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New Type of Organic Sensitizers with a Planar Amine Unit for Efficient Dye-Sensitized Solar Cells

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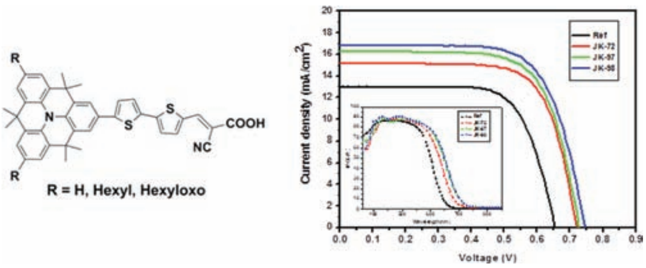
ABSTRACT



A new type of organic sensitizers incorporating a planar amine unit have been synthesized and demonstrated to be a highly efficient sensitizers, showing evidence of lateral interactions on the TiO_2 surface. Under standard global air mass 1.5 solar conditions, the JK-98 sensitized cell gave a short circuit photocurrent density (J_{sc}) of 16.78 mA cm^{-2}, an open-circuit voltage (V_{oc}) of 0.745 V, and a fill factor (*ff*) of 0.70, corresponding to an overall conversion efficiency (η) of 8.71%.

Increasing consumption of fossil fuels and their environmental pollution has led to an enhanced interest in the development of renewable energy sources.[1] Among the available technologies, dye-sensitized solar cells (DSSCs) have attracted significant attention due to their high conversion efficiencies over 11% in standard air mass 1.5 and good stability. In these cells as one of the key components ruthenium and metal-free organic dyes are used as light absorbers. The main disadvantage of ruthenium sensitizers is the relatively low molar extinction coefficient and lack of absorption in the red region. Some organic dyes have been utilized as promising sensitizers, and impressive photovoltaic performance has been reported with coumarin,[2] tetrahydroquinoline,[3] merocyanine,[4] triphenyl amine,[5] indoline,[6] phenothiazine,[7] and fluorenyl amine[8] dyes. Although organic sensitizers exhibit excellent spectral

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properties with high molar extinction coefficients, they tend to form aggregates on the semiconductor surface, resulting in self-quenching of the dye excited stated.[9] However, a controlled aggregation has been proven to enhance the photocurrent generation as a result of the larger spectral window.[10] Another disadvantage of organic sensitizers is easy interfacial recombination dynamics.[11] Many attempts have been made to design efficient organic sensitizers through structural modifications in order to prevent the aggregation of dyes and to diminish the charge recombination between the electrons on TiO_2 film and acceptors. A successful approach was achieved by incorporating a planar amine with bulky substituents,[12] which not only increased the life of the charge-separated state by the delocalization of the generated cation over a planar amine unit but also inhibited dye-aggregation. In this work, we report a novel class of organic sensitizers, consisting of a planar amine electron donor with alkyl or alkoxy chains and an electron-acceptor moiety, connected by thiophene units (Figure 1). The planar donor units show evidence of intermolecular interactions on TiO_2 films, which provide a significantly red-shifted spectral and photovoltaic response.

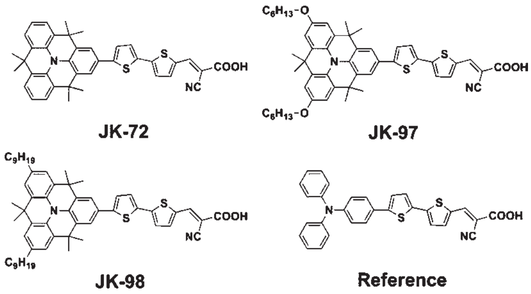

Figure 1. Structure of the dyes.

Scheme 1 illustrates the synthetic procedures of organic sensitizers (**JK-72**, **JK-97**, and **JK-98**) starting from a bridged triphenylamine(BTPHA) **1**,[13] in which three phenyl rings are bridged by a methylene unit. The key step in the synthesis of **JK-97** and **JK-98** is the alkylation and alkoxylation of **1**. The 2-bromo-6,10-dinonyl-BTPHA **4** was synthesized by bromination of **1** with NBS in CH_2Cl_2 and acylation of **2**, followed by reduction of **3** with hydrazine. The 2-bromo-6,10-dihexyloxo-BTPHA **7** was also synthesized by dibromination of **1** and dialkoxylation by salt elimination reaction of **5**, followed by bromination of **6**. The Suzuki coupling reaction[14] of **2**, **7**, and **4** with 4,4,5,5-tetramethyl-2-(5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)thiophen-2-yl)-1,3,2-dioxaborolane yielded **8**, **9**, and **10**, respectively. Subsequent cleavage of the 1,3-dioxalane protecting group in TFA gave the aldehyde **11**, **12**, and **13**. Reactions of the aldehydes with cyanoacetic acid in the presence of piperidine in CH_3CN produced the dyes **JK-72**, **JK-97**, and **JK-98**.

Scheme 1. Schematic Diagram for the Synthesis of Dyes

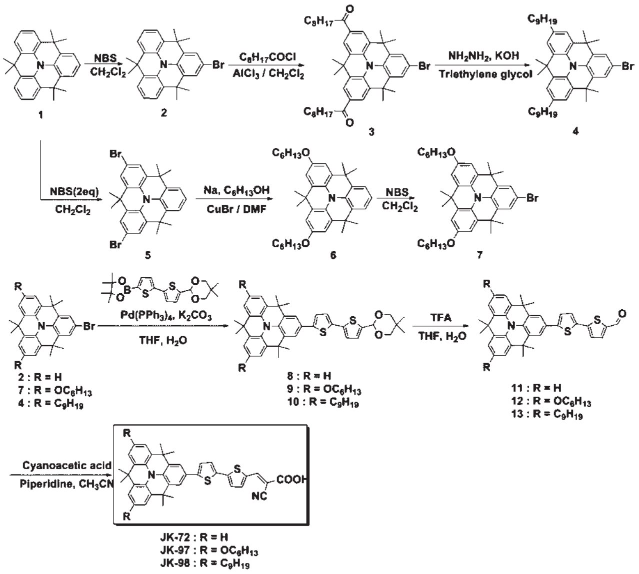

Figure 2 shows the UV−vis spectra of the four dyes measured in THF/EtOH (1:2) solution, and those absorbed on TiO_2 films are shown in the Supporting Information. The absorption spectrum of **JK-72** exhibits an intense peak at 455 nm, which is due to the $\pi-\pi^*$ transition of the conjugate molecule. Under similar conditions the **JK-98** sensitizer shows an absorption band at 463 nm that

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is red-shifted relative to that of **JK-72**. A red shift of **JK-98** relative to **JK-72** can be readily interpreted by the molecular modeling studies. The ground-state structure of **JK-98** has twist angles of 0.1° and 13.4°, respectively, between the aminophenyl and thiophene units and two thiophene moieties, indicating that the dye **JK-98** has a more planar configuration due to a small torsion angle. On the other hand, the dye **JK-72** exhibits the wide dihedral angles (3.4° and 27.8°), giving rise to a more twisted nonplanar geometry. Similar distortions have been reported for other organic sensitizers.[15]

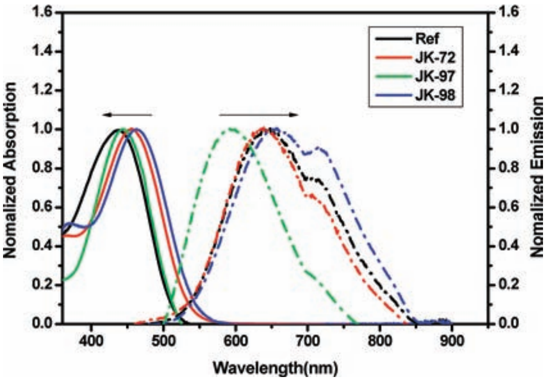

Figure 2. Absorption spectra of ref (black line), **JK-72** (red line), **JK-97** (green line), and **JK-98** (blue line) in THF/EtOH (1:2).

Cyclic voltammetry measurements were used to study the redox behavior of the three dyes in CH_3CN (Table 1). Electrochemical data for three dyes **JK-72**, **JK-97**, and **JK-98** display quasi-reversible couples. The oxidation potential of three sensitizers is around 1.00 eV, while the reduction potential of **JK-97** relative to **JK-72** and **JK-98** was shifted cathodically by 0.15 V due to the hexyl donor substitution. The electrochemical data are consistent with the UV–vis spectral data of **JK-97** with the increased HOMO–LUMO gap, which is caused by the higher LUMO level of **JK-97**.

The highest-occupied molecular orbitals (HOMOs) and lowest-unoccupied molecular orbitals (LUMOs) of **JK-72**, **JK-97**, and **JK-98** were performed with the B3LYP/3-21G*. The calculation indicates that the HOMO of three dyes is delocalized over the π-conjugated system via a bridged planar triphenylamine and the LUMO is delocalized over the cyanoacrylic unit through thiophene. From these results, we could induce that a photoinduced electron transfer from three dyes to TiO_2 electrode can efficiently occur by the HOMO–LUMO transition as shown in Figure 3.

The photovoltaic performances of the **JK-72**, **JK-97**, and **JK-98** sensitized cells are summarized in Table 1. The incident monochromatic photon-to-current conversion efficiency (IPCE) of three dyes exceeds 80% over the spectral region from 400 to 600 nm, reaching its maximum of 90% at 485 nm for **JK-72**. The band of **JK-98** tails off toward 740 nm, contributing to the broad spectral light harvesting. Under standard global air mass 1.5 solar condition, the **JK-72** sensitized cell gave a short circuit photocurrent density (J_{sc}) of 15.18 mA cm^{-2}, an open circuit voltage (V_{oc}) of 0.72 V, and a fill factor (*ff*) of 0.72, corresponding to an overall conversion efficiency (η) of 7.87%. Under the same conditions, the **JK-98** sensitized cell gave a J_{sc} of 16.78 mA cm^{-2}, a V_{oc} of 0.75 V, and a *ff* of 0.70, corresponding to an η value of 8.71%. From these results, we have observed that the η value of the **JK-98** based cell is higher than that of the **JK-72** based cell due to a large photocurrent and voltage. The large photocurrent in **JK-98** relative to **JK-72** originates from a broad and red-shifted absorption band (Figure 4). Of particular

Table 1. Optical, Redox, and DSSC Performance Parameters of Dyes

dye	λ_{abs},[a] nm (ε/M^{-1}cm^{-1})	E_{ox},[b] V	E_{0-0},[c] V	E_{LUMO},[d] V	J_{sc}, mA cm^{-2}	V_{oc}, V	*ff*	η, %
ref	438 (29420)	1.21	2.40	−1.19	13.0	0.66	0.71	6.00
JK-72	455 (20369)	1.07	2.32	−1.25	15.2	0.72	0.72	7.87
JK-97	444 (20289)	1.00	2.43	−1.43	16.3	0.73	0.70	8.28
JK-98	463 (12614)	1.01	2.29	−1.28	16.8	0.75	0.70	8.71

[a] Absorption spectra were measured in THF/EtOH(1:2). [b] Redox potential of dyes on TiO_2 were measured in CH_3CN with 0.1 M $(n\text{-}C_4H_9)_4NPF_6$ with a scan rate of 50 mV s^{-1} (vs Fc/Fc$^+$). [c] E_{0-0} was determined from intersection of absorption and emission spectra in THF/EtOH(1:2). [d] E_{LUMO} was calculated by $E_{ox} - E_{0-0}$.

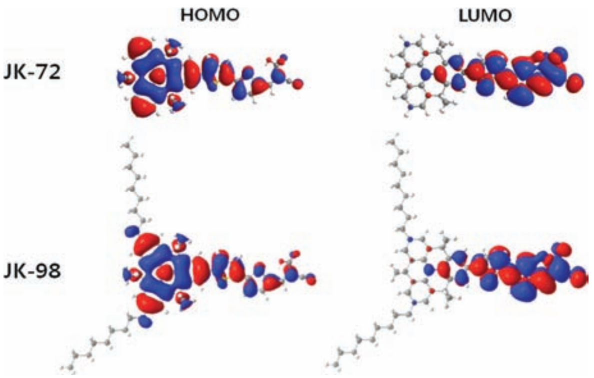

Figure 3. HOMO and LUMO surface plots for **JK-72** and **JK-98**.

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importance is the 20 mV increase in V_{oc} of the **JK-98** cell relative to the **JK-72** cell. It has been well documented that the alkyl substitution of the dye improved the V_{oc} due to the blocking effect of the charge recombination between electrons injected on the TiO_2 film and I_3^-.[16] The power conversion efficiency of **JK-72**, **JK-97**, and **JK-98** is higher than that of ref due to the *J*-aggregation by the intermolecular interaction of each three dyes.

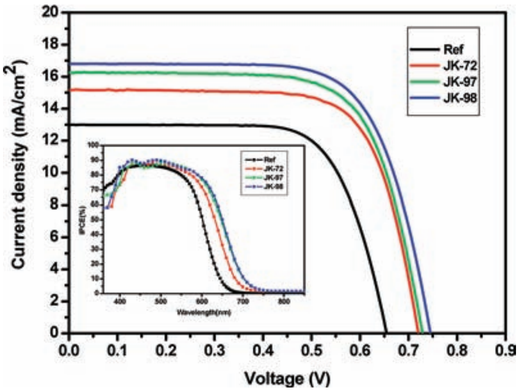

Figure 4. *J*– *V* curve and IPCE spectra of ref (black line), **JK-72** (red line), **JK-97** (green line), and **JK-98** (blue line).

Formation of tight **JK-72** aggregates has been simulated by adsorbing two dyes on adjacent Ti(IV) rows using DFT/TDDFT calculations, as shown in Figure 5. The lowest-energy configuration for **JK-72** is that having the two molecules aligned along the y direction with the π system almost perfectly stacked. The preferred configuration is one with the molecules separated by one Ti atom along the x-axis. The two dyes are separated by shortest contacts of ca. 3 Å between the donor units. Such close packing, implying a strong electronic coupling, induces a new transition of partial intermolecular transfer character in the optical absorption spectrum, which is 0.13 eV red-shifted compared to the dye in solution, consistent with the observed 0.20 eV shift.

Figure 6 shows the electron diffusion coefficients (D_e) and lifetimes (τ_c) of the DSSCs employing different dyes ref, **JK-72**, **JK-97**, and **JK-98** displayed as a function of the J_{sc} and V_{oc}, respectively. No significant differences among the D_e values were seen at the identical short-circuit current conditions, showing the similar trend to those of coumarin dyes. This result demonstrates that the D_e values are hardly affected by structural changes in the dye molecules. On the other hand, the τ_c values show a significant gap among the dyes, resulting in the increasing order **JK-98** > **JK-97** > **JK-72** > ref.[17] The different τ_c values might be caused by the different molecular structure of the dyes. Introduction of the alkyl chain on **JK-98** and **JK-97** largely enhanced both the open-circuit voltages and electron lifetimes of the DSSCs. The results of the electron lifetime are well consistent with those of the V_{oc}.

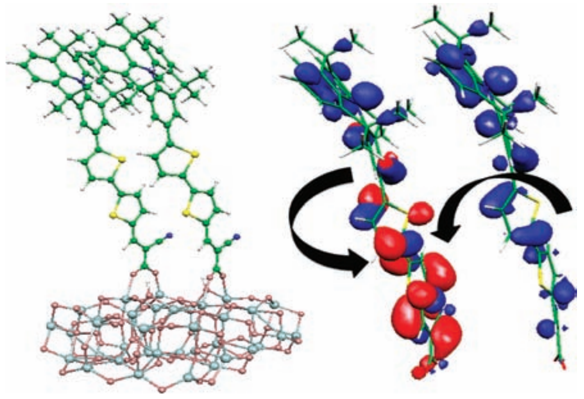

Figure 5. (Left) Optimized geometry of **JK-72** dimeric aggregate on TiO_2. Notice the dye protons transferred to the surface. (Right) Charge transfer analysis of the low-energy transition obtained for the **JK-72** dimer.

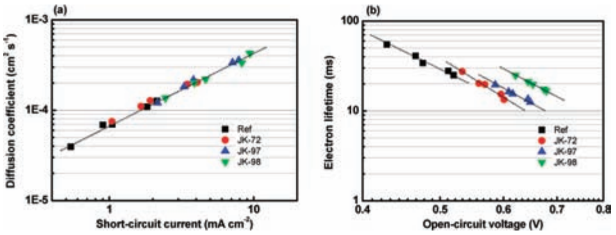

Figure 6. (a) Electron diffusion coefficients and (b) lifetime of the DSSCs employing **JK-72**, **JK-97**, and **JK-98**.

In summary, we have developed novel type of organic sensitizers incorporating a planar amine unit with long alkyl chains that achieve over 8.71% power conversion efficiency. Introduction of alkyl chains on a donor unit enhances the electron lifetime by leading to an effective spatial separation of the charges, which aids the retardation of charge recombination. We believe that the development of highly efficient organic sensitizers is possible through molecular modifications.

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Supporting Information Available. ^1H and ^{13}C NMR spectra of **JK-72**, **JK-97**, and **JK-98**. This material is available free of charge via the Internet at http://pubs.acs.org.