Molecular engineering of panchromatic unsymmetrical squaraines for dye-sensitized solar cell applications

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Three unsymmetrical squaraine dyes **JK-64**, **JK-65**, and **JK-64Hx**, containing a bulky spirobifluorene or hexyloxyphenyl unit are designed and synthesized. These sensitizers, when anchored onto a TiO_2 surface, exhibit decreased aggregation as well as enhanced unidirectional flow of electrons. Under standard global AM 1.5 solar conditions, an optimized **JK-64Hx** sensitized cell gave a short-circuit photocurrent density (J_{sc}) of 12.82 mA cm^{-2}, an open-circuit voltage (V_{oc}) of 0.54 V and a fill factor (*ff*) of 0.75, corresponding to an overall conversion efficiency (η) of 5.20%.

Introduction

Global warming and depletion of fossil fuels have led to a greater interest in clean renewable energy sources in recent years. Dye-sensitized solar cells (DSSCs) have attracted significant attention as an alternative to conventional solar cells due to their low cost and high efficiency.[1] In these cells, the sensitizer is one of the key components for high power-conversion efficiency. Several polypyridyl ruthenium complexes have achieved power conversion efficiencies of over 11% in standard air mass 1.5 sunlight.[2] In spite of this, the main drawback of these sensitizers is the lack of absorption in the red region of the visible spectrum, and also low molar extinction coefficients. An essential requirement for efficient conversion of solar energy is the good spectral match of the sensitizer absorption to the emission spectrum of solar radiation. In this regard, the ruthenium sensitizers' spectral response in the lower energy regions are not sufficient.

To further improve the efficiency of this system, an enhanced spectral response of the sensitizer in the lower energies is required. Amongst the different classes of red absorbing chromophores, squaraine dyes have received considerable attention in recent years because of their intense absorption in the red/near-IR regions.[3] Several groups[4] have utilized squaraines as sensitizers in DSSCs and obtained rather low conversion efficiencies. A major factor responsible for the lower power conversion efficiency of the squaraine-based solar cell is absorption; although very efficient (extinction coefficients often exceeding 300 000 mol cm^{-1} l^{-1}), it is limited to one relatively narrow band located in the aforementioned 600–800 nm region, and there is a lack of unidirectional flow of electrons on excitation of squaraines. The recent report on a photovoltaic device using the unsymmetrical squaraine dyes exhibited an improved high efficiency through a unidirectional flow of electrons on excitation of unsymmetrical squaraine dyes.[5] Here, we report a structural engineering strategy of squaraine sensitizers where functionalization of the squaraine core with an electron donor, and withdrawing units enabling the appearance of a second, high energy band in the absorption spectrum. Fig. 1 shows the structures of the new squaraines (**JK-64**, **JK-65**, and **JK-64Hx**), which contain spirobifluorenyl amino or hexyloxyphenyl amino units. These donor groups not only induce high energy bands but also suppress aggregation.[6–9]

Results and discussion

The three unsymmetrical squaraine dyes **JK-64**, **JK-64Hx** and **JK-65** were synthesized by the stepwise synthetic protocol (Scheme 1). The (*E*)-3-(4-(bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino)styryl)-4-isopropoxycyclobut-3-ene-1,2-dione **1** was synthesized by the condensation reaction of 4-(bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino)benzaldehyde with 3-isopropoxy-4-methylcyclobut-3-ene-1,2-dione. The hydrolysis of **1** with HCl afforded hydroxycyclobut-3-ene-1,2-dione derivative **3**. The condensation of **3** with 5-carboxy-2,3,3-trimethyl-1-octyl-3*H*-indolium was

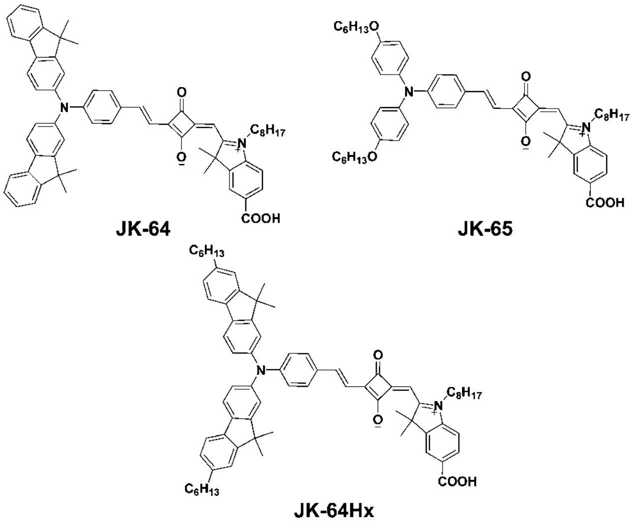

Fig. 1 Structure of the dyes of **JK-64**, **JK-65** and **JK-64Hx**.

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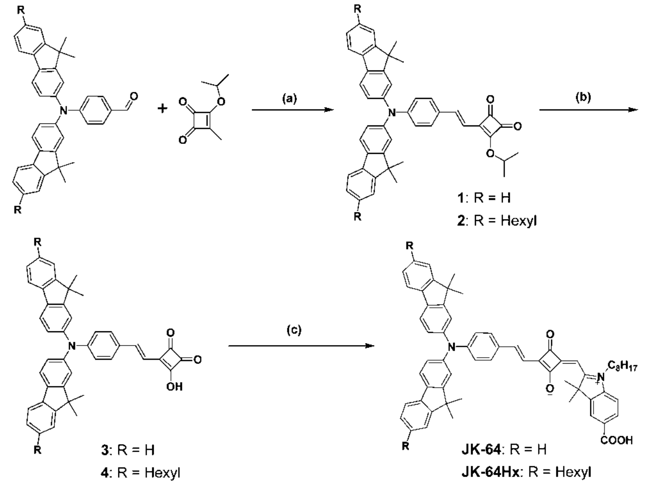

Scheme 1 Synthesis of **JK-64** and **JK-64Hx**. Reagents: (a) NEt_3, Ac_2O, THF; (b) 12 N HCl, dioxane; (c) 5-carboxy-2,3,3-trimethyl-1-octyl-3*H*-indolium, *n*-BuOH/Bz.

readily performed to give **JK-64**. The sensitizers **JK-64Hx** and **JK-65** were similarly synthesized using the **JK-64** procedure.

The UV-vis and emission spectra of **JK-64**, **JK-64Hx** and **JK-65** in ethanol are shown in Fig. 2, together with the corresponding dyes adsorbed on TiO_2 film. The absorption spectrum of **JK-64** exhibits two absorptions at 470 and 656 nm, which can be assigned as the vinylene squaraine moiety **F** and **JK-64**, respectively (Fig. 3). To support the assignment, we measured the UV-vis spectrum of compound **3**. The absorption spectrum of **3** exhibits λ_{abs} at 446 nm, which is in agreement with the high energy absorption band of **JK-64**. In order to study the intramolecular energy transfer from the unit **F** to the acceptor unit, we measured the emission spectra by exciting the sensitizer **JK-64** in EtOH at 460 nm, which exhibited two different emission bands with λ_{em} at 544 and 798 nm (Fig. 4). The emission band at 544 nm is relatively weak and the other strong emission band at 798 nm is similar to that excited at 640 nm. The emission band at 544 nm may be assigned as the vinylene squaraine moiety **F**.

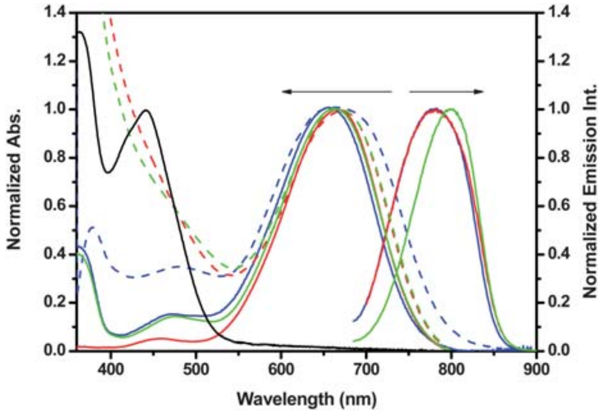

Fig. 2 Absorption and emission spectra of **JK-64** (blue solid line), **JK-65** (red solid line), **JK-64Hx** (green solid line) and **3** (black solid line) in EtOH, and absorption spectra of **JK-64** (blue dash line), **JK-65** (red dash line) and **JK-64Hx** (green dash line) on TiO_2 film. The emission spectra were obtained using the same solution by exciting at 640, 660 and 662 nm for **JK-64** (blue solid line), **JK-65** (red solid line) and **JK-64Hx** (green solid line) at 298 K, respectively.

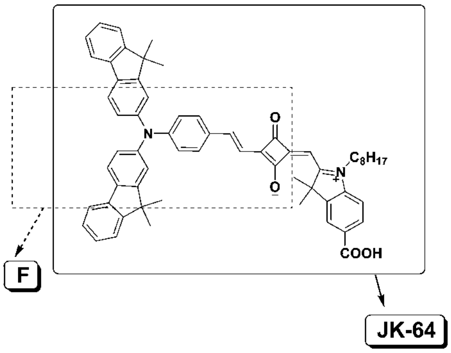

Fig. 3 The schematic drawing of the two donor systems of **JK-64**.

To validate the assignment, the emission spectrum of compound **3** was measured by exciting at 460 nm, and it exhibited an emission band at 598 nm that is in agreement with that of unit **F**. Under the same conditions, the emission band at 798 nm obtained by exciting **JK-64** at 460 nm is relatively weak. The observation of the band indicates the intramolecular energy transfer from the **F** unit to the acceptor unit. It is noted that the apparent peak at 544 nm can be attributable to a partial energy transfer, due to the incomplete overlap of the emission spectrum of unit **3** with the absorption spectrum of **JK-64**. Such a Förster energy transfer[10] was observed in triphenylamine organic dye.[11] When the **JK-64** dye was adsorbed on a TiO_2 electrode, a slight red shift from 656 to 668 nm was found due to the *J*-aggregation on the TiO_2 electrode.[12] The absorption spectra of the three dyes on the TiO_2 electrode are broad. Such a broadening of the absorption spectra is attributable to an interaction between the dyes and TiO_2.

To evaluate the feasibility of electron transfer from the excited-state of the dye to the conduction band of the TiO_2 electrode, cyclic voltammetry was employed to determine the oxidation potential of the sensitizers (Table 1). The redox potentials of the three dyes were measured in MeCN using 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. The cyclic voltammograms of the three sensitizers adsorbed on a TiO_2 film show quasi-reversible couples. The oxidation potentials of **JK-64**, **JK-65**, and **JK-64Hx** were measured to be 0.98, 0.93, and 0.95 V *versus* NHE, respectively. The high

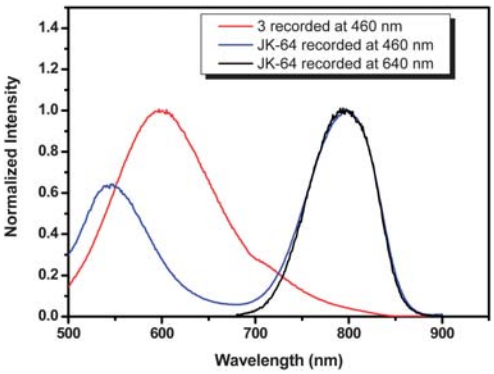

Fig. 4 The normalized emission spectra of **3** and **JK-64** in EtOH solutions.

Table 1 Optical, redox and DSSC performance parameters of dyes

Dye	$\lambda_{abs}{}^{a}$/nm (ε/M^{-1} cm^{-1})	E_{redox}/V^{b}	E_{0-0}/V^{c}	E_{LUMO}/V^{d}	J_{sc}/mA cm^{-2}	V_{oc}/V	FF	η (%)^{e}
JK-64	470 (6620), 656 (43 000)	0.98	1.72	−0.74	13.60	0.493	70.13	4.70
JK-65	460 (2800), 667 (54 000)	0.93	1.71	−0.77	7.50	0.500	71.91	2.70
JK-64Hx	472 (7860), 662 (55 000)	0.95	1.68	−0.73	12.17	0.509	79.36	4.91
JK-64/Al$_2$O$_3$					13.85	0.510	70.77	5.00
JK-65/Al$_2$O$_3$					7.28	0.516	79.21	2.98
JK-64HX/Al$_2$O$_3$					12.82	0.542	74.87	5.20

[a] Absorption spectra were measured in THF solution. [b] Redox potential of dyes on TiO$_2$ were measured in CH$_3$CN with 0.1 M (n-C$_4$H$_9$)$_4$NPF$_6$ with a scan rate of 50 mV s^{-1} (*vs.* NHE). [c] E_{0-0} was determined from intersection of absorption and emission spectra in ethanol. [d] E_{LUMO} was calculated by $E_{ox} - E_{0-0}$. [e] Performances of DSSCs were measured with 0.18 cm^2 working area. Electrolyte: 0.6 M DMPImI, 0.05 M I$_2$, and 0.1 M LiI in acetonitrile.

oxidation potential of these three sensitizers relative to that of the triiodide/iodide couple (+0.5 V) could lead to fast dye regeneration.[13] The reduction potentials of the three sensitizers calculated from the oxidation potentials and the E_{0-0} determined from the intersection of the absorption and emission spectra are listed in Table 1. The excited-state oxidation potential (E^{*}_{OX}) of the dyes (**JK-64**: −0.74 V *vs.* NHE; **JK-65**: −0.77 V *vs.* NHE; **JK-64Hx**: −0.73 V *vs.* NHE) are more negative than the conduction band level of TiO$_2$ at −0.5 V *vs.* NHE. Therefore, the downhill energy offset of the LUMO in the three dyes ensures enough of a driving force for electron injection.

In order to evaluate the geometrical configuration and electron distributions, molecular orbital calculations of **JK-64** were performed with the TD-DFT on B3LYP/3-21G* (Fig. 5). The calculation reveals that the HOMO−1 is located with the squaraine unit, while the HOMO is delocalized over the π-conjugated system through the phenyl amino group. The LUMO of **JK-64** contains the delocalized π* framework, with a sizable electron density distribution arising from the carboxylic group. On the other hand, LUMO+1 is localized within the carboxylic group. As light excitation should be associated with vectorial electron flow from the HOMO to the LUMO or LUMO+1 for efficient electron transfer, the examination of HOMO–LUMO in unsymmetrical sensitizer **JK-64** illustrates that HOMO–LUMO excitation moves the electron distribution from the phenyl amino unit to the anchoring group, resulting in efficient directional electron transfer. A relatively high efficiency in unsymmetrical **JK-64** and **JK-64Hx** can be explained as a good match of vectorial electron flow from the HOMO to the LUMO.

Fig. 6 shows the photocurrent action spectra of the **JK-64-**, **JK-65-** and **JK-64Hx**-sensitized cells using an acetonitrile-based electrolyte. In order to suppress the aggregation of sensitizers, 3α,7α-dihydroxy-5β-cholic acid (CDCA) has been used as co-adsorbent. The cell was fabricated using a double layer of 20 μm thick TiO$_2$ (20 nm) and 4 μm thick scattering TiO$_2$ (400 nm). The incident photon-to-current conversion efficiency (IPCE) of **JK-64** shows a plateau of over 50% from 450 to 740 nm, reaching the maximum of 65% at 650 nm. The high energy hump is due to the intramolecular energy transfer of unit **F**. Under standard global AM 1.5 solar conditions, the **JK-64**-sensitized cell gave a short-circuit photocurrent density (J_{sc}) of 13.60 mA cm^{-2}, an open-circuit voltage (V_{oc}) of 0.49 V, and a fill factor of 0.70, corresponding to η of 4.70% (Fig. 5). The overlap integral of the IPCE with the standard global AM 1.5 solar emission spectrum

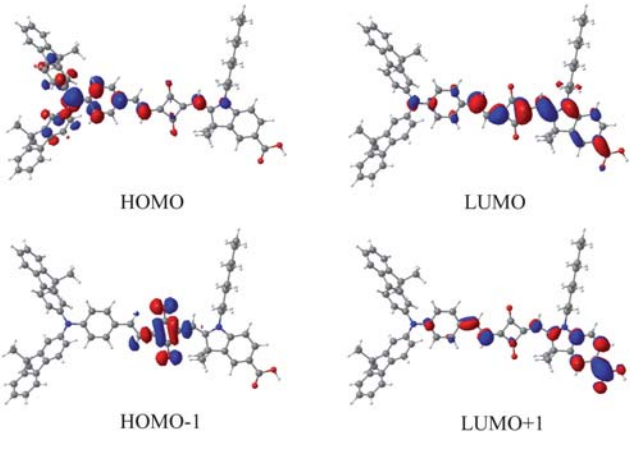

Fig. 5 Isodensity surface plots of the HOMO, HOMO−1, LUMO and LUMO+1 of **JK-64**.

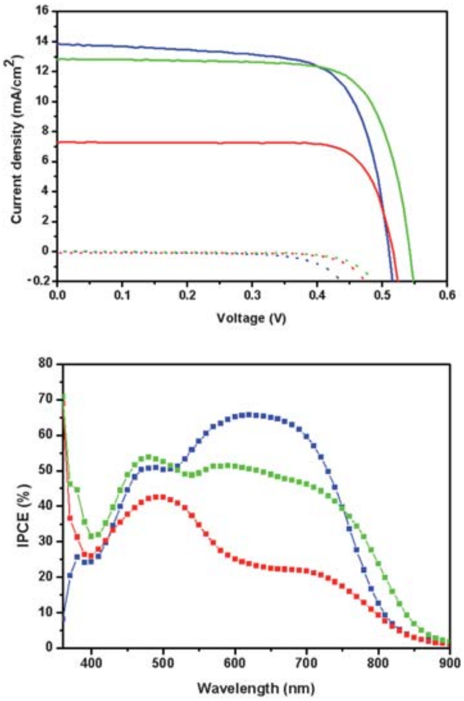

Fig. 6 *J–V* curve (top) and IPCE spectra (bottom) of **JK-64** (blue line), **JK-65** (red line) and **JK-64Hx** (green line). Dark current–bias potential relationship is shown as dotted curves.

yields a calculated photocurrent of 13.35 mA cm^{-2}, which is in good agreement with the measured photocurrent density. The low efficiency of the **JK-64**-sensitized solar cell is due to low open-circuit potential, which needs to be increased. Kroeze *et al.*[14] reported that alkyl substitution of the dye improved the V_{oc}, due to the blocking effect of the charge recombination between I_3^- and electrons injected in the nanocrystalline electrode. Therefore, we have incorporated long alkyl chain into the **JK-64**. The **JK-64Hx**-sensitized cell gave a J_{sc} value of 12.17 mA cm^{-2}, a V_{oc} of 0.51 V, and an *ff* of 0.79, corresponding to an η value of 4.91%. From these results (Table 1), we have observed that the η value of the **JK-64Hx**-based cell is higher than that of the **JK-64**-based cell. Of particular importance is the 20 mV increase in V_{oc} of the **JK-64Hx**-based cell. Therefore, the V_{oc} variation indicates that the charge recombination was suppressed by the blocking effect, due to the combination of the hexyl unit and CDCA. To further increase the efficiency, the interface charge recombination losses need to be minimized. The general strategy to reduce such losses involves the coating of inorganic barrier layers between the sensitizer and electrolyte.[15] The Al_2O_3 layer was coated by the hydrolysis of aluminium isopropoxide on a **JK-64Hx**-sensitized TiO_2 film. Under standard global air mass 1.5 solar conditions, the **JK-64Hx**/Al_2O_3-sensitized cell gave a J_{sc} value of 12.82 mA cm^{-2}, a V_{oc} of 0.54 V, and an *ff* of 0.75, corresponding to an η of 5.20%. The efficiency of 5.20% is one of the highest ever reported for DSSCs based on the squaraine sensitizer.[5a,b] The data demonstrate that the molecular modification of squaraines results in a panchromatic response. On the other hand, the **JK-65**-sensitized cell gave a J_{sc} of 7.5 mA cm^{-2}, V_{oc} of 0.50 V, and a fill factor of 0.72, corresponding to η of 2.70%. The power conversion efficiency of **JK-65** is quite low relative to those of **JK-64** and **JK-64Hx** (Table 1). To clarify the above result, we have measured the amount of dyes adsorbed on the TiO_2 film. The adsorbed amounts of 2.02×10^{-6} mmol cm^{-2} for **JK-64**, 2.18×10^{-6} mmol cm^{-2} for **JK-65**, and 1.94×10^{-6} mmol cm^{-2} for **JK-64Hx** were measured. Therefore, the high efficiencies of **JK-64** and **JK-64Hx** relative to that of **JK-65** may be due to their broad and red-shifted absorption bands on TiO_2 film. In order to evaluate the effect of the high molar extinction coefficient of the three squaraine sensitizers on photovoltaic performance, we have fabricated solar cells using the TiO_2 film consisting of a different thickness of transparent layer and a 4 μm scattering layer. The photocurrent increased with the thickness of TiO_2 film. On the other hand, the photovoltage slightly decreased with the increase of thickness. In this cell, the power conversion efficiency slightly increased with the increase of thickness. Further optimization was achieved by using various concentrations of CDCA as a co-adsorbent. Table 2 shows the photovoltaic performance of **JK-64** sensitized cells with different concentrations of CDCA. For the 10 + 4 μm TiO_2 film, the cell using a CDCA concentration of 10 mM showed a photocurrent density (J_{sc}) of 9.89 mA cm^{-2}, an open circuit voltage (V_{oc}) of 0.46 V and a fill factor (*ff*) of 0.64, corresponding to η of 3.20%, When the concentration of CDCA was increased from 10 to 40 mM, the open circuit voltage rose from 0.46 to 0.49 V. The photocurrent was 10.21 mA cm^{-2} and the fill factor attained 0.69, corresponding to η of 3.86%. Substantial increase of η is due to reduced aggregation of sensitizers.

Table 2 Current–voltage characteristics obtained with various TiO_2 (20 nm) thickness layers with fixed thickness (4 μm) of TiO_2 (400 nm) and CDCA concentration

TiO_2 thickness/μm	CDCA concentration/mM	J_{sc}/mA cm^{-2}	V_{oc}/V	FF (%)	η (%)
3 + 4	10	6.58	0.478	67.8	2.30
3 + 4	40	6.57	0.510	68.5	2.47
7 + 4	10	6.89	0.463	67.8	2.28
7 + 4	40	7.85	0.506	67.8	2.83
10 + 4	10	9.89	0.463	64.3	3.20
10 + 4	40	10.21	0.494	69.0	3.86
20 + 4	40	13.60	0.493	70.1	4.70

Fig. 7 shows the AC impedance spectra of the DSSCs measured under illumination. Under illumination at open circuit condition (100 mW cm^{-2}), the radius of the intermediate-frequency semicircle in the Nyquist plot decreased in the order of **JK-65** (42.2 Ω) > **JK-64Hx** (37.9 Ω) > **JK-64** (26.9 Ω), indicating the improved electron generation and transport. These results reflect well the trends observed in the short circuit photocurrent density.

In conclusion, we have designed and synthesized three unsymmetrical squaraine dyes containing *N*,*N*-bis(9,9-dimethylfluoren-2-yl)amino or bis(hexyloxyphenyl)amino units, which show an extra new absorption band in the high energy region resulting in a panchromatic response, as well as enhanced unidirectional flow of electrons. We believe that the development of highly efficient unsymmetrical squaraine dyes with low band gap and high absorption coefficient is possible through sophisticated modification, and work on these is now in progress.

Experimental

All reactions were carried out under an argon atmosphere. Solvents were distilled from appropriate reagents. All reagents were purchased from Sigma-Aldrich. 4-(Bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino)benzaldehyde,[7c] *N*-(4-bromophenyl)-7-hexyl-*N*-(7-hexyl-9,9-dimethyl-9*H*-fluoren-2-yl)-9,9-dimethyl-9*H*-fluoren-2-amine,[6c] 4-(bis(4-(hexyloxy)phenyl)amino)benzaldehyde,[16] 3-isopropoxy-4-methylcyclobut-3-ene-1,2-dione[17] and 5-carboxy-2,3,3-trimethyl-1-octyl-3*H*-indolium[7a] were synthesized

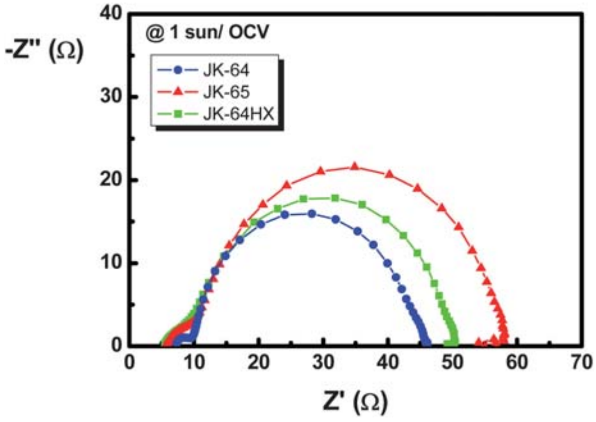

Fig. 7 Electrochemical impedance spectra measured under illumination (1 sun) for the cells with different dye adsorption conditions (*i.e.* **JK-64** (blue), **JK-65** (red), **JK-64Hx** (green)).

using modified procedures of previous references. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer. Elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA 1108 analyzer. Mass spectra were recorded on a JEOL JMS-SX102A instrument. The absorption and photoluminescence spectra were recorded on a Perkin-Elmer Lambda 2S UV-visible spectrometer and a Perkin LS fluorescence spectrometer, respectively.

Cyclic voltammetry was carried out with a BAS 100B (Bioanalytical Systems, Inc.). A three-electrode system was used and consisted of a gold disk, working electrode, and a platinum wire electrode. The redox potential of dyes on TiO_2 were measured in CH_3CN with 0.1 M $(n\text{-}C_4H_9)_4N\text{-}PF_6$ a scan rate of 50 mV s^{-1} (*vs.* Fc/Fc$^+$).

The ac impedance measurements were carried out under illumination (1 sun) using an impedance analyzer (PARSTAT 2273, USA).

Photoelectrochemical data were measured using a 1000 W xenon light source (Oriel, 91193) that was focused to give 1000 W m^{-2}, the equivalent of one sun at Air Mass (AM) 1.5, at the surface of the test cell. The light intensity was adjusted with a Si solar cell that was double-checked with an NREL-calibrated Si solar cell (PV Measurement Inc.). The applied potential and measured cell current were measured using a Keithley model 2400 digital source meter. The current–voltage characteristics of the cell under these conditions were determined by biasing the cell externally and measuring the generated photocurrent. This process was fully automated using Wavemetrics software.

(*E*)-3-(4-(Bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino)styryl)-4-isopropoxycyclobut-3-ene-1,2-dione (1)

To a mixture of 4-(bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino)-benzaldehyde (1.91 g, 3.77 mmol), 3-isopropoxy-4-methyl-cyclobut-3-ene-1,2-dione (0.58 g, 3.77 mmol) and triethylamine (0.554 ml, 3.96 mmol) in THF (5 ml) was added dropwise acetic anhydride (0.369 ml, 3.96 mmol). The mixture was heated to 70 °C for 12 h, diluted with H_2O, and extracted with AcOEt. The collected organic layer was washed with water (50 mL), dried over magnesium sulfate, and filtered. The solvent was removed under reduced pressure. The pure product **1** was obtained by silica gel chromatography (eluent EA : Hx = 1 : 5, R_f 0.4) to afford **1** in 51% yield. Mp: 194 °C. ^1H NMR ($CDCl_3$): δ 7.83 (d, J = 16.0 Hz, 1H), 7.66 (t, J = 7.8 Hz, 2H), 7.64 (d, J = 8.7 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 7.5 Hz, 2H), 7.31 (t, J = 7.8 Hz, 2H), 7.25 (d, J = 7.5 Hz, 2H), 7.24 (s, 2H), 7.15 (d, J = 8.7 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 6.84 (d, J = 16.0 Hz, 1H), 5.51 (sept, J = 6.3 Hz, 1H), 1.50 (d, J = 6.3 Hz, 6H), 1.42 (s, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 193.6, 192.2, 191.4, 174.4, 155.4, 153.7, 150.4, 146.2, 142.2, 138.7, 135.6, 129.6, 128.3, 127.2, 127.0, 124.3, 122.7, 121.8, 120.9, 119.8, 119.7, 110.3, 79.3, 47.0, 27.1, 22.8. MS: *m*/*z* 641 [M$^+$]. Anal. Calc. for $C_{45}H_{39}NO_3$: C, 84.21; H, 6.12. Found: C, 84.01; H, 5.92.

(*E*)-3-(4-(Bis(7-hexyl-9,9-dimethyl-9*H*-fluoren-2-yl)amino)styryl)-4-isopropoxycyclobut-3-ene-1,2-dione (2)

n-BuLi (1.03 ml, 1.6 M solution in hexane) was added into *N*-(4-bromophenyl)-7-hexyl-*N*-(7-hexyl-9,9-dimethyl-9*H*-fluoren-2-yl)-9,9-dimethyl-9*H*-fluoren-2-amine (1 g, 1.37 mmol) solution in dry THF at −78 °C under argon. After 1 h, DMF (1 ml) was added dropwise at −78 °C under argon. The mixture was stirred at 20 °C for 1 h, and quenched with H_2O (30 mL), and extracted with EtOAc three times. The organic layer was separated and dried in $MgSO_4$. The solvent was removed *in vacuo*. The pure product 4-(bis(7-hexyl-9,9-dimethyl-9*H*-fluoren-2-yl)amino)benzaldehyde was obtained by chromatographic work-up (eluent MC : Hx = 1 : 3, R_f 0.4). **2** was synthesized by a similar procedure to **1**, except that 4-(bis(7-hexyl-9,9-dimethyl-9*H*-fluoren-2-yl)amino)-benzaldehyde (0.91 g, 1.350 mmol) was used in place of 4-(bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino)benzaldehyde. Yield: 20%. Mp: 191 °C. ^1H NMR ($CDCl_3$): δ 7.82 (d, J = 15.9 Hz, 1H), 7.59 (d, J = 8.7 Hz, 2H), 7.56 (d, J = 7.5 Hz, 2H), 7.45 (d, J = 8.7 Hz, 2H), 7.22 (d, J = 8.7 Hz, 2H), 7.20 (s, 2H), 7.14 (d, J = 7.5 Hz, 2H), 7.12 (s, 2H), 7.11 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 15.9 Hz, 1H), 5.49 (sept, J = 6.9 Hz, 1H), 2.66 (t, J = 8.1 Hz, 4H), 1.64 (m, 4H), 1.47 (s, 12H), 1.40 (m, 4H), 1.25 (m, 8H), 0.88 (t, J = 6.9 Hz, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 193.1, 192.2, 191.4, 175.9, 155.3, 153.9, 150.6, 145.7, 142.3, 142.2, 136.3, 135.8, 129.6, 128.0, 127.4, 124.4, 122.7, 121.4, 120.5, 119.9, 119.5, 110.1, 79.3, 46.7, 36.4, 31.8, 31.1, 29.2, 27.2, 23.0, 22.7, 14.2. MS: *m*/*z* 809 [M$^+$]. Anal. Calc. for $C_{57}H_{63}NO_3$: C, 84.51; H, 7.84. Found: C, 84.21; H, 7.65.

(*E*)-3-(4-(Bis(4-(hexyloxy)phenyl)amino)styryl)-4-isopropoxy-cyclobut-3-ene-1,2-dione (5)

5 was synthesized by a similar procedure to **1**, except that 4-(bis(4-(hexyloxy)phenyl)amino)benzaldehyde (2.16 g, 4.56 mmol) was used instead of 4-(bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino)benzaldehyde. Yield: 20%. Mp: 189 °C. ^1H NMR ($CDCl_3$): 7.60 (d, 1H, J = 16.2 Hz), 7.32 (d, 2H, J = 8.4 Hz), 6.95 (d, 4H, J = 8.7 Hz), 6.90 (d, 1H, J = 16.2 Hz), 6.84 (d, 4H, J = 9.0 Hz), 6.77 (d, 2H, J = 8.07 Hz), 5.38 (septet, 1H, J = 6.0 Hz) 3.87 (t, 4H, J = 6.6 Hz), 1.72 (m, 4H), 1.47–1.42 (m, 10H), 1.31 (m, 8H), 0.90 (t, 6H, J = 6.9 Hz). ^{13}C NMR (CD_3OD): 208.4, 199.5, 178.4, 157.5, 151.1, 142.4, 138.7, 137.2, 129.7, 129.4, 128.2, 120.4, 116.5, 112.9, 79.1, 68.8, 31.5, 30.4, 27.9, 23.7, 22.8, 14.6. Anal. Calc. for $C_{38}H_{45}NO_5$: C, 76.61; H, 7.61. Found: C, 76.76; H, 7.53.

(*E*)-3-(4-(Bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino)styryl)-4-hydroxycyclobut-3-ene-1,2-dione (3)

A solution of **1** (0.24 g, 0.374 mmol) in dioxane (10 ml) and concd HCl (2.5 ml) was refluxed for 4 h. The mixture was evaporated *in vacuo* to give **3**. The pure product **3** was obtained by silica gel chromatography (eluent Mc : MeOH = 10 : 1, R_f 0.4) to afford **3** in 90% yield. Mp: 187 °C. ^1H NMR ($CDCl_3$): δ 7.91 (d, J = 16.0 Hz, 1H), 7.66 (t, J = 7.8 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.6 Hz, 1H s, 2H), 7.41 (d, J = 7.6 Hz, 2H), 7.31 (t, J = 7.8 Hz, 2H), 7.25 (d, J = 7.6 Hz, 2H), 7.24 (s, 2H), 7.15 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 16.0 Hz, 1H), 1.42 (s, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 194.3, 192.2, 191.2, 176.5, 155.4, 153.7, 150.7, 146.1, 143.5, 138.7, 135.7, 129.9, 127.2, 127.0, 125.0, 124.4, 122.7, 121.7, 120.9, 120.5, 119.9, 110.5, 47.0, 27.1.

MS: *m*/*z* 599 [M$^+$]. Anal. Calc. for $C_{42}H_{33}NO_3$: C, 84.11; H, 5.55. Found: C, 83.91; H, 5.34.

(*E*)-3-(4-(Bis(7-hexyl-9,9-dimethyl-9*H*-fluoren-2-yl)amino)styryl)-4-hydroxycyclobut-3-ene-1,2-dione (4)

4 was synthesized by a similar procedure to **3**, except that **2** (0.2 g, 0.246 mmol) was used instead of **1**. Yield: 90%. Mp: 193 °C. ^{1}H NMR ($CDCl_3$): δ 7.88 (d, $J = 16.2$ Hz, 1H), 7.59 (d, $J = 8.7$ Hz, 2H), 7.56 (d, $J = 7.5$ Hz, 2H), 7.47 (d, $J = 7.8$ Hz, 2H), 7.22 (d, $J = 8.7$ Hz, 2H), 7.20 (s, 2H), 7.14 (d, $J = 7.8$ Hz, 2H), 7.12 (s, 2H), 7.11 (d, $J = 7.5$ Hz, 2H), 6.92 (d, $J = 16.2$ Hz, 1H), 2.66 (t, $J = 8.1$ Hz, 4H), 1.64 (m, 4H), 1.43 (s, 12H), 1.40 (m, 4H), 1.25 (m, 8H), 0.88 (t, $J = 6.9$ Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 193.1, 192.5, 191.4, 175.5, 155.1, 153.3, 150.2, 146.7, 142.3, 142.1, 137.3, 136.8, 129.3, 128.0, 127.4, 124.2, 122.4, 121.6, 120.5, 119.9, 119.3, 111.7, 46.8, 36.4, 31.8, 31.1, 29.2, 27.2, 22.7, 14.2. MS: *m*/*z* 767 [M$^+$]. Anal. Calc. for $C_{54}H_{57}NO_3$: C, 84.45; H, 7.48. Found: C, 84.13; H, 7.25.

(*E*)-3-(4-(Bis(4-(hexyloxy)phenyl)amino)styryl)-4-hydroxycyclobut-3-ene-1,2-dione (6)

6 was synthesized by a similar procedure to **3**, except that **5** (0.2 g, 0.33 mmol) was used instead of **1**. Yield: 90%. Mp: 191 °C. ^{1}H NMR ($CDCl_3$): 7.57 (d, 1H, $J = 16.2$ Hz), 7.31 (d, 2H, $J = 8.4$ Hz), 6.97 (d, 4H, $J = 8.7$ Hz), 6.90 (d, 1H, $J = 16.2$ Hz), 6.82 (d, 4H, $J = 9.0$ Hz), 6.76 (d, 2H, $J = 8.07$ Hz), 3.90 (t, 4H, $J = 6.6$ Hz), 1.74 (m, 4H), 1.46 (m, 4H), 1.34 (m, 8H), 0.92 (t, 6H, $J = 6.9$ Hz). ^{13}C NMR (CD_3OD): 209.4, 200.5, 179.4, 157.5, 151.1, 141.3, 136.8, 129.7, 129.4, 128.2, 120.4, 116.5, 112.9, 69.3, 32.8, 30.4, 26.9, 23.7, 14.4. Anal. Calc. for $C_{36}H_{41}NO_5$: C, 76.16; H, 7.28. Found: C, 76.20; H, 7.26.

(*E*)-2-((*E*)-4-(Bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino)styryl)-4-((5-carboxy-3,3-dimethyl-1-octyl-3*H*-indolium-2-yl) methylene)-3-oxocyclobut-1-enolate (JK-64)

0.19 g (0.317 mmol) of **3** and 0.14 g (0.317 mmol) of 5-carboxy-2,3,3-trimethyl-1-octyl-3*H*-indolium were dissolved in a mixture of 50 ml benzene and 50 ml *n*-butanol. The mixture was refluxed with a Dean–Stark apparatus for 18 h. The solvent was partly removed until the product precipitated. The pure product **JK-64** was obtained by silica gel chromatography (eluent Mc : MeOH = 10 : 1, R_f 0.4) to afford **JK-64** in 81% yield. Mp: 197 °C. ^{1}H NMR (DMSO-d_6): δ 8.21 (s, 1H), 8.06 (d, $J = 7.2$ Hz, 1H), 7.78 (t, $J = 7.8$ Hz, 2H), 7.76 (d, $J = 8.7$ Hz, 2H), 7.65 (m, 1H), 7.61 (d, $J = 7.6$ Hz, 2H), 7.49 (d, $J = 8.7$ Hz, 2H), 7.33 (s, 2H), 7.30 (t, $J = 7.8$ Hz, 2H), 7.29 (d, $J = 7.8$ Hz, 2H), 7.28 (m, 1H), 7.11 (d, $J = 7.6$ Hz, 2H), 7.02 (d, $J = 7.2$ Hz, 1H), 6.99 (d, $J = 7.8$ Hz, 2H), 6.24 (s, 1H), 4.37 (m, 2H), 1.95 (m, 2H), 1.75 (s, 6H), 1.47 (m, 2H), 1.36 (s, 12H), 1.35–1.30 (m, 4H), 1.28 (m, 4H), 0.88 (t, $J = 6.9$ Hz, 3H). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 184.7, 184.3, 179.1, 176.5, 175.0, 172.3, 169.9, 167.0, 155.4, 155.0, 153.3, 150.7, 146.1, 145.7, 143.5, 138.7, 138.1, 135.7, 135.0, 131.6, 129.9, 128.7, 127.1, 125.0, 124.4, 122.7, 121.7, 120.9, 120.5, 110.5, 54.9, 46.5, 44.8, 33.7, 31.1, 28.5, 27.3, 26.7, 26.0, 22.0, 20.8, 13.9. MS: *m*/*z* 896 [M$^+$]. Anal. Calc. for $C_{62}H_{60}N_2O_4$: C, 83.00; H, 6.74. Found: C, 82.81; H, 6.54.

(*E*)-2-((*E*)-4-(Bis(7-hexyl-9,9-dimethyl-9*H*-fluoren-2-yl)-amino)styryl)-4-((5-carboxy-3,3-dimethyl-1-octyl-3*H*-indolium-2-yl)methylene)-3-oxocyclobut-1-enolate (JK-64Hx)

JK-64Hx was synthesized by a similar procedure to **JK-64**, except that **4** (200 mg, 0.26 mmol) was used instead of **3**. Yield: 85%. Mp: 193 °C. ^{1}H NMR (DMSO-d_6): δ 8.21 (s, 1H), 8.06 (d, $J = 7.2$ Hz, 1H), 7.85 (d, $J = 16.0$ Hz, 1H), 7.69 (d, $J = 8.5$ Hz, 2H), 7.66 (d, $J = 7.7$ Hz, 2H), 7.49 (d, $J = 7.8$ Hz, 2H), 7.22 (d, $J = 8.5$ Hz, 2H), 7.23 (s, 2H), 7.16 (d, $J = 7.8$ Hz, 2H), 7.16 (s, 2H), 7.11 (d, $J = 7.7$ Hz, 2H), 6.92 (d, $J = 16.0$ Hz, 1H), 6.99 (d, $J = 7.2$ Hz, 1H), 6.24 (s, 1H), 4.37 (m, 2H), 2.66 (t, $J = 8.1$ Hz, 4H), 1.95 (m, 2H), 1.75 (s, 6H), 1.64 (m, 4H), 1.47 (m, 6H), 1.36 (s, 12H), 1.35–1.30 (m, 4H), 1.28 (m, 12H), 0.88 (t, $J = 6.9$ Hz, 3H), 0.87 (t, $J = 6.9$ Hz, 6H). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 191.0, 183.0, 176.9, 177.5, 172.3, 169.7, 166.8, 154.6, 153.5, 149.1, 145.2, 144.6, 142.9, 141.4, 137.6, 135.7, 135.2, 130.2, 129.7, 129.2, 128.6, 127.2, 124.2, 123.6, 122.6, 120.9, 119.6, 118.5, 112.9, 60.2, 46.5, 44.8, 35.5, 33.7, 31.8, 31.4, 31.1, 29.2, 28.5, 27.3, 26.7, 26.0, 22.7, 22.0, 20.8, 14.2, 13.9. MS: *m*/*z* 1064 [M$^+$]. Anal. Calc. for $C_{74}H_{84}N_2O_4$: C, 83.42; H, 7.95. Found: C, 82.91; H, 7.52.

(*E*)-2-((*E*)-4-(Bis(4-(hexyloxy)phenyl)amino)styryl)-4-((5-carboxy-3,3-dimethyl-1-octyl-3*H*-indolium-2-yl)methyl-ene)-3-oxocyclobut-1-enolate (JK-65)

JK-65 was synthesized by a similar procedure to **JK-64**, except that **6** (110 mg, 0.19 mmol) was used instead of **3**. Yield: 85%. Mp: 189 °C. ^{1}H NMR ($CDCl_3$): 8.20 (d, 1H, $J = 8.1$ Hz), 8.17 (s, 1H), 8.08 (d, 1H, $J = 15.6$ Hz), 7.43 (d, 2H, $J = 8.4$ Hz), 7.20 (d, 1H, $J = 8.4$ Hz), 7.07 (m, 5H), 6.86 (d, 4H, $J = 8.1$ Hz), 6.82 (d, 2H, $J = 8.4$ Hz), 6.3 (s, 1H), 4.21 (t, 2H, $J = 6.0$ Hz), 3.94 (t, 4H, $J = 6.3$ Hz), 1.85 (s, 6H), 1.75 (m, 6H), 1.46 – 1.23 (m, 22H), 0.88 (m, 9H). ^{13}C NMR ($CDCl_3$): 189.7, 185.5, 181.3, 178.1, 176.4, 169.4, 156.8, 151.5, 145.6, 143.2, 139.1, 130.6, 130.3, 128.4, 128.1, 127.8, 127.6, 118.7, 118.2, 115.9, 115.6, 115.4, 68.4, 50.8, 31.7, 29.4, 29.2, 27.7, 27.0, 26.7, 26.4, 26.2, 25.9, 22.8, 22.7, 14.3, 14.2, 14.1. Anal. Calc. for $C_{56}H_{68}N_2O_6$: C, 77.74; H, 7.92. Found: C, 77.68; H, 7.90.

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