

Highly Efficient and Thermally Stable Organic Sensitizers for Solvent-Free Dye-Sensitized Solar Cells**

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Increasing energy demands and concerns about global warming have led to a greater focus on renewable energy sources during the last years. Dye-sensitized solar cells (DSSCs) have a significant potential to be used as low-cost devices for conventional p–n junction solar cells.^[1] Several Ru^{II} polypyridyl complexes have achieved power conversion efficiencies above 11% in standard global air mass 1.5, thereby showing a good stability.^[2] Some organic dyes with interesting photophysical and electrochemical properties can be used as promising sensitizers. Recently, an impressive photovoltaic performance was obtained using organic dyes that showed efficiencies between 6 and 9%.^[3] However, organic dyes are known to be less stable than ruthenium complexes, which is probably a result of the formation of excited triplet states and unstable radicals under light irradiation. Another disadvantage of organic dyes in DSSCs is the formation of aggregates on the semiconductor surface, which leads to self-quenching and reduces electron injection into TiO₂.^[4] Therefore, engineering of organic sensitizers with an enhanced stability and a reduced tendency toward aggregation is paramount. Recently, a successful approach was introduced by incorporating a nonplanar bis-dimethylfluorenylamino moiety^[5] and a terthiophene unit^[6] into the organic framework, which not only suppresses aggregate formation but also increases the molar extinction coefficient of the organic sensitizer. Herein, we report novel organic sensitizers, coded as JK-45 and JK-46, which consist of: 1) a

tailored dimethylfluorenylamino moiety that ensures greater resistance to degradation when exposed to light and/or high temperatures, because it possesses a bipolar character that allows the formation of both stable cation and anion radicals;^[7] 2) conducting thiophene units with aliphatic chains that enhance the interface and the tolerance towards water in the electrolytes; 3) a cyanoacrylic acid moiety, which acts as acceptor and anchoring group.

The sensitizers JK-45 and JK-46 are readily synthesized in three steps, which are illustrated in Scheme 1. The Suzuki coupling of **1**^[8] and **2**^[9] with 1.2 equivalents of 2-(3',4,3''-trihexyl-2,2':5',2''-terthio-phen-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane^[10] yields **3** and **4**. The terthiophene derivatives were converted into their corresponding carbaldehydes **5** and **6** by means of a Vilsmeier–Haack reaction.^[11] The aldehydes **5** and **6**, upon reaction with cyanoacetic acid in the presence of piperidine in acetonitrile, produced the JK-45 and JK-46 dyes.

The visible absorption spectrum of JK-45 exhibits two maxima at 430 nm ($\epsilon = 34\,800\text{ M}^{-1}\text{ cm}^{-1}$) and 369 nm ($\epsilon = 60\,200\text{ M}^{-1}\text{ cm}^{-1}$), which are attributed to the $\pi\text{--}\pi^*$ transitions of the conjugated molecule. Under similar conditions, the JK-46 sensitizer exhibits absorption bands at 430 nm ($\epsilon = 29\,200\text{ M}^{-1}\text{ cm}^{-1}$) and 372 nm ($\epsilon = 35\,000\text{ M}^{-1}\text{ cm}^{-1}$; Figure 1). Their molar extinction coefficients are higher than that of the standard N719 dye ($14\,000\text{ M}^{-1}\text{ cm}^{-1}$).^[13] When JK-45 and JK-46 are excited within their $\pi\text{--}\pi^*$ bands, they exhibit a strong luminescence maximum at around 650 nm, with E_{0-0} transition energies of 2.50 and 2.35 eV, respectively. The excited-state oxidation potentials (E_{ox}^*) of the dyes (JK-45: -1.48 V and JK-46: -1.36 V , versus NHE, normal hydrogen electrode) are much more negative than the conduction-band edge of TiO₂, which is located at -0.5 V (vs. NHE), thus providing a thermodynamic driving force for efficient electron injection.

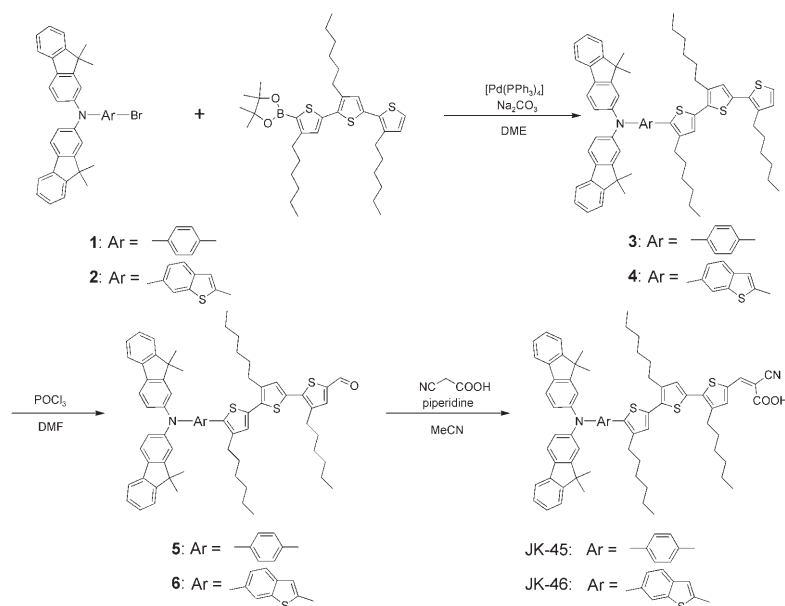
Molecular-orbital calculations illustrate that the HOMO of JK-46 is localized over the fluorenylamino unit through benzo [b]thiophene and the LUMO is localized over the cyanoacrylic unit through thiophene (Figure 2). Examination of the HOMO and LUMO of both sensitizers indicates that the HOMO–LUMO excitation moves the electron distribution from the bis(9,9-dimethylfluoren-2-yl)amino unit to the cyanoacrylic acid moiety, thus allowing an efficient photo-induced electron transfer from the dye to the TiO₂ electrode.

The photocurrent action spectra of the devices composed of JK-45 and JK-46 were obtained using an electrolyte comprising 0.6 M 1,2-dimethyl-3-*n*-propylimidazolium iodide (DMPImI), 0.1 M LiI, 0.05 M I₂, and 0.5 M 4-*tert*-butylpyridine in acetonitrile (Figure 3). The incident-photon-to-current conversion efficiency (IPCE) of JK-46 exceeds 70% in the

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Scheme 1. Synthesis of JK-45 and JK-46.

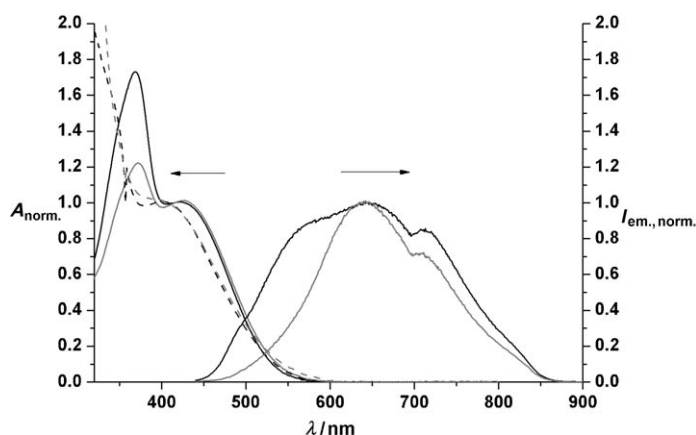


Figure 1. Absorption and emission spectra of JK-45 (black solid line) and JK-46 (gray solid line) in THF and absorption spectra of JK-45 (black dashed line) and JK-46 (gray dashed line) adsorbed on a TiO₂ film. The emission spectra were obtained using the same solution by exciting at 430 nm at 298 K.

spectral range: 400–610 nm, thereby reaching its maximum value (namely, 82%) at 482 nm. Under solar-simulated light irradiation (that is, 100 mW cm⁻²; 1.5 AM Global), the JK-46-based DSSC exhibited a short-circuit current (J_{sc}) of 17.45 mA cm⁻², an open-circuit voltage (V_{oc}) of 0.664 V, and a fill factor (FF) of 0.742, which corresponds to an overall efficiency of 8.60%. Using solvent-free ionic-liquid electrolytes composed of 0.2 M I₂, 0.5 M NMBI, and 0.1 M GuNCS in PMII/EMINCS (13:7), the JK-46 sensitizer yielded a strikingly high conversion efficiency of 7%. To the best of our knowledge, this is the highest efficiency ever reported for DSSCs based on organic sensitizers.^[14] Figure 4 shows the photovoltaic performance during long-term accelerated aging of JK-45 and JK-46 sensitized solar cells using an ionic liquid at AM 1.5 and 60 °C. The values of J_{sc} , V_{oc} , FF, and the overall

efficiency (η) were recorded over a period of 1000 h. After 1000 h of light soaking, the V_{oc} of JK-46 decreased by 77 mV, but the loss was compensated by an increase in the short-circuit current density from 11.71 to 13.44 mA cm⁻², while the fill factor was very stable. The long-term stability of the device is remarkable, because the initial efficiency of 6.82% slightly increased to 7.03% during the 1000 h light soaking test. Only three ruthenium polypyridyl sensitizers have resisted light-soaking stress for 1000 h while retaining an efficiency over 7%.^[15] This is the first time that organic-sensitized DSSCs with an efficiency above 7% have passed the light-soaking test. The enhanced stability of JK-45 and JK-46 can be attributed to the bis-dimethylfluorenyl-amino moiety coupled to the substituted hexyl chains, which prevents water-induced dye desorption from the TiO₂ surface. The JK-2 sensitizer reported in reference [7] does not contain hexyl chains and is hence less stable than JK-45 and JK-46.

To understand the electron-injection property and the change in V_{oc} of JK-45 and JK-46 more clearly, we measured the electron-diffusion coefficients and lifetimes of the photoelectrode. Figure 5 shows the electron-diffusion coefficients (D_e) and the lifetimes (τ_e) of DSSCs prepared using different dyes (namely, N719, JK-45, and JK-46) as a function of J_{sc} . The D_e values were obtained using a time constant (τ_c), which was determined by fitting the decay of the photocurrent transient to $\exp(-t/\tau_c)$ and the TiO₂ film thickness (ω) using the equation: $D_e = \omega^2/(2.77\tau_c)$. The τ value was also determined by fitting the decay of the photovoltage transient to $\exp(-t/\tau)$. The J_{sc} values in the x axis increased with an increase in the initial laser intensity controlled by ND filters with different optical densities. The D_e values of the photoanodes adsorbing the JK-45 and JK-46 dyes are very similar to those of N719 under identical short-circuit-current conditions, which demonstrates that the

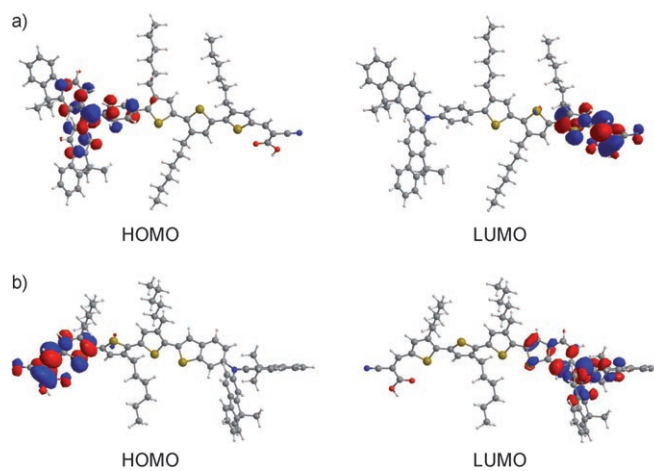


Figure 2. Isodensity surface plots of the HOMO and LUMO of a) JK-45 and b) JK-46.

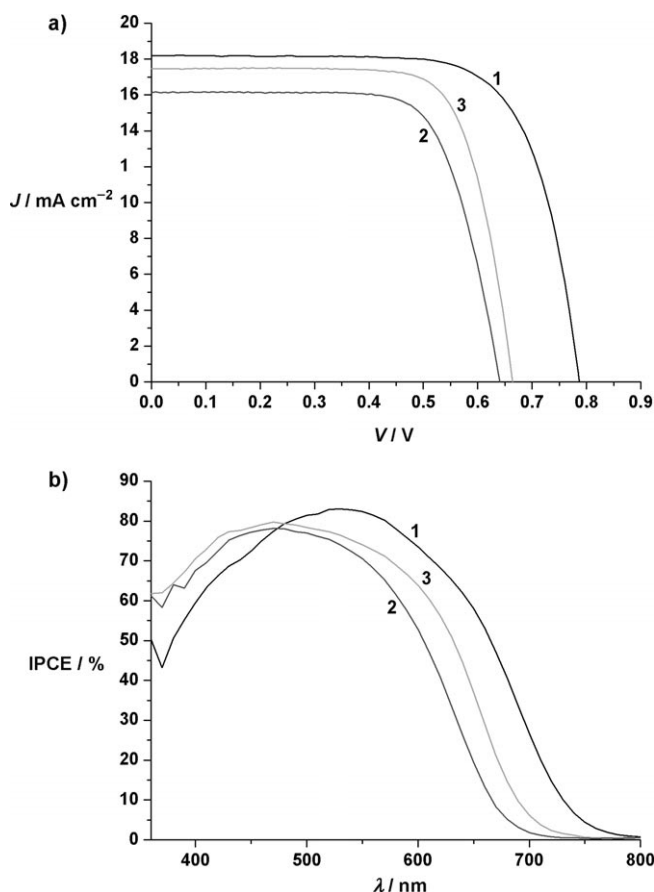


Figure 3. a) J - V curve and b) IPCE spectra of N719 (1), JK-45 (2), and JK-46 (3).

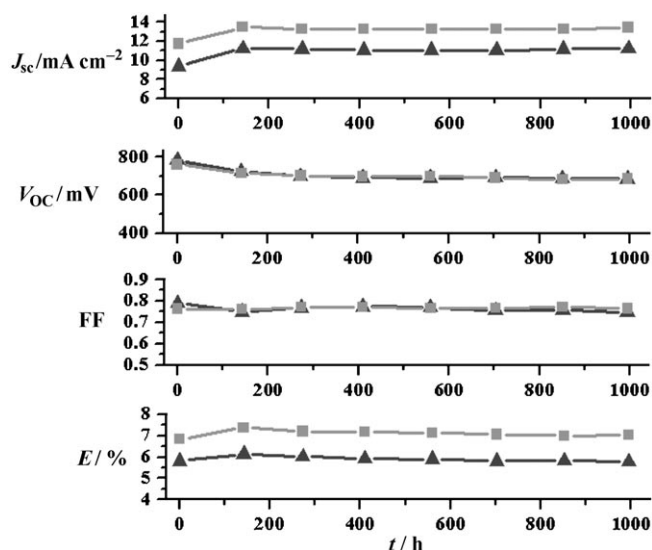


Figure 4. Evolution of the solar-cell parameters with JK-45 (▲) and JK-46 (■) during visible-light soaking (AM 1.5G, 100 mW cm^{-2}) at 60°C . A 420-nm cut-off filter was placed on the cell surface during illumination. Ionic-liquid electrolyte: 0.2 M iodine, 0.5 M NMBl, 0.1 M GuNCS in PMII/EMINCS (13/7).

electron-injection properties of JK-45 and JK-46 are good enough for application in DSSCs. Differences in the τ_e values

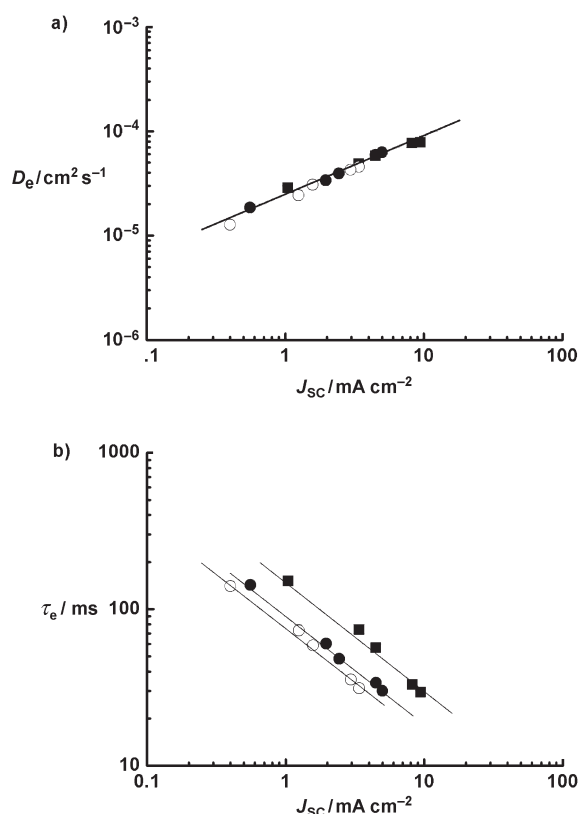


Figure 5. Electron-diffusion coefficients D_e (a) and lifetimes τ_e (b) in the photoelectrodes adsorbing different dyes. ■: N719, ○: JK-45, ●: JK-46.

were observed between the cells that used different dyes. The electron-recombination rates seem to be determined by the molecular structures of the dyes as a result of their different coverage on the TiO_2 surface. The electron lifetimes are consistent with the V_{oc} values shown in Table 1. The presence of hexyl groups in the JK-45 and JK-46 dyes increases the electron lifetime (τ) as a result of the steric hindrance, which leads to an increase in V_{oc} and the solar-to-electric conversion efficiency.^[12]

In conclusion, we designed and synthesized two novel organic dyes (namely, JK-45 and JK-46). A solar-cell device based on the sensitizer JK-46 and a volatile electrolyte yielded an overall conversion efficiency of 8.60%, whereas the conversion efficiency of a device based on the same sensitizer and a solvent-free ionic-liquid electrolyte was 7% (both devices were tested under AM 1.5 sunlight). The JK-46-based solar cells fabricated using a solvent-free ionic-liquid electrolyte exhibited an excellent stability under light soaking at 60°C for 1000 h.

Experimental Section

Electron-transport measurements: The electron-diffusion coefficients and lifetimes were measured by means of stepped light-induced transient measurements of photocurrent and voltages (SLIM-PCV).^[12] The transients were induced by a stepwise change in the laser intensity. A diode laser ($\lambda = 635 \text{ nm}$), which served as light

Table 1: Optical, redox, and DSSC performance parameters of the dyes.

Dye	$\lambda_{\text{abs}}^{[a]}$ [nm] (ϵ [$\text{M}^{-1}\text{cm}^{-1}$])	$E_{\text{redox}}^{[b]}$ [V]	$E_{0-0}^{[c]}$ [V]	$E_{\text{LUMO}}^{[d]}$ [V]	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF	$\eta^{[e]}$ [%]
JK-45	369 (60 200), 430 (34 800)	1.02	2.50	−1.48	16.13	0.641	0.718	7.42
JK-46	372 (35 000), 430 (29 200)	0.99	2.35	−1.36	17.45	0.664	0.742	8.60
N719					18.19	0.787	0.720	10.31

[a] The absorption spectra were measured in THF solution. [b] The redox potentials of the dyes on TiO_2 were measured in CH_3CN with 0.1 M $(n\text{-C}_4\text{H}_9)_4\text{NPF}_6$ at a scan rate of 50 mV s^{-1} (vs. NHE). [c] E_{0-0} was determined from the intersection of the absorption and the emission spectra in THF. [d] E_{LUMO} was calculated by $E_{\text{ox}} - E_{0-0}$. [e] The performances of the DSSCs were measured using a working area of 0.18 cm^2 . Electrolyte: 0.6 M DMPIII, 0.05 M I_2 , 0.1 M LiI, and 0.5 M *tert*-butylpyridine in acetonitrile.

source, was modulated using a function generator. The initial laser intensity was 90 mW cm^{-2} (constant) and was then attenuated (to approximately 10 mW cm^{-2}) by using an ND filter which was positioned at the front side of the fabricated samples (0.04 cm^2). For the SLIM-PCV measurements, the TiO_2 thickness was controlled at approximately $8\text{ }\mu\text{m}$. The photocurrent and photovoltage transients were monitored using a digital oscilloscope through an amplifier. A total of five points were measured to determine the electron-diffusion coefficients and lifetimes.

Dye-sensitized solar cells: Fluorine-doped tin oxide (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 and then rinsed with water and ethanol. Then, the 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 was prepared on the FTO glass plates by using a doctor blade printing TiO_2 paste (Solaronix, Ti-Nanoxide T/SP), which was 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 containing 400-nm-sized anatase particles (CCIC, PST-400C) was deposited by means of doctor blade printing, to obtain the scattering layer, 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 film was composed of a $20\text{-}\mu\text{m}$ -thick transparent layer and a $4\text{-}\mu\text{m}$ -thick scattering layer. The TiO_2 electrodes were treated again with TiCl_4 at 70°C for 30 min and sintered at 500°C for 30 min. Then, they were immersed in JK-45 and JK-46 solutions (0.3 mm in tetrahydrofuran, THF) and kept at room temperature for 24 h. FTO plates for the counter electrodes were cleaned in an ultrasonic bath in H_2O , acetone, and 0.1 M aqueous HCl, subsequently. The counter electrodes were prepared by placing a drop of an H_2PtCl_6 solution (2 mg Pt in 1 mL ethanol) on an FTO plate and heating it (at 400°C) for 15 min. The dye-adsorbed TiO_2 electrodes and the Pt counter electrodes were assembled into a sealed sandwich-type cell by heating at 80°C using a hot-melt ionomer film (Surllyn) as a spacer between the electrodes. A drop of the electrolyte solution was placed in the drilled hole of the counter electrode and was driven into the cell via vacuum backfilling. Finally, the hole was sealed using additional Surllyn and a cover glass (0.1 mm thickness).

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