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Aqueous electrolyte based dye-sensitized solar cells using organic sensitizers†

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Two novel organic sensitizers containing a 2-(2-methoxyethoxy)ethyl unit are designed and synthesized. Under standard global AM 1.5 solar conditions, the **JK-262** sensitized cell in conjunction with an aqueous electrolyte gave a short-circuit photocurrent density (J_{sc}) of 3.78 mA cm^{-2}, an open-circuit voltage (V_{oc}) of 0.68 V, and a fill factor of 0.82, affording an overall conversion efficiency (η) of 2.10%. The η of **JK-262** is higher than that of **JK-259** due to the larger J_{sc}. The improved J_{sc} value is attributable to the broad and red-shifted absorption band as well as the dense packing of **JK-262** on the TiO_2 film.

Introduction

The photovoltaic technology has been considered as an effective way to solve the current energy and environmental crisis.[1] Dye-sensitized solar cells are attracting wide-spread interest for the conversion of sunlight into electricity because of their low cost and high efficiency.[2] A typical DSSC consists of three main parts: dye-sensitized TiO_2 photoanode, electrolyte with I^-/I_3^- redox couple, and catalytic counter electrode. In these cells, the electrolyte is one of the key components for high power conversion efficiency. The use of organic volatile electrolytes and organic dyes as sensitizers in DSSCs is achieved a power conversion efficiency in the range of 8–10%.[3] However, organic based electrolytes with volatility and flammability degrade the durability and safety of the cell.[4] The best option for the electrolyte is to use water because water-based DSSCs are less expensive and environmentally benign. Since 1990, it has been generally accepted that the water present in the organic electrolyte of DSSCs is poisonous for efficient solar energy conversion.[5] Therefore, water permeation on organic based DSSCs should be prevented by barrier layers.[6] Recently, O'Regan and co-workers[7] have shown that high water content in the electrolyte is not inseparably linked to poor efficiency and/or instability in DSSCs. So far, most of work on water-based electrolytes have centered on the ruthenium dyes.[8] Recently, Spiccia and co-workers have described an aqueous dye-sensitized solar cell based on the $Fe(CN)_6^{4-/3-}$ redox couple using an organic sensitizer, showing a high conversion efficiency of 4.1%.[9] This finding encouraged us to revisit the water-based DSSCs using the organic sensitizers in conjunction with aqueous electrolytes. In this work, we report water-based DSSCs using the organic sensitizers (**JK-259** and **JK-262**) containing 4-(2-(2-methoxyethoxy)ethoxy)phenylamine as the electron donor and cyanoacrylic acid as the electron acceptor bridged by the 9,9-bis(2-(2-methoxyethoxy)ethyl)-9*H*-fluorenyl linker (Fig. 1). We introduced a 2-(2-methoxyethoxy)ethyl unit on an organic unit to increase water solubility.

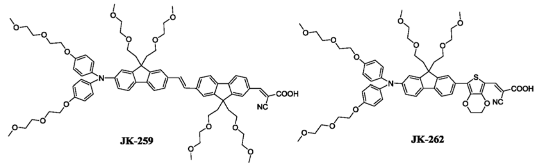

Fig. 1 Structure of the dyes (**JK-259** and **JK-262**).

Result and discussion

Scheme 1 illustrates the synthetic procedures of organic sensitizers (**JK-259** and **JK-262**) starting from a 2-bromo-7-iodo-9*H*-fluorene **1**. The 2-bromo-7-iodo-9,9-bis(2-(2-methoxyethoxy)ethyl)-9*H*-fluorene **2** was synthesized by alkylation of **1** with 1-iodo-2-(2-methoxyethoxy)ethane in the presence of *t*-BuOK. *N*-Phenylation of **2** with bis(4-(2-(2-methoxyethoxy)ethoxy)phenyl)amine was performed under Buchwald reaction.[10] Compound **5** was prepared from **4** by a lithiation with 1.2 equiv. of *n*-butyllithium and subsequent quenching with DMF. The Heck reaction[11] of **5** with vinylboronic acid pinacol ester led to **6**. The attachment of **6** to **3** was achieved by the Suzuki coupling reaction.[12]

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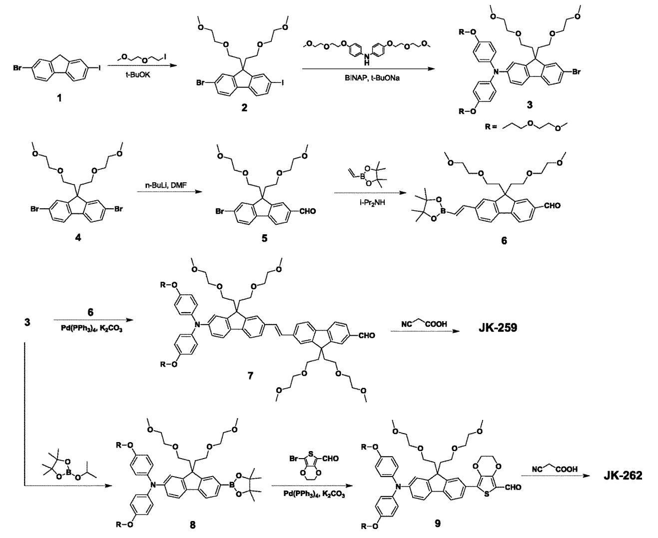

Scheme 1 Schematic diagram for the synthesis of dyes.

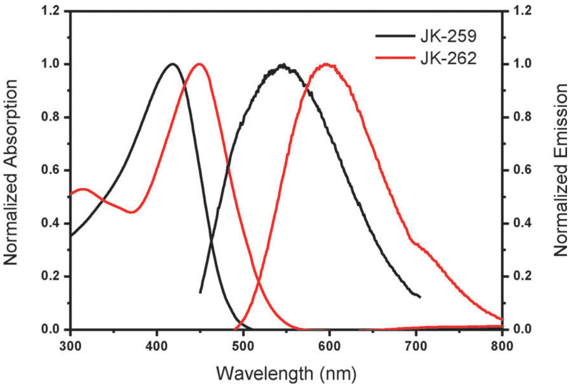

Fig. 2 Absorption and emission spectra of **JK-259** (black solid lines) and **JK-262** (red solid lines) in THF.

The Knoevenagel condensation[13] of the aldehydes **7** and **9** with cyanoacetic acid in the presence of piperidine yielded the sensitizers **JK-259** and **JK-262**.

Fig. 2 shows the electronic absorption and emission spectra of the **JK-259** and **JK-262** sensitizers measured in THF. The absorption spectrum of **JK-259** exhibits an intense absorption peak at 418 nm (ε = 83 400 $dm^3\ mol^{-1}\ cm^{-1}$), which is due to the π–π* transition of the conjugate molecule. Obviously, the absorption coefficient is enhanced with the increase of the conjugation length. Under the same conditions, the **JK-262** sensitizer with a 3,4-ethyldioxythiophenyl unit on the spacer framework exhibits a strong absorption band at 449 nm, which is 31 nm red-shifted relative to that of **JK-259**. The red-shift derives from the presence of an electron-rich 3,4-ethylenedioxythiophenyl unit[14] and a small distortion angle with respect to the fluorenyl unit (24.4°). When the **JK-259** and **JK-262** sensitizers are excited within their π–π* band in an air-equilibrated solution at 298 K, the photoluminescence spectra of **JK-259** and **JK-262** exhibit strong luminescence maxima of 542 and 598 nm, respectively.

Electrochemical properties of the sensitizers **JK-259** and **JK-262** were scrutinized in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate using TiO_2 film with absorbed dyes as working electrodes. The two organic sensitizers adsorbed on a TiO_2 film showed quasi-reversible couples. The oxidation potentials of **JK-259** and **JK-262** were measured to be 0.90 and 0.94 V *vs.* NHE, respectively. The high oxidation potential relative to that of the triiodide/iodide couple (+0.5 V) could lead to fast dye regeneration. The reduction potentials of two dyes calculated from the oxidation potentials and the E_{0-0} determined from the intersection of normalized absorption and emission spectra[15] were calculated to be −1.78 and −1.46 V *vs.* NHE. Therefore, the downhill energy offset of the LUMO in the two dyes ensures an ample driving force for electron injection.[16]

The highest-occupied molecular orbitals (HOMOs) and lowest-unoccupied molecular orbitals (LUMOs) of **JK-259** and **JK-262** were performed with the B3LYP/6-21G* (Fig. 3). The calculation reveals that the HOMO is delocalized over the π-conjugated system *via* the diphenylamino group through the fluorenyl unit and the LUMO is delocalized over the cyanoacrylic unit through fluorenyl and 3,4-ethyldioxythiophenyl groups. The examination of HOMO–LUMO illustrates that the photoinduced electron transfer from **JK-259** or **JK-262** dyes to TiO_2 electrodes can efficiently occur by the HOMO–LUMO transition as shown in Fig. 3.

Table 1 demonstrates the device performance of two cells constructed with the addition of up to 100% water to the electrolyte. The electrolyte used in both cells consists of 2 M 1-propyl-3-methylimidazolium iodide (PMMI), 0.05 M iodine, 0.1 M guanidinium thiocyanate (GuSCN), and 0.5 M *tert*-butylpyridine (TBP) in methoxypropionitrile (MPN). In order to prevent phase separation in the 100% water electrolyte, 1% Triton X-100 was added to the electrolytic solution.[17] At water containing electrolyte in both dyes,

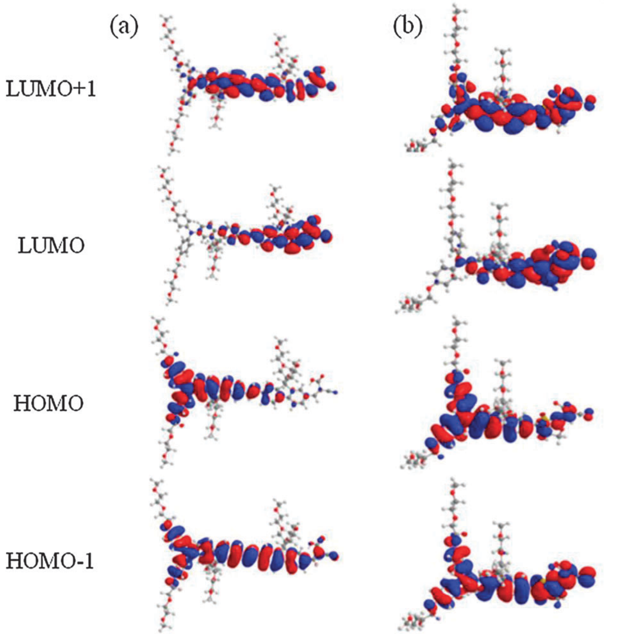

Fig. 3 Isodensity surface plots of the HOMO − 1, HOMO, LUMO, LUMO + 1 of (a) **JK-259** and (b) **JK-262**.

Table 1 Photovoltaic performance of DSSCs with three dyes and electrolytes with different water contents

Dye	Water content (%)	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	η (%)
JK-259	0	5.60	0.70	0.77	3.00
	20	4.54	0.65	0.72	2.12
	40	3.34	0.62	0.72	1.48
	60	2.73	0.65	0.77	1.38
	80	2.31	0.66	0.81	1.24
	100	2.28	0.66	0.79	1.16
JK-262	0	8.10	0.74	0.73	4.39
	20	6.29	0.66	0.71	2.93
	40	5.54	0.66	0.73	2.65
	60	4.90	0.67	0.76	2.51
	80	4.37	0.67	0.77	2.21
	100	3.78	0.68	0.82	2.10
JK-2	0	9.60	0.75	0.76	5.46
	20	6.62	0.74	0.82	4.02
	60	4.30	0.75	0.77	2.48
	100	3.31	0.74	0.82	2.01

TBP treatment on the TiO_2 films improved the photovoltaic performance and stability. The sensitizers without any addition of TBP were easily decomposed. A large increase in V_{oc} and J_{sc} occurred for both dyes when 0.5 M TBP was added into the electrolyte. A similar phenomenon was observed in organic electrolyte-based DSSCs.[18] As shown in Table 1, the fill factor (ff) and open-circuit voltage in the water-containing electrolyte gradually increased with the incremental addition of water, but the short-circuit photocurrent (J_{sc}) sharply decreased under the same conditions. The decrease of photocurrent may be contributable to the dye detachment,[19] formation of iodates[20] as well as decrease in electron lifetime.[17]

The incident monochromatic photon-to-current conversion efficiency (IPCE) with a sandwich type cell based on **JK-259** and **JK-262** is shown in Fig. 4. IPCE values higher than 20% were observed in the range of 370–470 nm with a maximum value of 26% at 455 nm for the device based on **JK-259** in 100% water based electrolyte. Under the same conditions, the action spectrum of **JK-262** is red-shifted by 100 nm compared to that of **JK-259** due to an apparent red-shift in the absorption spectrum. Under standard global air mass 1.5 solar conditions, the **JK-259** sensitized cell in 100% water containing electrolyte gave a short circuit photocurrent density (J_{sc}) of 2.28 mA cm^{-2}, an open circuit voltage (V_{oc}) of 0.66 V, and a fill factor (ff) of 0.79, corresponding to an overall conversion efficiency (η) of 1.16%. Under the same conditions, the **JK-262** sensitized cell gave a J_{sc} of 3.78 mA cm^{-2}, a V_{oc} of 0.68 V, and a ff of 0.82, corresponding to an η value of 2.10%, which is the highest one in the water based DSSCs with I^-/I_3^- electrolytes. The increased fill factor upon the incremental addition of water may be attributable to the fast catalytic characteristic, resulting in the reduced resistance. For comparison, we fabricated the cell using the sensitizer with hydrophobic nature (**JK-2**). Upon the incremental addition of water, the efficiency was sharply dropped from 5.46% in no water electrolyte to 2.10% in 100% water electrolyte. Therefore, the molecular engineering of organic sensitizers with hydrophilic terminals demonstrates some advantage for aqueous electrolyte based DSSCs. From these results, we have observed that the η value of the **JK-262** based cell is higher than that of the **JK-259** based cell due to a large photocurrent. The large photocurrent in **JK-262** relative to **JK-259** originates from a broad and red-shifted absorption band (Fig. 2) and the dense packing of **JK-262** on the TiO_2 films. To check the effect of packing on both sensitizers, we measured the amount of dyes adsorbed on the TiO_2 films by desorbing the dyes from the TiO_2 surface with KOH. The amount of two dyes adsorbed on the TiO_2 film were measured to be 7.01 × 10^{-6} and 8.84 × 10^{-6} mmol cm^{-2}

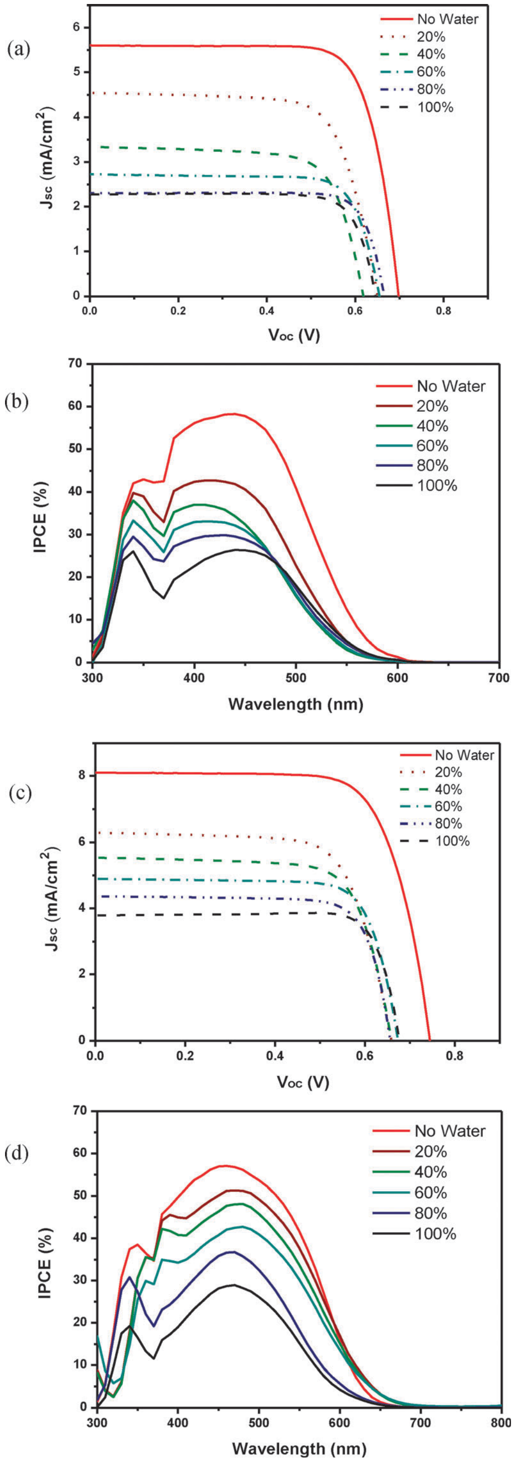

Fig. 4 (a) *J–V* curve and (b) IPCE spectra of **JK-259** and (c) *J–V* curve and (d) IPCE spectra of **JK-262**.

for **JK-259** and **JK-262**, respectively. The low adsorption of **JK-259** may be attributable to the presence of two bulky (2-methoxy-ethoxy)ethyl units. The bulky sensitizer requires more space on the TiO_2 surface and penetrates less easily in the small cavities of the TiO_2 than the less hindered sensitizer. Therefore, the electron recombination can be facilitated along with the insufficient coverage on the TiO_2 surface, resulting in the decrease in the τ_e value.[21]

Fig. 5 shows the lifetimes (τ_e) of the DSSCs employing W00 (no water) and W100 (100% water) for **JK-259** and W00 and W100 for **JK-262** displayed with a function of J_{sc} and V_{oc}. The τ_e values show a big gap among the dyes, giving W00 of **JK-262** > W00 of **JK-259** > W100 of **JK-262** > W100 of **JK-259**. The different τ_e values might be derived from the different dye structures. The τ_e values of **JK-262** were longer than those of **JK-259** due to the relatively poor dye adsorption on the TiO_2 film. The electron recombination can be facilitated along with the insufficient coverage on the TiO_2 surface for **JK-259** dye, resulting in the decrease in the τ_e values.[21] The result of the electron lifetime in both dyes is consistent with that of V_{oc} shown in Table 1.

The electrocatalytic activity of CE in DSSCs can be conveniently evaluated by using symmetrical dummy cells, in which a thin layer of electrolyte solution is sandwiched between two identical electrodes.[22–25] Fig. 6a shows the Nyquist plots of the symmetrical dummy cells consisting of two Pt-coated FTO electrodes with different amounts of water in the electrolyte. The experimental data could be fitted into the equivalent circuit shown in the inset of Fig. 6a, which is well known as a Randles-type circuit, where R_S is ohmic serial resistance, R_{CT} is charge transport resistance at the interface between electrode surface and electrolyte, Z_D is the Nernst diffusion impedance in the bulk electrolyte solution between the two identical electrodes, and CPE is a constant phase element describing deviation from the ideal capacitance due to the surface roughness of the electrodes.[26,27]

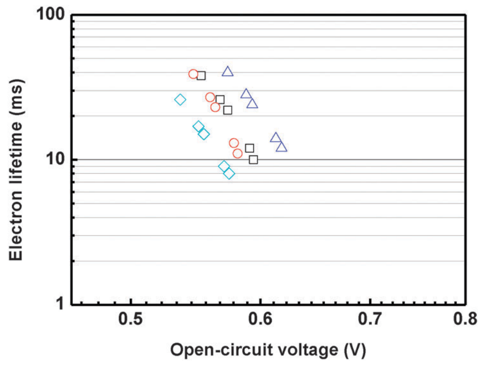

Fig. 5 Lifetimes in the photoelectrodes different dyes (△ W00 of **JK-262**; ○ W00 of **JK-259**; □ W100 of **JK-262**; ◇ W100 of **JK-259**).

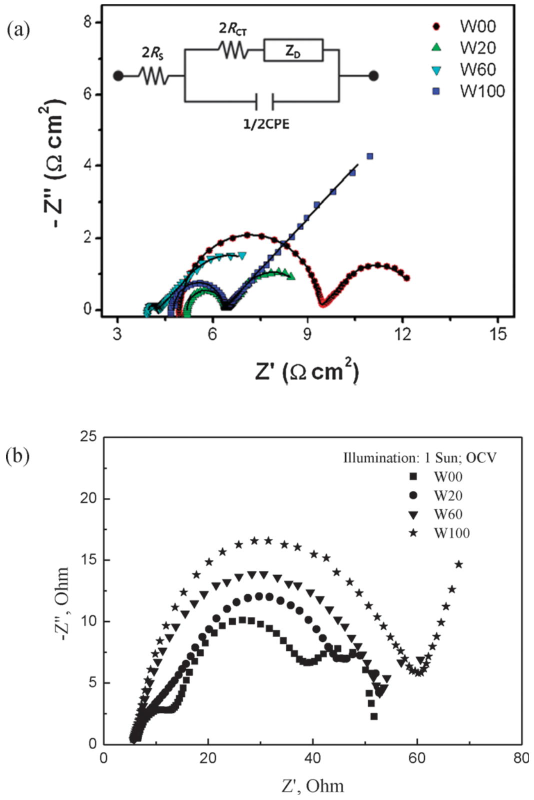

Fig. 6 (a) Nyquist plots of electrochemical impedance spectra (EIS) measured at 0 V from 10^6 Hz to 0.1 Hz on dummy cells with two identical Pt-coated FTO electrodes with an AC amplitude of 10 mV. The inset is equivalent circuit diagram for fitting the EIS data. Solid lines are fitted curves to the equivalent circuit. (b) Electrochemical impedance spectra measured under the illumination (100 mW cm^{-2}) for **JK-262** employing different dyes (■ W00, ● W20, ▼ W60, ★ W100).

Table 2 Electrochemical parameters obtained by fitting the EIS data of the reference and water-added dummy cells, using an equivalent circuit

Electrolyte	R_S (Ω cm^2)	R_{CT} (Ω cm^2)	CPE:β
W00	2.47	2.21	0.96
W20	2.59	0.14	0.96
W60	1.98	0.08	0.96
W100	2.34	0.81	0.94

The corresponding electrochemical parameters, obtained by fitting the plots with ZView software based on the equivalent circuit, are listed in Table 2. The resulted R_{CT} values imply that the charge transfer resistance of the water-added dummy cells is decreased compared to that of the reference dummy cell, which is in agreement with the report by Sakaguchi *et al.* on quasi-solid state DSSCs with chemically cross-linked gelators.[28] The R_{CT} is an important parameter to evaluate the catalytic performance of counter electrode (CE) in DSSCs. It is because the exchange current density, J_0 (*i.e.*, the equal cathodic and anodic currents normalized to the projected electrode area at equilibrium), should be akin to photocurrent density on the TiO_2 photoanode working under full sun illumination on a CE. The J_0 varies inversely with the R_{CT}.[29] A lower R_{CT} implies a more facile electron transfer from the CE to the I_3^- ions and, therefore, the J_{sc} of the DSSC increases relative to that of the reference DSSC. In fact, there is one report that J_{sc} increases with increasing water content, as a result of the decreased charge transfer resistance,[30] in contrast to the decrease in J_{sc} noted in other reports.[31,32] Fig. 6b shows the Nyquist plots of the DSSCs at open circuit condition under 1 sun illumination. In typical EIS analysis, the R_S of DSSCs is generally composed of at least three internal resistances. The semicircles in the different frequency regimes indicate the Nernst diffusion limited impedance of the redox species in the electrolyte, impedance by transport and recombination competition at the TiO_2/dye/electrolyte interface (R_{TR}), and electrochemical charge transfer resistance at the CE/electrolyte interface (R_{CT}). The semicircle at the highest frequency regime in Fig. 6b is related to the CE/electrolyte event, and the R_{CT} at the CE/electrolyte interface can be obtained from the real component values. As shown in Fig. 6b, R_{CT} of the DSSCs with W60 and W100 is so active that cannot be fitted, but R_{CT} of the DSSCs with W20 and W00 exhibits 6.8 and 6.1, respectively. The presence of water in the electrolyte solution increases its hydrophilicity and thus would facilitate the charge transfer at the electrode/electrolyte interface due to the enhanced movement of the ionic species. The increased fill factor of the water added DSSCs except for the DSSC with W20 compared to that of the reference DSSC in Table 1 also supports this observation. It is known that the fill factor depends on the resistances of the photoanode, electrolyte and CE. The increase in the fill factor in the case of the cell with W60 and W100 is attributed to its lower charge transfer resistance, relative to that of the cell without water additives.

In contrast to the expectation based on the decrease in R_{CT} as shown in Fig. 6a, however, the J_{sc} values of the water-added DSSCs were decreased compared to that of the DSSC with W00, as shown in Table 1. R_{TR} of the intermediate frequency semicircles in the Nyquist plots for **JK-262** decreased in the order of W100 (50.5 Ω) > W60 (46.2 Ω) > W20 (33.6 Ω) > W00 (22.1 Ω), indicating the improved charge generation and transport. This result is consistent with that of short circuit photocurrent shown in Table 1. In summary, we can conclude that the decrease in the J_{sc} values of the water-containing DSSCs in the electrolyte could be explained by the detachment of the adsorbed dye through the hydrolysis of the TiO_2–water surface linkage.

Experimental

2-Bromo-7-iodo-9*H*-fluorene (**1**),[33] 1-iodo-2-(2-methoxyethoxy)-ethane,[34] and 7-bromo-2,3-dihydrothieno[3,4-*b*][1,4]dioxine-5-carbaldehyde[35] were synthesized according to the procedures in the literatures.

^1H and ^{13}C NMR spectra were recorded using a Varian Mercury 300 spectrometer. MALDI-TOF Mass spectrometry was performed using Voyager™ DE-STR, 4700 Proteomics. Optimized structures were calculated by TD-DFT using the B3LYP functional and the 6-21G* basis set. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies were determined using minimized singlet geometries to approximate the ground state. UV-vis data were measured using a Perkin-Elmer Lambda 2S UV-visible spectrometer. Photoluminescence spectra were recorded on a Perkin LS fluorescence spectrometer. Cyclic voltammetry (CV) was performed using VersaSTAT 3 (Princeton Applied Research). Anhydrous acetonitrile was used as the solvent and 0.1 M of tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte. TiO_2 films stained with the sensitizers were used as working electrodes, a platinum wire as the counter electrode, and a Ag/Ag$^+$ electrode as the reference electrode. The measurements were done using a scan rate of 50 mV s^{-1} and ferrocenium/ferrocene redox couple was used as an internal reference.

Electron transport measurements

The electron lifetimes (τ_e) in the TiO_2 photoelectrode were measured by the stepped light-induced transient measurements of photocurrent and voltage (SLIM-PCV).[36–39] The transients were induced by a stepwise change in the laser intensity. A diode laser (λ = 635 nm) as a light source was modulated using a function generator. The initial laser intensity was constant 90 mW cm^{-2} and was attenuated up to approximately 10 mW cm^{-2} using a ND filter which was positioned at the front side of the fabricated samples (TiO_2 film thickness = *ca.* 6 μm; active area = 0.04 cm^2). The photocurrent and photovoltage transients were monitored using a digital oscilloscope through an amplifier. The τ_e value was determined by fitting a decay of photovoltage transient with $\exp(-t/\tau_e)$.[36] All experiments were conducted at room temperature.

Fabrication of cell

FTO glass plates (Pilkington TEC Glass-TEC 8, Solar 2.3 mm thickness) were cleaned in a detergent solution using an ultrasonic bath for 30 min, rinsed with water and ethanol. The FTO glass plates were immersed in 40 mM $TiCl_4$ (aqueous) at 70 °C for 30 min and washed with water and ethanol. A transparent nanocrystalline layer on the FTO glass plate was prepared by doctor blade printing TiO_2 paste (Solaronix, Ti-Nanoxide T/SP) and then dried for 2 h at 25 °C. The TiO_2 electrodes were gradually heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 15 min. The thickness of the transparent layer was measured by using an Alpha-step 250 surface profilometer (Tencor Instruments, San Jose, CA), a paste for the scattering layer containing 400 nm sized anatase particles (CCIC, PST-400C) was deposited by doctor blade printing and then dried for 2 h at 25 °C. The TiO_2 electrodes were gradually heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 15 min. The resulting layer was composed of 20 μm thickness of transparent layer and 4 μm thickness of scattering layer. The TiO_2 electrodes were treated again by $TiCl_4$ at 70 °C for 30 min and sintered at 500 °C for 30 min. The TiO_2 electrodes were immersed into the **JK-259** and **JK-262** (0.3 mM in acetonitrile : *tert*-butanol : ethanol = 2 : 1 : 1) and kept at room temperature for 16 h. The FTO plate (Pilkington TEC Glass-TEC 8, Solar 2.3 mm thickness) for counter electrodes cleaned with an ultrasonic bath in H_2O, acetone and 0.1 M HCl aq., subsequently. Counter electrodes were prepared by coating with a drop of H_2PtCl_6 solution (2 mg of Pt in 1 mL of ethanol) on a FTO plate and heating at 400 °C for 15 min. The dye adsorbed TiO_2 electrode and Pt-counter electrode were assembled into a sealed sandwich-type cell by heating at 80 °C with a hot-melt ionomer film (Surlyn SX 1170-25, Solaronix) as a spacer between the electrodes. A drop of electrolyte solution (2 M 1-propyl-3-methylimidazolium iodide (PMMI), 0.05 M iodine, 0.1 M guanidinium thiocyanate (GuSCN), 0.5 M *tert*-butylpyridine (TBP) in methoxypropionitrile (MPN) and water) was placed on the drilled hole in the counter electrode of the assembled cell and was driven into the cell *via* vacuum backfilling. Finally, the hole was sealed using additional Surlyn and a cover glass (0.1 mm thickness).

2-Bromo-7-iodo-9,9-bis(2-(2-methoxyethoxy)ethyl)-9*H*-fluorene (2)

Compound **1** (1.5 g, 4.04 mmol) was dissolved in anhydrous THF (20 mL) and cooled to 0 °C under a nitrogen atmosphere. To this solution, *tert*-BuOK (1.36 g, 12.12 mmol) was added in several portions. After stirring for 30 min, 1-iodo-2-(2-methoxyethoxy)ethane (5.43 g, 16.16 mmol) was added to the solution and stirred at RT for overnight. The resulting mixture was extracted with ethyl acetate, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified with silica column chromatography using ethyl acetate/CH_2Cl_2 (3 : 7) as eluent to obtain as viscous oil in 60% yield. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 2.36 (6H, t, J = 7.5 Hz), 2.75 (6H, t, J = 7.5 Hz), 3.18 (4H, m), 3.30 (10H, m), 7.39 (1H, d, J = 8.4 Hz), 5.31 (1H, br s), 6.82 (4H, d, J = 9.3 Hz), 6.91 (4H, d, J = 4.8 Hz). 7.46 (1H, dd, J = 8.1 Hz, J = 1.5 Hz), 7.51 (1H, d, J = 8.1 Hz), 7.53 (1H, d, J = 1.2 Hz), 7.67 (1H, dd, J = 7.8 Hz, J = 1.5 Hz), 7.74 (1H, d, J = 1.2 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 39.45, 51.82, 59.02, 66.78, 69.93, 71.71, 93.07, 121.16, 121.19, 121.75, 126.64, 130.58, 132.55, 136.47, 138.36, 138.97, 150.61, 150.94.

7-Bromo-*N*,*N*-bis(4-(2-(2-methoxyethoxy)ethoxy)phenyl)-9,9-bis(2-(2-methoxy-ethoxy)ethyl)-9*H*-fluorene-2-amine (3)

Bis(4-(2-(2-methoxyethoxy)ethoxy)phenyl)-amine (0.33 g, 0.814 mmol), compound **2** (0.56 g, 0.974 mmol), tris(dibenzylidene-acetone)dipalladium(0) (1.85 mg, 0.00202 mmol), 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (3.80 mg, 0.0061 mmol) and sodium tertiary butoxide (0.11 g, 1.15 mmol) in anhydrous toluene (10 mL) were refluxed overnight. After cooling, a crude product was extracted with ethyl acetate, dried over Na_2SO_4, filtered by a glass filter and concentrated under reduced pressure. The residue was purified with silica column chromatography using ethyl acetate/CH_2Cl_2 (3 : 7) as eluent to obtain as a brown oil in 50% yield. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 2.20–2.24 (4H, m), 2.75–2.86 (4H, m), 3.21–3.26 (4H, m), 3.30 (6H, s), 3.34 (4H, t, J = 4.5 Hz), 3.40 (6H, s), 5.42 (1H, s), 7.46 (1H, dd, J = 8.1 Hz, J = 1.8 Hz), 7.50–7.56 (4H, m), 7.65 (1H, d, J = 8.7 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 31.12, 39.53, 51.44, 59.19, 59.27, 67.27, 67.84, 69.98, 70.08, 70.92, 71.94, 72.14, 115.61, 119.77, 120.50, 126.40, 126.50, 130.40, 132.19, 139.67, 141.23, 149.01, 149.91, 150.90, 155.10, 156.92. MALDI-TOF, *m*/*z*: calcd, 851.32; found, 851.36 (M^+).

7-Bromo-9,9-bis(2-(2-methoxyethoxy)ethyl)-9*H*-fluorene-2-carbaldehyde (5)

2,7-Dibromo-9,9-bis(2-(2-methoxyethoxy)ethyl)-9*H*-fluorene (1.55 g, 2.93 mmol) was dissolved in anhydrous THF (30 mL) and cooled to −78 °C under a nitrogen atmosphere. A solution of *n*-butyllithium (1.83 mL of a 1.6 M solution in hexane, 2.93 mmol) was added dropwise. After stirring at −78 °C for 1 h, DMF (0.49 mL, 6.33 mmol) was added to the solution and allowed to warm to room temperature for 2 h. The reaction was quenched by the addition of water, extracted with ethyl acetate, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was used for the following reaction without further purification as viscous oil in 90% yield. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 2.38–2.52 (4H, m), 2.74–2.80 (4H, m), 3.15 (4H, m), 3.27 (10H, m), 7.52 (1H, dd, J = 8.1 Hz, J = 1.5 Hz), 7.62 (1H, s), 7.63 (1H, d, J = 8.1 Hz), 7.80 (1H, d, J = 8.1 Hz), 7.89 (1H, dd, J = 8.1 Hz, J = 1.5 Hz), 7.93 (1H, s), 10.05 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 39.25, 51.80, 58.84, 66.71, 69.79, 71.55, 120.12, 122.15, 123.00, 124.09, 126.95, 130.07, 130.73, 135.58, 137.80, 145.40, 149.46, 152.47, 191.57.

(*E*)-9,9-Bis(2-(2-methoxyethoxy)ethyl)-7-(2-(4,4,5,5-tetra-methyl-1,3,2-dioxaborol-an-2-yl)vinyl)-9*H*-fluorene-2-carbaldehyde (6)

Compound **5** (0.87 g, 1.82 mmol), vinylboronic acid pinacol ester (0.31 mL, 1.82 mmol), diisopropylamine (1.04 mL, 7.37 mmol) and bis(tri-*tert*-butylphosphine)palladium(0) (47.5 mg, 0.092 mmol) were dissolved in dry toluene (10 mL) and stirred at 80 °C for 24 h. After cooling, the resulting mixture was extracted with ethyl acetate, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The product **6** was obtained by silica gel column chromatography using EA as eluent in 60% yield. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 1.33 (12H, s), 2.41–2.50 (4H, m), 2.70–2.80 (4H, m), 2.14 (4H, m), 3.25 (10H, m), 6.26 (1H, d, J = 18.6 Hz), 7.44–7.57 (3H, m), 7.70–7.81 (2H, m), 7.88 (1H, d, J = 8.4 Hz), 7.94 (1H, s), 10.05 (1H, s). Anal. calcd for $C_{32}H_{43}BO_7$: C, 69.82; H, 7.87. Found: C, 69.58; H, 7.72%.

(*E*)-7-(2-(7-(Bis(4-(2-(2-methoxyethoxy)ethoxy)phenyl)-amino)-9,9-bis(2-(2-methoxyethoxy)ethyl)-9*H*-fluoren-2-yl)vinyl)-9,9-bis(2-(2-methoxyethoxy)ethyl)-9*H*-fluorene-2-carbaldehyde (7)

Compound **3** (0.85 g, 0.997 mmol), compound **6** (0.55 g, 0.999 mmol), potassium carbonate (0.55 g, 3.98 mmol) in distilled water (2.0 mL) and tetrakis(tri-phenylphosphine)palladium(0) (58 mg, 0.050 mmol) in anhydrous THF (10 mL) were refluxed at 80 °C for 24 h. After cooling, THF was evaporated under reduced pressure. A crude product was extracted with ethyl acetate, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The product **7** was obtained by silica gel column chromatography using EA as eluent as an yellow oil in 32% yield. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 2.18–2.41 (4H, m), 2.50 (4H, m), 2.73–2.91 (8H, m), 3.16–3.36 (28H, m), 3.40 (6H, s), 3.59 (4H, m), 3.74 (4H, m), 3.87 (4H, t, J = 4.8 Hz), 4.14 (4H, t, J = 4.8 Hz), 6.85 (4H, d, J = 9.0 Hz), 6.90 (1H, dd, J = 8.1 Hz, J = 2.1 Hz), 7.00 (1H, d, J = 2.1 Hz), 7.04 (4H, d, J = 9.0 Hz), 7.24 (1H, d, J = 8.1 Hz), 7.46 (3H, t, J = 8.1 Hz), 7.54–7.57 (3H, m), 7.64 (1H, s), 7.76 (1H, d, J = 7.8 Hz), 7.81 (1H, d, J = 7.8 Hz), 7.89 (1H, dd, J = 7.8 Hz, J = 1.2 Hz), 7.95 (1H, s), 10.05 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 39.76, 51.05, 51.52, 59.13, 59.25, 67.10, 67.43, 67.83, 69.97, 70.06, 70.89, 71.83, 71.93, 72.13, 115.58, 115.81, 119.22, 120.12, 120.61, 121.05, 121.48, 124.31, 126.34, 126.64, 127.48, 130.06, 130.31, 132.99, 135.14, 135.37, 138.37, 138.74, 140.74, 141.32, 146.59, 148.76, 149.22, 150.14, 150.52, 151.08, 155.04.

3-(7-((*E*)-2-(7-(Bis(4-(2-(2-methoxyethoxy)ethoxy)phenyl)-amino)-9,9-bis(2-(2-methoxyethoxy)ethyl)-9*H*-fluoren-2-yl)vinyl)-9,9-bis(2-(2-methoxyethoxy)ethyl)-9*H*-fluoren-2-yl)-2-cyanoacrylic acid (JK-259)

Compound **7** (100 mg, 0.084 mmol) and cyanoacetic acid (28.4 mg, 0.334 mmol) were dissolved in dry CH_3CN (40 mL) and THF (40 mL). To this mixture, piperidine (0.1 mL) was added under a nitrogen atmosphere and the solution was refluxed at 80 °C for 24 h. After cooling, 1 M HCl solution (10 mL) was added and the solution was stirred at RT for 3 h. The resulting mixture was extracted with ethyl acetate, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The product **JK-259** was obtained by silica gel column chromatography using ethyl acetate/methanol (9 : 1) as eluent. Red solid in 44% yield. ^{1}H NMR (CD_3OD, 300 MHz, ppm): δ 2.15–2.36 (4H, m), 2.45 (4H, m), 2.88 (8H, m), 3.12–3.28 (28H, m), 3.36 (6H, s), 3.56 (4H, m), 3.68 (4H, m), 3.82 (4H, t, J = 4.5 Hz), 4.09 (4H, t, J = 4.5 Hz), 6.83 (1H, d, J = 2.4 Hz), 6.87 (4H, d, J = 9.0 Hz), 7.01 (4H, d, J = 9.0 Hz), 7.19 (1H, d, J = 2.1 Hz), 7.34 (1H, d, J = 6.3 Hz), 7.43–7.56 (4H, m), 7.70–7.74 (2H, m), 7.79–7.81 (2H, m), 7.92 (1H, d, J = 8.1 Hz), 8.15 (1H, s), 8.22 (1H, s). ^{13}C NMR (CD_3OD, 75 MHz, ppm): δ 40.37, 52.31, 52.82, 59.10, 68.21, 68.43, 68.89, 70.72, 70.83, 71.49, 72.74, 72.94, 110.52, 116.57, 119.54, 121.17, 121.56, 122.05, 125.74, 127.37, 131.38, 133.00, 134.36, 136.86, 139.59, 140.06, 141.64, 142.43, 145.07, 149.97, 150.56, 151.32, 151.77, 152.05, 156.41, 168.56. MALDI-TOF, *m*/*z*: calcd, 1262.63; found, 1262.63 (M^+). Anal. calcd for $C_{74}H_{90}N_2O_{16}$: C, 70.34; H, 7.18. Found: C, 70.08; H, 7.11%.

N,*N*-Bis(4-(2-(2-methoxyethoxy)ethoxy)phenyl)-9,9-bis-(2-(2-methoxyethoxy)ethyl)-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-fluorene-2-amine (8)

Compound **3** (0.16 g, 0.188 mmol) was dissolved in anhydrous THF (20 mL) and cooled to −78 °C under a nitrogen atmosphere. A solution of *n*-butyllithium (0.14 mL of a 1.6 M solution in hexane, 0.23 mmol) was added dropwise. After stirring at −78 °C for 30 min, 2-iso-propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.058 mL, 0.282 mmol) was added to the solution and allowed to warm to room temperature for 2 h. The reaction was quenched by the addition of water, extracted with ethyl acetate, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was used for the following reaction without further purification. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 1.36 (12H, s), 2.16–2.38 (4H, m), 2.73–2.80 (4H, m), 3.21 (4H, m), 3.28 (6H, s), 3.33 (4H, t, J = 4.5 Hz), 3.39 (6H, s), 3.58 (4H, m) 3.73 (4H, m), 3.85 (4H, t, J = 4.5 Hz), 4.12 (4H, t, J = 5.1 Hz), 6.83 (4H, dt, J = 8.7 Hz, J = 1.8 Hz), 6.87 (1H, dd, J = 8.4 Hz, J = 1.8 Hz), 6.98 (1H, d, J = 2.1 Hz), 7.02 (4H, dt, J = 9.0 Hz, J = 2.1 Hz), 7.45 (1H, d, J = 8.1 Hz), 7.52 (1H, d, J = 7.2 Hz), 7.74 (2H, d, J = 9.6 Hz).

7-(7-(Bis(4-(2-(2-methoxyethoxy)ethoxy)phenyl)amino)-9,9-bis(2-(2-methoxy-ethoxy)ethyl)-9*H*-fluoren-2-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxine-5-carbaldehyde (9)

Compound **8** (0.27 g, 0.300 mmol), 7-bromo-2,3-dihydrothieno[3,4-b]-[1,4]dioxine-5-carbaldehyde (0.11 g, 0.441 mmol), 2 M solution of potassium carbonate (0.17 g, 1.23 mmol) in distilled water (0.6 mL) and tetrakis(triphenyl-phosphine)palladium(0) (17 mg, 0.015 mmol) in anhydrous THF (30 mL) were refluxed at 80 °C for 24 h. After cooling, THF was evaporated under reduced pressure. A crude product was extracted with ethyl acetate, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The product **9** was obtained by silica gel column chromatography using ethyl acetate/CH_2Cl_2 as eluent in 25% yield. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 2.18–2.37 (4H, m), 2.79–2.90 (4H, m), 3.23–3.26 (4H, m), 3.28 (6H, s), 3.29–3.35 (4H, m), 3.40 (6H, s), 3.59 (4H, m), 3.74 (4H, m), 3.87 (4H, t, J = 4.5 Hz), 4.14 (4H, t, J = 4.5 Hz), 4.43 (4H, s), 6.85 (4H, d, J = 8.7 Hz), 6.89 (1H, dd, J = 8.1 Hz, J = 1.8 Hz), 6.97 (1H, d, J = 2.1 Hz), 7.04 (4H, d, J = 8.7 Hz), 7.45 (1H, d, J = 8.1 Hz), 7.54 (1H, d, J = 8.1 Hz), 7.69 (1H, d, J = 9.0 Hz), 7.84 (1H, s), 7.93 (1H, s). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 31.08, 39.48, 51.21, 59.13, 59.22, 64.74, 65.29, 67.37, 67.81, 69.94, 70.03, 70.87, 71.89, 72.10, 115.24, 115.44, 115.59, 119.16, 120.32, 120.72, 121.50, 125.85, 126.22, 126.47, 129.48, 129.85, 132.36, 137.53, 141.12, 141.41, 149.13, 149.21, 150.74, 155.15, 179.51.

(*E*)-3-(7-(7-(Bis(4-(2-(2-methoxyethoxy)ethoxy)phenyl)-amino)-9,9-bis(2-(2-methoxyethoxy)ethyl)-9*H*-fluoren-2-yl)-2,3-dihydrothieno-[3,4-b][1,4]dioxin-5-yl)-2-cyanoacrylic acid (JK-262)

Compound **9** (70 mg, 0.074 mmol) and cyanoacetic acid (25.0 mg, 0.29 mmol) were dissolved in dry CH_3CN (20 mL) and THF (20 mL). To this mixture, piperidine (0.1 mL) was added under a nitrogen atmosphere and the solution was refluxed at 80 °C for 24 h. After cooling, 1 M HCl solution (10 mL) was added and the solution was stirred at RT for 3 h. The resulting mixture was extracted with ethyl acetate, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The product **JK-262** was obtained by silica gel column chromatography using ethyl acetate/methanol (9 : 1) as eluent in 34% yield. ^{1}H NMR (CD_3OD, 300 MHz, ppm): δ 2.15–2.32 (4H, m), 2.88 (4H, m), 3.20–3.30 (14H, m), 3.37 (6H, s), 3.57 (4H, m), 3.70 (4H, m), 3.83 (4H, t, J = 4.5 Hz), 4.11 (4H, t, J = 4.2 Hz), 4.44 (4H, s), 6.84 (1H, d, J = 2.4 Hz), 6.89 (4H, d, J = 9.0 Hz), 7.00 (1H, d, J = 1.5 Hz), 7.03 (4H, d, J = 9.0 Hz), 7.50 (1H, d, J = 8.1 Hz), 7.57 (1H, d, J = 8.1 Hz), 7.72 (1H, d, J = 8.7 Hz), 7.83 (1H, s), 8.30 (1H, s). ^{13}C NMR (CD_3OD, 75 MHz, ppm): δ 30.73, 40.27, 52.54, 59.07, 59.13, 66.08, 66.67, 68.40, 68.89, 70.71, 70.82, 71.48, 72.72, 72.92, 110.98, 116.57, 119.96, 120.22, 121.32, 121.75, 122.16, 126.75, 127.48, 131.00, 133.84, 139.06, 142.14, 142.34, 148.65, 150.32, 150.51, 151.95, 156.51. MALDI-TOF, *m*/*z*: calcd, 1008.41; found, 1008.48 (M^+). Anal. calcd for $C_{55}H_{64}N_2O_{14}S$: C, 65.46; H, 6.39. Found: C, 65.27; H, 6.24.

Conclusions

We have meticulously designed and synthesized a new class of fluorenyl-bridged organic sensitizers for aqueous electrolytes. A solar-cell device based on the organic sensitizer **JK-262** in conjunction with an aqueous electrolyte gave an overall conversion efficiency of 2.10%. The power conversion efficiency of the DSSCs based on the two sensitizers was shown to be sensitive to the bridged units. Using a water-based electrolyte, a greener process for DSSCs fabrication can be developed for the realization of environmentally benign dye solar cells.

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Notes and references

1 N. Robertson, *Angew. Chem., Int. Ed.*, 2006, **45**, 2338.

2 (*a*) B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737; (*b*) M. Grätzel, *Nature*, 2001, **414**, 338; (*c*) P. Wang, C. Klein, T. Humphry-Baker, S. M. Zakeeruddin and M. Grätzel, *J. Am. Chem. Soc.*, 2005, **127**, 808.

3 (*a*) W. Zeng, Y. Cao, Y. Bai, Y. Wang, Y. Shi, M. Zhang, F. Wang, C. Pan and P. Wang, *Chem. Mater.*, 2010, **22**, 1915; (*b*) Z. S. Wang, Y. Cui, K. Hara, Y. Dan-oh, C. Kasada and A. Shinpo, *Adv. Mater.*, 2007, **19**, 1138; (*c*) H. Choi, I. Raabe, D. Kim, F. Teocoli, C. Kim, K. Song, J.-H. Yum, J. Ko, M. K. Nazeeruddin and M. Grätzel, *Chem.–Eur. J.*, 2010, **16**, 1193; (*d*) S. Ito, H. Miura, S. Uchida, M. Takata, K. Sumioka P. Liska, P. Comte, P. Péchy and M. Grätzel, *Chem. Commun.*, 2008, 5194; (*e*) H. Choi, C. Baik, S. O Kang, J. Ko, M. S. Kang, M. K. Nazeeruddin and M. Grätzel, *Angew. Chem., Int. Ed.*, 2008, **47**, 327.

4 (*a*) A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, *Chem. Rev.*, 2010, **110**, 6595; (*b*) K. Hara, T. Horiguchi, T. Kinoshita, K. Sayama and H. Arakawa, *Sol. Energy Mater. Sol. Cells*, 2001, **70**, 151.

5 S. Mikoshiba, S. Murai, H. Sumino, T. Kato, K. Kosugi and S. Hayase, *Curr. Appl. Phys.*, 2005, **5**, 152.

6 T. N. Murakami, H. Saito, S. Uegusa, N. Kawashima and T. Miyasaka, *Chem. Lett.*, 2003, 1154.

7 C. H. Law, S. C. Pathirana, X. Li, A. Y. Anderson, P. R. F. Barnes, A. Listorti, T. H. Ghaddar and B. O'Regan, *Adv. Mater.*, 2010, **22**, 4505.

8 (*a*) P. Liska, N. Vlachopoulos, M. K. Nazeeruddin, P. Comte and M. Grätzel, *J. Am. Chem. Soc.*, 1988, **110**, 3686; (*b*) B. O'Regan, J. Moser, M. Anderson and M. Grätzel, *J. Phys. Chem.*, 1996, **94**, 8720.

9 T. Daeneke, Y. Uemura, N. W. Duffy, A. J. Mozer, N. Koumura, U. Bach and L. Spiccia, *Adv. Mater.*, 2012, **24**, 1222.

10 R. Martin, C. H. Larsen, A. Cuenca and S. L. Buchwald, *Org. Lett.*, 2007, **9**, 3379.

11 K. Itami, K. Tonogaki, Y. Ohashi and J.-I. Yoshida, *Org. Lett.*, 2004, **6**, 4093.

12 (*a*) C.-H. Hwang, N. D. McClenaghan, A. Kuhn, J. W. Hofstraat and D. M. Bassan, *Org. Lett.*, 2005, **7**, 3409; (*b*) K. J. Hoffmann, E. Bakken, E. J. Samuelesen and P. H. Carlen, *Synth. Met.*, 2000, **113**, 39; (*c*) M. Trubiez, P. Frére, M. Allain, C. Videlot, J. Ackermann and J. Roncali, *Chem.–Eur. J.*, 2005, **11**, 3742.

13 E. Knoevenagel, *Ber. Dtsch. Chem. Ges.*, 1898, **31**, 2596.

14 (*a*) G. Zhang, H. Bala, Y. Cheng, D. Shi, X. Lv, Q. Yu and P. Wang, *Chem. Commun.*, 2009, 2198; (*b*) M. Xu, S. Wenger, H. Bala, D. Shi, R. Li, Y. Zhou, S. M. Zakeeruddin, M. Grätzel and P. Wang, *J. Phys. Chem. C*, 2009, **113**, 2966.

15 X. Li, X. Hou, F. Duan and C. Huang, *Inorg. Chem. Commun.*, 2006, **9**, 394.

16 (*a*) A. M. Bond, G. B. Deacon, J. Howitt, D. R. MacFarlane, L. Spiccia and G. Wolfbauer, *J. Electrochem. Soc.*, 1999, **146**, 648; (*b*) P. Wang, S. M. Zakeeruddin, J.-E. Moser and M. Grätzel, *J. Phys. Chem. B*, 2003, **107**, 13280.

17 Y.-S. Jung, B. Yoo, M. K. Lim, S. Y. Lee and K.-J. Kim, *Electrochim. Acta*, 2009, **54**, 6286.

18 (*a*) H. Choi, C. Baik, S. O. Kang, J. Ko, M.-S. Kang, M. K. Nazeeruddin and M. Grätzel, *Angew. Chem., Int. Ed.*, 2008, **47**, 327; (*b*) S. Kim, D. Kim, H. Choi, M.-S. Kang, K. Song, S. O. Kang and J. Ko, *Chem. Commun.*, 2008, 4951.

19 Y. Liu, A. Hagfeldt, X. R. Xiao and S. E. Lindquist, *Sol. Energy Mater. Sol. Cells*, 1998, **55**, 3267.

20 B. Macht, M. Turrion, A. Barkschat, P. Salvador, K. Ellmer and H. Tributch, *Sol. Energy Mater. Sol. Cells*, 2002, **73**, 163.

21 K. Hara, K. Miyamoto, Y. Abe and M. Yanagida, *J. Phys. Chem. B*, 2005, **109**, 23776.

22 A. Hauch and A. Georg, *Electrochim. Acta*, 2001, **46**, 3457–3466.

23 X. Fang, T. Ma, G. Guan, M. Akiyama, T. Kida and E. Abe, *J. Electroanal. Chem.*, 2004, **570**, 257–263.

24 T. N. Murakami, S. Ito, Q. Wang, M. K. Nazeeruddin, T. Bessho, I. Cesar, P. Liska, R. Humphry-Baker, P. Comte, P. Pechy and M. Grätzel, *J. Electrochem. Soc.*, 2006, **153**, A2255–A2261.

25 H. Bönnemann, G. Khelashvili, S. Behrens, A. Hinsch, K. Skupien and E. Dinjus, *J. Cluster Sci.*, 2007, **18**, 141–155.

26 M. Liberatore, F. Decker, L. Burtone, V. Zardetto, T. M. Brown, A. Reale and A. Di Carlo, *J. Appl. Electrochem.*, 2009, **39**, 2291–2295.

27 G. Wang, W. Xing and S. Zhou, *J. Power Sources*, 2009, **194**, 568–573.

28 S. Sakaguchi, H. Ueki, T. Kato, T. Tado, R. Shiratuchi, W. Takashima, K. Kaneto and S. Hayase, *J. Photochem. Photobiol., A*, 2004, **164**, 117.

29 A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, *Chem. Rev.*, 2010, **110**, 6595–6663.

30 S. Mikoshiba, S. Murai, H. Sumino, T. Kabo, D. Kosigi and S. Hayase, *Curr. Appl. Phys.*, 2005, **5**, 152.

31 H. Zhao, X. Yin, H. Li, Y. Lin and Y.-X. Weng, *Chin. Phys. Lett.*, 2007, **24**, 3272.

32 Y. Liu, A. Hagfeldt, X.-R. Xiao and S.-E. Lindquist, *Sol. Energy Mater. Sol. Cells*, 1998, **55**, 267.

33 J. J. Peterson, M. Werre, Y. C. Simon, E. B. Coughlin and K. R. Carter, *Macromolecules*, 2009, **42**, 8594–8598.

34 J. D. Prugh, G. D. Hartman, P. J. Mallorga, B. M. McKeever, S. R. Michelson, M. A. Murcko, H. Schwam, R. L. Smith and J. M. Sondey, *J. Med. Chem.*, 1991, **34**, 1805–1818.

35 M. Jessing, M. Brandt, K. J. Jensen, J. B. Christensen and U. Boas, *J. Org. Chem.*, 2006, **71**, 6734–6741.

36 S. Nakade, T. Kanzaki, Y. Wada and S. Yanagida, *Langmuir*, 2005, **21**, 10803.

37 M.-S. Kang, K.-S. Ahn, J.-W. Lee and Y. S. Kang, *J. Photochem. Photobiol., A*, 2008, **195**, 198.

38 K.-S. Ahn, M.-S. Kang, J.-K. Lee, B.-C. Shin and J.-W. Lee, *Appl. Phys. Lett.*, 2006, **89**, 013103.

39 K.-S. Ahn, M.-S. Kang, J.-W. Lee and Y. S. Kang, *J. Appl. Phys.*, 2007, **101**, 084312.