the mixture was washed with methylene chloride and water. After removal of the organic solvent, the residue was purified by column chromatography on a silica gel using methylene

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-*d*₆) δ 3.85 (s, 3H, -Ph-OCH₃), 3.96 (s, 3H, -Ph-OCH₃), 7.11 (d, *J* = 8.8 Hz, 2H, -Ph-N-Naph₂), 7.24 (s, 1H, -Ph-CH=CH-Ph-), 7.33 (m, 3H, -Ph-CH=CH-Ph-), 7.42 (m, 4H, -Ph-N-Naph₂), 7.55 (m, 6H, -Ph-N-Naph₂), 7.74 (d, 2H, -Ph-N-Naph₂), 7.88 (m, 4H, -Ph-N-Naph₂), 10.31 (s, 1H, CHO-Ph-); ¹³C NMR (100.64 MHz, DMSO-*d*₆) 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-(dinaphthalen-2-ylamino)styryl)-2,5-dimethoxyphenyl)acrylic acid (Di-Naph-DM-CA): Piperidine (4.154 mL, 42.054 mmol) was added into an acetonitrile solution (50 mL) of compound **3** (1.00 g, 2.103 mmol) and cyanoacetic acid (3.577 g, 42.054 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-*d*₆) δ 3.84 (s, 3H, -Ph-OCH₃), 3.94 (s, 3H, -Ph-OCH₃), 7.10 (d, *J* = 8.4 Hz, 2H, -Ph-N-Naph₂), 7.30 (d, *J* = 2 Hz, 1H, -Ph-CH=CH-Ph-), 7.32 (d, *J* = 2 Hz, 1H, =CH-Ph-CH=), 7.37 (s, 1H, =CH-Ph-CH=), 7.41 (m, 4H, -Ph-N-Naph₂), 7.46 (s, 1H, -Ph-CH=CH-Ph-), 7.56 (m, 5H, -Ph-N-Naph₂), 7.74 (d, *J* = 7.2 Hz, 2H, -Ph-N-Naph₂), 7.88 (m, 5H, -Ph-N-Naph₂), 8.49 (s, 1H, -Ph-CH=C-COOH); ¹³C NMR (100.64 MHz, THF-*d*₆) 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 C₄₀H₃₀N₂O₄: C, 79.72; H, 5.02; N, 4.65; O, 10.62. Found: C, 79.25; H, 5.05; N, 4.68; O, 11.04.

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