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Donor–Acceptor Organic Photosensitizers for Dye-Sensitized Solar Cells

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Donor–acceptor type organic dyes (TA-EDOT-CA and TA-DM-EDOT-CA) containing thiophenevinylene spacer with 3,4-ethylenedioxythiophene (EDOT) substituent were synthesized and characterized for dye-sensitized solar cells (DSSCs). TA-EDOT-CA and TA-DM-EDOT-CA showed 26700 and 28000 $M^{-1} \cdot cm^{-1}$ of molar absorption coefficient at 458 nm and 459 nm of UV/vis absorption maximum wavelength, respectively. The overall solar-to-energy conversion efficiency of TA-EDOT-CA and TA-DM-EDOT-CA was 8.26% and 7.23% under AM 1.5 illumination (100 mW cm^{-2}) without mask, respectively.

Keywords: Dye-Sensitized Solar Cell, 3,4-Ethylenedioxythiophene, Organic Photosensitizer.

1. INTRODUCTION

Dye-sensitized solar cells (DSSCs) have attracted great attention by presenting an alternative to conventional silicon solar cells due to their low cost and ease to production. The photosensitizer is one of the most influential components to achieve high performance DSSCs. Recently, power conversion efficiency (PCE) of ruthenium -based photosensitizers has been obtained up to 11% under AM 1.5G irradiation.[1] Although ruthenium complexes exhibited high PCE, they have some disadvantages for commercialization such as high cost due to expensive ruthenium metal and inconvenient purification. Compared with Ru-based photosentizers, metal-free organic dyes provide facile control of properties such as the absorption wavelength, molar extinction coefficient, and HOMO–LUMO energy levels by tuning molecular designs with relatively low cost.[2] For high efficient DSSCs, organic sensitizers have been designed containing a donor-π-bridge-acceptor (D-π-A) structure for effective intramolecular charge transfer and panchromatic UV/vis absorption,[3] which is consist of a donor (such as diphenylamine,[4] or indolin[5] derivatives), a π-conjugated bridge (such as thiophene,[6] or benzene[7] derivatives), and an acceptor unit (such as cyanoacrylic acid[8] or rhodanine-3-acetic acid[9]). These efficient organic dyes include characteristic structural units such as coumarin,[10] indolin,[5] polyene,[11] hemicyanine,[12] squaraine,[13] thiophene,[14] perylene,[15] porphyrin,[16] benzothiadiazole,[17] merocyanine[18] or cyanine moiety.[19] Recently, 11.9% of PCE was reported using porphyrin-containing photosensitizer with $Co^{(II/III)}$-based redox electrolyte,[19] which indicates that finely tuned organic photosensitizers have great possibility to achieve high energy conversion without expensive noble metal.

In this study, we designed and synthesized D-π-A type organic photosensitizers named TA-EDOT-CA and TA-DM-EDOT-CA with 3,4-ethylenedioxythiophene (EDOT) unit as a π-conjugated spacer, which induces low bandgap properties for conjugated materials.[21] These organic dyes were used as a photosensitizer for DSSC application, and their photoelectrochemical performances were investigated.

2. MATERIALS AND EXPERIMENTAL

2.1. Materials

4-(N,N'-diphenylamino)benzaldehyde, 3,4-ethylenedioxythiophene, N-bromosuccinimide, cyanoacetic acid, di-*tert*-butyl-p-cresol, piperidine, diphenylamine, potassium *tert*-butoxide, methyltriphenylphosphonium iodide, copper (I) oxide, silver nitrate, methanol, N,N'-dimethylacetamide (DMAc), acetonitrile and iodine were purchased from Aldrich and used as received. Tetrahydrofuran (THF) was used after distillation under sodium and benzophenone. Spectroscopic-grade solvents from Aldrich were used for spectral measurements. Distilled water was obtained from a Millipore Nanopure water system.

2.2. Methods

2.2.1. Instruments

^{1}H and ^{13}C NMR spectra were recorded on a Varian UNITY INOVA 400 at 400 and 100 MHz, respectively.

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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. Dithranol was used as the matrix. UV-vis spectra were recorded on Hewlett-Packard 8452A spectrophotometer. Photocurrent–voltage were measured using a class-A solar simulator (Yamashita Denso, model YSS-200A) equipped with a 1600 W Xenon lamp and AM 1.5 G filter, where light intensity was adjusted with a Fraunhofer ISE-calibrated mono Si solar cell with KG-3 filter for approximating 1 sun light intensity. During photocurrent–voltage measurement, DSSC was covered with a black mask with an aperture to avoid additional light coming through lateral space. IPCE was measured as a function of wavelength from 300 to 800 nm using a specially designed IPCE system for dye-sensitized solar cell (PV Measurements, Inc.). A 75 W Xenon lamp was used as a light source for generating monochromatic beam. Calibration was performed using a silicon photodiode, which was calibrated using the NIST-calibrated photodiode G425 as a standard, and IPCE values were collected under bias light at a low chopping speed of 10 Hz.

2.2.2. DSSC Fabrication

DSSCs were fabricated as follows. FTO-coated conducting glass substrates (TEC8, Pilkington, 8 ohm/square, glass thickness of 2.3 mm) were pre-cleaned ultrasonically in ethanol. The surface on 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 ($\sim$20 nm) with ethyl cellulose (Aldrich), lauric acid (Fluka) and terpineol (Fluka). The prepared TiO_2 paste was coated on a FTO glass substrate, which was annealed at 500 °C for 30 min. A light scattering overlayer, composed of anatase TiO_2 particles ($\sim$400 nm, CCIC), was formed on the nanocrystalline TiO_2 film. The annealed TiO_2 film was treated with 0.2 M TiCl4 at 30 °C for 16 h, which was heated at 500 °C for 30 min. The annealed nanocrystalline TiO_2 underlayer was determined to be about 10 μm and the scattering overlayer was about 5 μm as measured with Alpha-step IQ surface profiler (KLA Tencor). For dye adsorption, the annealed TiO_2 films were immersed in ethanol containing 0.5 mM of TA-EDOT-CA and TA-DM-EDOT-CA for 24 h at ambient temperature. N719 dye ($Ru[LL'(NCS)_2]$, $L =$ 2,2′-bypyridyl-4,4′-dicarboxylic acid, $L' =$ 2,2′-bypyridyl-4,4′-ditetrabutylammonium carboxylate) was also used for comparison. A counter electrode was prepared by dropping a 7 mM of H2PtCl6 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 (v/v, 85:15). 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.

2.3. Synthesis

2.3.1. Synthesis of Compounds 1 and 2

2-Bromo-(3,4-ethylenedioxythiophene)-5-carbadehyde (**1**) and N,N′-diphenyl-4-vinylaniline (**2**) were prepared using a reference procedure.[24, 25]

2.3.2. Synthesis of Compound 3

A DMAc solution of **1** (3.74 g, 15.00 mmol), **2** (6.11 g, 22.50 mmol), sodium carbonate (4.77 g, 45.00 mmol), 2,6-di-*tert*-butylcresol (0.66 g, 3.00 mmol), and trans-di(μ-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl] dipalladium(II) (0.14 mg, 0.15 mmol) was stirred at 110 °C for 16 h under nitrogen. After cooling, the solution was poured into methylene chloride and washed with distilled water. The mixture in the organic layer was purified by column chromatography on a silica gel using *n*-hexane/methylene chloride (3:1, v/v) as an eluent. Further purification was performed by repeated precipitation from methylene chloride into methanol to give **3** as a brown solid. (Yield 3.82 g, 52%). mp 218–220 °C. ^{1}H NMR (400 MHz, DMSO-d6) δ 4.28 (t, 4H), 6.58 (d, 2H), 6.63 (d, 4H), 6.81 (d, 2H), 6.95 (dd, 1H), 6.99 (d, 1H), 7.20 (m, 4H), 7.65 (m, 2H), 9.84 (s, 1H); ^{13}C NMR (100.64 MHz, DMSO-d6) δ 64.9, 65.3, 121.9, 123.9, 124.9, 125.7, 126.8, 129.6, 129.7, 130.4, 131.9, 133.4, 138.2, 145.1, 145.9, 147.8, 182.4.

2.3.3. Synthesis of TA-EDOT-CA

An acetonitrile solution of **3** (3.00 g, 6.83 mmol), cyanoacetic acid (11.61 g, 136.50 mmol) and piperidine (11.62 g, 136.50 mmol) was stirred at 90 °C for 24 h under nitrogen. After cooling, the solution was poured into methylene chloride and washed with aqueous solution (pH 2, adjusted by phosphoric acid). The organic layer was separated and dried over Na_2SO_4. After removal of the solvent at reduced pressure, the crude product was purified by column chromatography over silica gel using THF/methylene chloride (3:1, v/v) as an eluent. Further purification was performed by precipitation from THF into *n*-hexane (1:20, v/v) to obtain TA-EDOT-CA as a red solid. (Yield 0.81 g, 24%), mp 283–287 °C. ^{1}H NMR (400 MHz, DMSO-d_6)δ

4.28 (t, 4H), 6.58 (d, 2H), 6.63 (d, 4H), 6.81 (d, 2H), 6.95 (dd, 1H), 6.99 (d, 1H), 7.20 (m, 4H), 7.65 (m, 2H), 8.61 (s, 1H); ^{13}C NMR (100.64 MHz, DMSO-d$_6$)δ 65.3, 92.8, 117.7, 118.6, 124.9, 125.7, 126.8, 129.6, 129.7, 130.40 131.9, 133.4, 137.5, 145.1, 145.9, 159.8; MS (MALD-TOF) calcd 506.67, found 506.42 [m+H]$^+$.

2.3.4. Synthesis of Compound 4

2,5-dimethoxy-N, N'-diphenyl-4-vinylaniline (**4**) was prepared using a reference procedure.[24, 25]

2.3.5. Synthesis of Compound 5

A DMAc solution (130 ml) of **4** (7.46 g, 22.50 mmol), **1** (3.74 g, 15.00 mmol), sodium carbonate (4.77 g, 45.00 mmol), 2,6-di-*tert*-butyl-*p*-cresol (0.66 g, 3.00 mmol), and trans-di(μ-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl] dipalladium(II) (140.60 mg, 0.15 mmol) was stirred at 110 °C for 16 h. After removal of the solvent, the mixture was poured into methylene chloride and washed with distilled 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. Further purification was performed by precipitation from methylene chloride into methanol (1:20, v/v) to obtain **5** as a brown solid. Yield (4.39 g, 58%). mp 208–210 °C. ^{1}H NMR (400 MHz, DMSO-d_6)δ3.83 (s, 6H), 4.28 (t, 4H), 6.02 (s, 1H), 6.57 (s, 1H), 6.63 (m, 4H), 6.81 (t, 2H), 6.84 (d, 1H), 7.20 (m, 4H), 7.22 (d,1H), 9.89 (s, 1H); ^{13}C NMR (100.64 MHz, DMSO-d$_6$)δ 55.8, 56.8, 64.9, 65.3, 106.7, 110.3, 112.4, 121.9, 123.9, 125.7, 126.8, 129.6, 130.4, 131.5, 133.4, 138.2, 145.9, 147.8, 150.8, 182.4.

2.3.6. Synthesis of TA-DM-EDOT-CA

Piperidine (10.22 g, 120.01 mmol) was added into an acetonitrile solution (200 ml) of **5** (3.00 g, 6.01 mmol) and cyanoacetic acid (10.21 g, 120.01 mmol). The solution was stirred at 90 °C for 24 h. After removal of the solvent, the reaction mixture was poured into methylene chloride and washed with aqueous phosphoric acid (2.0 M in distilled 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 THF (1:3, v/v) as an eluent. Further purification was performed by precipitation from THF into *n*-hexane (1:20, v/v) to obtain TA-DM-EDOT-CA as a red solid. Yield (1.20 g, 40 %). mp 275–278 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$)δ 3.83 (s, 6H), 4.28 (t, 4H), 6.02 (s, 1H), 6.57 (s, 1H), 6.63 (m, 4H), 6.81 (t, 2H), 6.8s (d, 1H), 7.20 (m, 4H), 7.22 (d,1H), 8.61 (s, 1H); ^{13}C NMR (100.64 MHz, DMSO-d_6)δ 55.8, 56.2, 65.3, 92.8, 106.7, 110.3, 112.4, 117.7, 118.6, 125.7, 126.8, 129.6, 130.4, 131.5, 133.4, 137.5, 145.9, 146.2, 150.8, 159.8; MS (MALD-TOF) calcd 566.62, found 566.43 [m+H]$^+$.

3. RESULTS AND DISCUSSION

The EDOT-containing organic dyes, TA-EDOT-CA and TA-DM-EDOT-CA, with triphenylamine (TA-EDOT-CA) or methoxy-substituted triphenylamine unit (TA-DM-EDOT-CA) as an electron donor and cyanoacrylic acid as an acceptor moiety were prepared as shown in Figure 1. The methoxy unit was introduced to enhance the electron donating character into the π-conjugated photosensitizer. The compounds **1, 2** and **4** were prepared using reference procedures.[24, 25] Then, Heck coupling of **2** and **4** with **1** produced **3** and **5**, respectively. Then, Knoevenagel condensation of **3** and **5** with cyanoacetic acid in the presence of piperidine in acetonitrile produced TA-EDOT-CA and TA-DM-EDOT-CA, respectively.

As shown in Figure 2 and Table I, the UV/vis absorption spectrum of TA-EDOT-CA in ethanol exhibited an absorption maximum wavelength at 458 nm (ε = 26 700 M$^{-1}\cdot$cm^{-1}), and TA-DM-EDOT-CA at 459 nm (ε = 28 000 M$^{-1}\cdot$cm^{-1}). The red-shift of absorption maxi-

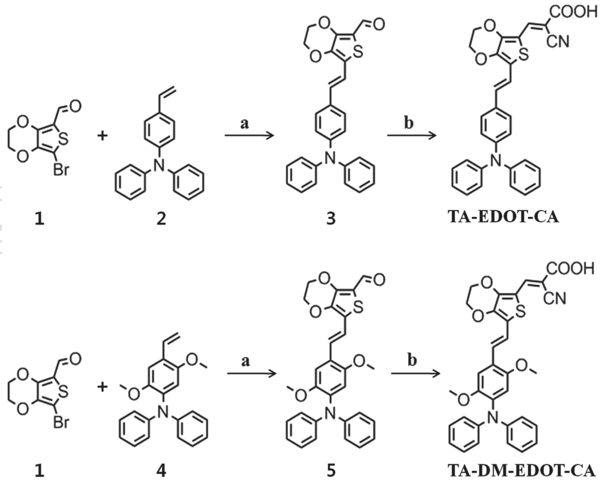

Fig. 1. Synthetic routes to TA-EDOT-CA and TA-DM-EDOT-CA. Conditions: (a) DMAc, Na$_2$CO$_3$, Pd cat, 110 °C, 16 h; (b) Acetonitrile, cyanoacetic acid, 90 °C, 24 h.

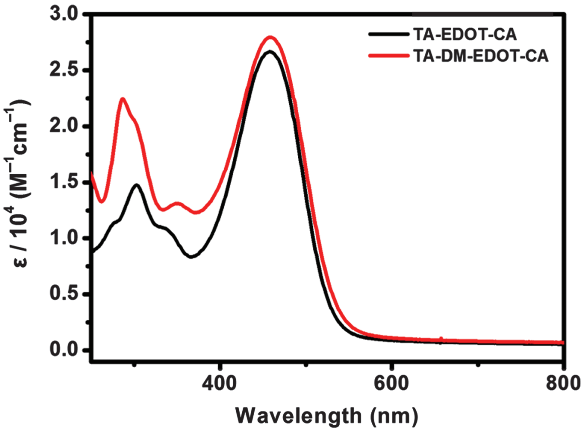

Fig. 2. Absorption spectra of TA-EDOT-CA and TA-DM-EDOT-CA in ethanol.

Table I. Electrochemical and photophysical properties of organic dyes.

Dye	E_{homo} (eV)[a]	E_{bandgap} (eV)[b]	E_{lumo} (eV)[c]	$\lambda_{\max,1}$ (nm)[d]	ε_1 ($M^{-1}\cdot cm^{-1}$)[d]	$\lambda_{\max,2}$ (nm)[d]	ε_1 ($M^{-1}\cdot cm^{-1}$)[d]
TA-EDOT- CA	−5.41	2.36	−3.05	303	14800	458	26700
TA-DM-EDOT-CA	−5.37	2.34	−3.03	287	22400	459	28000

[a] Estimated from the oxidation potential determined by cyclic voltammetry. [b] Estimated from the edge of absorption spectra. [c] Calculated from the bandgap and HOMO value. [d] Absorption spectra in ethanol.

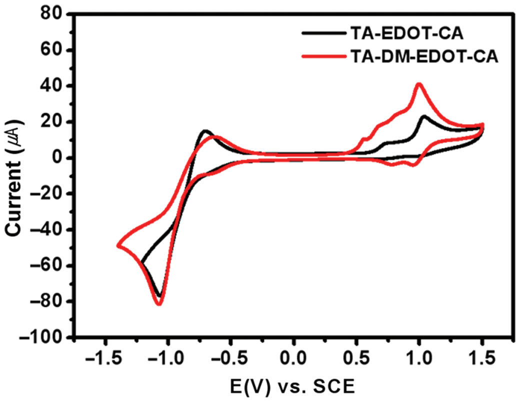

Fig. 3. Cyclic voltammetry of TA-EDOT-CA and TA-DM-EDOT-CA measured at a sweep rate of 100 mV sec^{-1}.

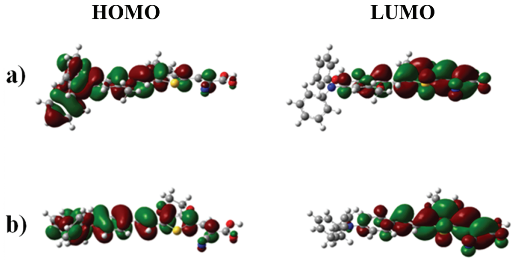

Fig. 4. The frontier HOMO and LUMO orbitals of TA-EDOT-CA (a) and TA-DM-EDOT-CA (b) organic dyes at the B3LYP/6-31G level.

mum and the enhancement of molar absorption coefficient of TA-DM-EDOT-CA were originated from the effect of methoxy unit in the donor moiety. The UV/vis absorption spectra of TA-EDOT-CA and TA-DM-EDOT-CA were red-shifted than that of TA-ST-CA (386 nm) of which the structure is similar to TA-EDOT-CA except the phenylene unit instead of EDOT moiety.[25] Therefore, the introduction of EDOT moiety is successful to induce the red-shift in the UV/vis absorption spectrum. The optical bandgap of TA-EDOT-CA and TA-DM-EDOT-CA estimated from the absorption edge of the absorption spectra were 2.36 eV and 2.34 eV, respectively.

To determine HOMO and LUMO levels of TA-EDOT-CA and TA-DM-EDOT-CA, the cyclic voltammetry was performed as shown in Figure 3 and Table II. 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 N,N′-dimethylformamide solution containing 0.1 M tetrabutylammonium tetrafluoroborate as an electrolyte. A ferrocene/ferrocenium (Fe/Fe+) system was used as a standard to calibrate the redox potential value. The HOMO levels of TA-EDOT-CA and TA-DM-EDOT-CA were −5.41 eV and −5.37 eV, respectively. The calculated LUMO values of TA-EDOT-CA and TA-DM-EDOT-CA from the HOMO levels and bandgap were −3.05 eV and −3.03 eV, respectively (Table I). These values are in the range of favorable energy matching with the conduction level of the TiO_2 particle for efficient electron transfer from the LUMO of the dyes to the conduction level of TiO_2.[20]

Figure 4 shows the frontier molecular orbitals of the dyes. At the HOMO state, the electrons are spread over the triphenylamine unit and the π-conjugated linker moiety. At the LUMO state, the excited electrons are transferred from the electron donor to the electron acceptor moiety of the dye, which indicates that the intramolecular charge transfer along the π-conjugated bridge effectively occurred by excitation induced by photon absorption. Therefore, we expect that the excited electrons of TA-EDOT-CA and TA-DM-EDOT-CA are effectively injected into the conduction band of TiO_2 from the excited dye.

Figure 5 shows the photocurrent density-photovoltage (I–V) curve of TA-EDOT-CA and TA-DM-EDOT-CA. The short circuit current density (J_{sc}) and the open circuit voltage (V_{oc}) of TA-EDOT-CA without mask were 21.45 mA/cm^2 and 614 mV with a fill factor (*ff*) of 0.628, respectively. The overall conversion efficiency (η) of TA-EDOT-CA was 8.26%, when the power conversion efficiency of N719 was 10.00% at the same experimental condition. TA-DM-EDOT-CA exhibited 19.12 mA/cm^2 of

Table II. Photovoltaic performance of the organic dyes.

	Without mask				With mask			
Dye	J_{sc} (mA/cm^2)	V_{oc} (mV)	*ff*	η (%)	J_{sc} (mA/cm^2)	V_{oc}(mV)	*ff*	η (%)
TA-EDOT-CA	21.45	614	0.628	8.26	13.45	587	0.657	5.18
TA-DM-EDOT-CA	19.12	606	0.624	7.23	12.85	587	0.647	4.88
N719	20.58	734	0.661	10.00	15.96	725	0.679	7.86

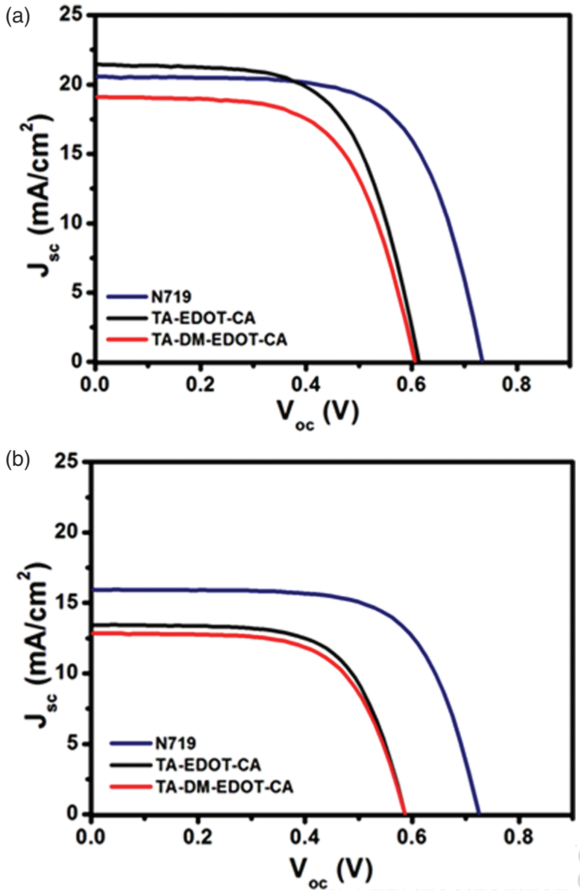

Fig. 5. Photocurrent density-photovoltage curves of TA-EDOT-CA and TA-DM-EDOT-CA without (a) and with mask (b) under AM 1.5 G 1 sun illumination (100 mW/cm^2). Electrolyte: 0.7 M 1-propyl-3-methylimidazolium iodide, 0.2 M LiI, 0.05 M iodine, 0.5 M *tert*-butylpyridine in acetonitrile/valeronitrile (85/15).

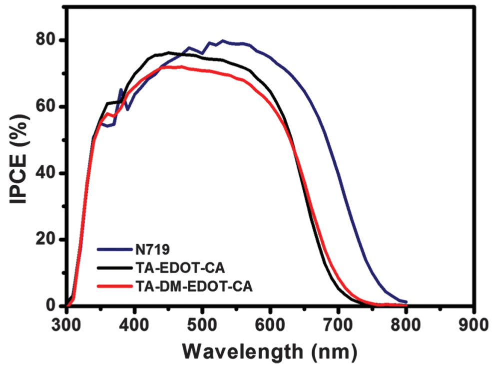

Fig. 6. IPCE spectra for the DSSC modules using N719, TA-EDOT-CA or TA-DM-EDOT-CA as a photosensitizer.

J_{sc}, 606 mV of V_{oc}, 0.624 of *ff*, and 7.23% of conversion efficiency. An apertured black mask was introduced on the cell to reduce the effect of scattered light from the edge of the glass electrodes on the TiO_2 layer.[22] In the presence of mask, the overall efficiency of the cells with the organic dyes decreased by about 30% as summarized in Figure 5 and Table II, which is comparable with the result obtained with other organic dyes.[4a]

Figure 6 shows the incident photon to current conversion efficiency (IPCE) data for TA-EDOT-CA, TA-DM-EDOT-CA and N719 as a reference. In the case of TA-EDOT-CA, the IPCE value exceeds 70% from 400 to 570 nm, reaching the maximum of 76% at 450 nm, and it is higher than N719 in the region from 350 nm to 470 nm. The IPCE spectrum of TA-DM-EDOT-CA showed slightly lower value compared with that of TA-EDOT-CA, which is possibly due to the weak charge separation of TA-DM-EDOT-CA.

In summary, we introduced EDOT moiety into the organic photosensitizer as a spacer to introduce low bandgap properties. The power conversion efficiencies of TA-EDOT-CA and TA-DM-EDOT-CA as a dye for DSSC were 8.26 and 7.23% without mask, respectively. Therefore, we expect that the EDOT moiety as a π-spacer would provide an opportunity for organic dyes to exhibit high energy conversion performances.

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