

Enhanced photovoltaic performance and long-term stability of quasi-solid-state dye-sensitized solar cells *via* molecular engineering†

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Organic dyes with long alkyl chains have been synthesized and demonstrated to be highly efficient sensitizers for liquid and quasi-solid-state solar cells, giving power conversion efficiencies of 8.31–8.39% and 7.03–7.31% under AM 1.5 G irradiation, respectively.

Increasing energy demands and global warming urge the development of cheap and accessible renewable energy sources. Dye-sensitized solar cells (DSSCs) are one of the promising candidates for an alternative form of solar cell.¹ Several ruthenium polypyridyl complexes have achieved power conversion efficiencies of 10–11%;² however, achieving of long-term stability has become a major challenge. The introduction of a long alkyl chain to the ruthenium polypyridyl unit has resulted in thermal and long-term stability.³ Some organic dyes have also been utilized as promising photosensitizers, and several groups have obtained impressive efficiencies in the range of 7–9%.⁴ However, the long-term stability of organic dye-based devices raises a serious problem. Another disadvantage of organic dyes in DSSCs is the formation of aggregates on the TiO₂ surface and the facile charge recombination that is responsible for their low photoconversion efficiency. Therefore, the molecular engineering of organic dyes with high efficiencies, and which meet the stability criteria, is required. Our strategy towards obtaining high photovoltaic performance from organic DSSCs is based upon the structural modification of the dye to minimize charge recombination. It is well documented that the introduction of long alkyl chains to amphiphilic ruthenium or organic dyes exerts an immense effect on their photovoltaic performance, and increases their stability due to the large distance between the TiO₂ and the hole conductors.⁵

Recently, successful molecular engineering was achieved by incorporating long alkyl units into the organic framework, which not only increased the photoconversion efficiency but also exhibited excellent stability under light soaking at 60 °C. Herein, we report the synthesis, photovoltaic properties and

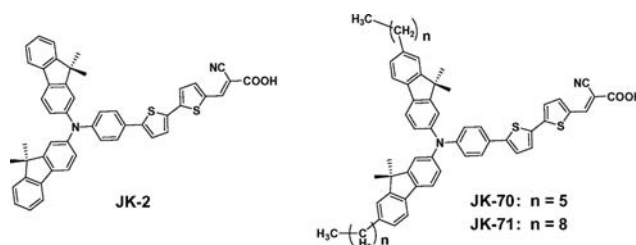


Fig. 1 The structures of JK-2, JK-70 and JK-71.

stability tests of two organic sensitizers, coded as JK-70 and JK-71 (Fig. 1).

The organic sensitizers, JK-70 and JK-71, were readily synthesized in eight steps (see the ESI†). The visible absorption spectrum of JK-70 exhibited two bands centered at 448 ($\epsilon = 42\,520\text{ M}^{-1}\text{ cm}^{-1}$) and 367 ($\epsilon = 51\,580\text{ M}^{-1}\text{ cm}^{-1}$) nm, which were assigned to the π – π^* transitions of the conjugated molecule (Fig. 2). Under similar conditions, the JK-71 sensitizer exhibited absorption bands at 447 ($\epsilon = 36\,630\text{ M}^{-1}\text{ cm}^{-1}$) and 368 ($\epsilon = 45\,090\text{ M}^{-1}\text{ cm}^{-1}$) nm. Excitation of the low energy π – π^* transition of JK-70 and JK-71 resulted in strong emissions centered at 583 and 608 nm, respectively. The excitation transition energy (E_{0-0}) of JK-70 and JK-71 was calculated to be 2.39 and 2.37 eV, respectively. The excited-state oxidation potentials (E^*_{ox}) of the dyes (JK-70: -1.35 V and JK-71: -1.31 V vs. the normal hydrogen electrode (NHE)) were much more negative with respect to the conduction band edge of TiO₂, providing the thermodynamic driving force for electron injection.

Molecular orbital calculations illustrated that the HOMO of both sensitizers was delocalized over the fluorenylamino unit,

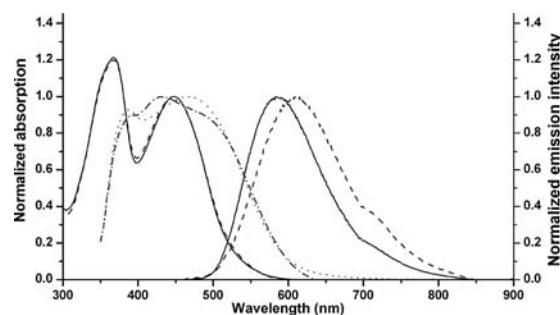


Fig. 2 The absorption and emission spectra of JK-70 (—) and JK-71 (--) in THF, and the absorption spectra of JK-70 (···) and JK-71 (-·-) absorbed on a TiO₂ film.

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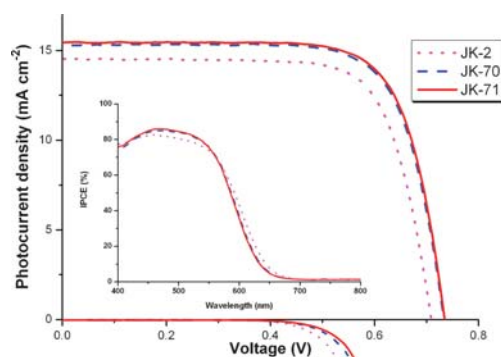


Fig. 3 A photocurrent–voltage curve obtained with a DSSC-based **JK-70** (---), **JK-71** (—) and **JK-2** (···) under AM 1.5 radiation (100 mW cm^{-2}).

arising from the nitrogen lone pair, and that the LUMO was delocalized over the thiophene and cyanoacrylic groups (see the ESI†). Examination of the HOMO and LUMO of these dyes indicated that HOMO–LUMO excitation moved the electron distribution from the triphenylamine moiety to the cyanoacrylic acid moiety, and that photoinduced electron transfer from the dye to the TiO_2 electrode could efficiently occur through the HOMO–LUMO transition.

The inset in Fig. 3 shows the photocurrent action spectra for DSSCs based on **JK-70** and **JK-71**, using an acetonitrile-based electrolyte composed of 0.6 M 3-hexyl-1,2-dimethyl-imidazolium iodide, 0.04 M I_2 , 0.025 M LiI, 0.05 M guanidinium thiocyanate and 0.28 M 4-*tert*-butylpyridine. The incident photon-to-current conversion efficiency (IPCE) of **JK-71** showed a plateau of over 80% from 430 to 560 nm, reaching a maximum of 83% at 483 nm. The photovoltaic performances of the **JK-70**- and **JK-71**-sensitized cells are shown in Table 1. Under standard global AM 1.5 solar conditions, the **JK-71**-sensitized cell gave a short circuit photocurrent density (J_{sc}) of 15.43 mA cm^{-2} , an open circuit voltage (V_{oc}) of 0.74 V and a fill factor (ff) of 0.74, corresponding to an overall conversion efficiency (η) of 8.39%. Under the same conditions, the **JK-2**-sensitized cell gave a J_{sc} value of 14.54 mA cm^{-2} , a V_{oc} of 0.70 V and an ff of 0.74, corresponding to an η value of 7.63%. From these results (Table 1), we have observed that the η values of the **JK-70**- and **JK-71**-based cells are higher than that of the **JK-2**-based cell. Of particular importance is the 40–50 mV increase in V_{oc} of the **JK-70**- and **JK-71**-based cells relative to the **JK-2**-based cell. The result can be interpreted as decreasing the electronic coupling

between the TiO_2 surface and the oxidizing hole by the introduction of long alkyl chains to the dyes, resulting in a long electron lifetime. The alkyl chains can lead to an effective spatial separation of the charges, which aids the retardation of charge recombination. The minimization of interfacial charge recombination losses in the device is also evident from the dark-current data for the cells.

Since long-term stability is a vital parameter for sustained cell operation, we substituted the liquid electrolyte with a quasi-solid-state one, because DSSCs that employ liquid electrolytes have drawbacks, such as leakage, evaporation of the solvent and corrosion of the Pt counter-electrode by the I^-/I_3^- couple. Fig. 4 shows the photovoltaic performance of **JK-2**-, **JK-70**- and **JK-71**-sensitized solar cells during long-term light soaking using a polymer gel electrolyte composed of 5 wt% poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), 0.6 M 1,2-dimethyl-3-propyl-imidazolium iodide (DMPII), 0.1 M I_2 and 0.5 M *N*-methyl-benzimidazole (NMBI) in 3-methoxypropionitrile (MPN). The **JK-71**-sensitized cell yielded a remarkably high conversion efficiency of 7.31%. To the best of our knowledge, this is the highest efficiency ever reported for DSSCs based on organic sensitizers. After 1000 h of light soaking at 60°C , the initial efficiency of 7.31% in **JK-71** decreased to 6.21%. On the other hand, the efficiency of **JK-2** decreased from 6.31 to

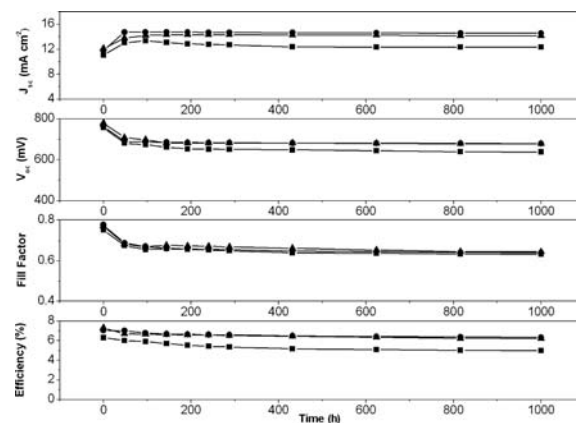


Fig. 4 Evolution of the solar cell parameters with **JK-2** (■), **JK-70** (●) and **JK-71** (▲) during visible light soaking (AM 1.5G, 100 mW cm^{-2}) at 60°C . A 420 nm cut-off filter was placed on the cell surface during illumination. Quasi-solid gel electrolyte: 5 wt% PVDF-HFP, 0.6 M DMPII, 0.1 M I_2 and 0.5 M NMBI in MPN.

Table 1 The optical, redox and DSSC performance parameters of **JK-2**, **JK-70** and **JK-71**

Dye	$\lambda_{\text{abs}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{ cm}^{-1}$) ^a	$\lambda_{\text{em}}/\text{nm}$ ^a	E_{ox}/V ($\Delta E_{\text{p}}/\text{V}$) ^b	E_{0-0}/V ^c	E_{LUMO}/V ^d	$J_{\text{sc}}/\text{mA cm}^{-2}$	V_{oc}/V	ff	η (%) ^e
JK-70	367 (51 580) 448 (42 520)	583	1.04 (0.17)	2.39	−1.35	15.29	0.73	0.74	8.31
JK-71	368 (45 090) 447 (37 630)	608	1.06 (0.15)	2.37	−1.31	15.43	0.74	0.74	8.39
JK-2	364 (44 000) 452 (39 000)	670	1.04 (0.15)	2.34	−1.30	14.54	0.70	0.74	7.63

^a The absorption spectra were measured in ethanol solution. ^b The oxidation potential of dyes on TiO_2 were measured in CH_3CN with 0.1 M (*n*- C_4H_9)₄NPF₆, with a scan rate of 50 mV s^{-1} (vs. NHE). ^c E_{0-0} was determined from the intersection of the absorption and emission spectra in ethanol. ^d E_{LUMO} was calculated as $E_{\text{ox}} - E_{0-0}$. ^e The performances of the DSSCs were measured with a 0.18 cm^2 working area, employing a mask.

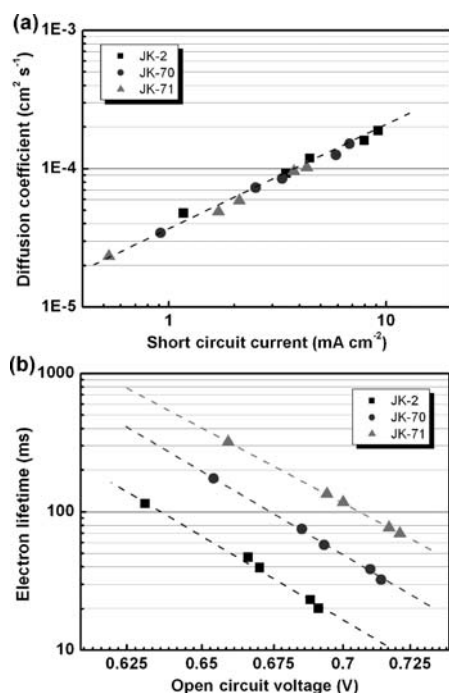


Fig. 5 The electron diffusion coefficients (a) and lifetimes (b) of the electrodes containing different adsorbed dyes (i.e. **JK-2**, **JK-70** and **JK-71**).

4.99% under the same conditions. Tolerance of such a severe light-soaking stress by a DSSC with an efficiency of over 6.2% is unprecedented. Only two ruthenium polypyridyl sensitizers have resisted light-soaking stress for 1000 h while retaining an efficiency of over 6%.⁶ This is the first time that organic dye-sensitized cells with an efficiency above 6.2% using a quasi-solid-state electrolyte have passed such a light-soaking test. The enhanced long-term stability of **JK-70** and **JK-71** can be attributed to the introduction of long alkyl chains to the bis-dimethylfluorenyl amino unit, which leads to the retardation of charge recombination.

Fig. 5 shows the electron diffusion coefficient (D_e) and lifetime (τ_e) of the DSSCs when employing different dyes (i.e. **JK-2**, **JK-70** and **JK-71**) as a function of J_{sc} and V_{oc} , respectively. The D_e and τ_e values were determined by the photocurrent and photovoltage transients, induced by a stepwise change in the laser light intensity, controlled with a function generator.^{7–9} The D_e value was obtained by a time constant (τ_c), determined by fitting a decay of the photocurrent transient with $\exp(-t/\tau_c)$ and the TiO_2 film thickness (ω) using the equation $D_e = \omega^2/(2.77 \times \tau_c)$.⁷ The τ_e value was also determined by fitting a decay of the photovoltage transient with $\exp(-t/\tau_e)$.⁷ The D_e values of the photoanodes containing the adsorbed organic dyes are shown to be very similar to each other under identical J_{sc} conditions, showing similar trends to those of coumarin dyes.¹⁰ Meanwhile, the difference in the τ_e values was clearly observed among cells employing different dyes. The increasing order of τ_e values was **JK-2** < **JK-70** < **JK-71** under

identical V_{oc} conditions, demonstrating that the electron recombination process was effectively controlled by the molecular structure of the dye. The results of the electron lifetime are also consistent with those of V_{oc} shown in Table 1.

In summary, we have developed novel organic dyes incorporating long alkyl chains that achieve over 7.31% power conversion efficiency and long-term stability using a polymer gel electrolyte; such a high efficiency is very impressive. We believe that the development of highly efficient organic dyes as alternatives to ruthenium complexes is possible through sophisticated structural modifications.

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