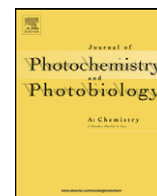




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Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Organic dyes with a novel anchoring group for dye-sensitized solar cell applications

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ARTICLE INFO

Article history:

Received 4 October 2007

Received in revised form 7 October 2008

Accepted 17 October 2008

Available online 6 November 2008

Keywords:

Anchoring group

Trialkylsilyl

Organic sensitizers

Dye-sensitized solar cells

ABSTRACT

Two novel trialkylsilyl-containing organic sensitizers (**JK-53** and **JK-54**) have been designed and synthesized. Nanocrystalline TiO₂-silica-based dye-sensitized solar cells (DSSCs) were fabricated using these dyes. Under standard global AM 1.5 solar conditions, the **JK-53**-sensitized cell gave a short-circuit photocurrent density (J_{sc}) of 6.37 mA cm⁻², an open-circuit voltage (V_{oc}) of 0.70 V, and a fill factor of 0.74. These values correspond to an overall conversion efficiency (η) of 3.31%. By comparison, the **JK-54**-sensitized cell resulted in a J_{sc} of 7.52 mA cm⁻², a V_{oc} of 0.71 V, and a fill factor of 0.75. These values give an overall conversion efficiency of 4.01%.

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1. Introduction

Increasing energy demands and concerns over global warming have led to a greater focus on renewable energy sources in recent years. Dye-sensitized solar cells (DSSCs) have significant potential as low-cost alternatives to conventional *p-n* junction solar cells [1]. In a dye-sensitized cell, the immobilization of the sensitizer on the nanocrystalline TiO₂ surface allows efficient electronic communication between the light-harvesting center and the semiconductor substrate. The immobilization of the sensitizer is achieved by attaching anchoring groups (e.g., carboxylate [2,3], phosphonate [4–8], salicylate [9], sulfonate [10,11], acetyl acetate [12], and catechol [13] groups) to the surfaces of the mesoporous TiO₂ nanoparticles. Siloxane derivatives are known to form self-assembled monolayers on substrates [14–16] and have therefore been widely used as anchoring groups in information storage applications, organic light-emitting diodes, and organic solar cells. However, they have not been used in TiO₂-based dye-sensitized solar cells because of synthetic difficulties and stability concerns in ambient conditions. Recently, Luh and coworkers reported silica-titania-organic-inorganic hybrid materials (OIHMs) for pho-

tovoltaic applications. However, these materials exhibited a low electric power conversion efficiency of 1.09% [17].

In this work, we successfully synthesized novel organic dyes, each having a triethoxysilyl unit as an anchoring group, Fig. 1 and investigated the photovoltaic performances of DSSCs employing them.

2. Experimental

2.1. General methods

All of the reactions were carried out under an argon atmosphere. The solvents used were all distilled before use. All of the reagents were purchased from Sigma-Aldrich. 5'-[N,N-bis(9,9-dimethylfluoren-2-yl)phenyl]-2,2'-bithiophene (**1**) [18,19] and 6-amino benzo[*b*]thiophene (**3**) [20–22] were synthesized via procedures similar to those described in previous reports. ¹H and ¹³C NMR spectra were recorded on a Varian Mercury 300 spectrometer. Elemental analyses were performed using a Carlo Erba Instruments CHNS-O EA 1108 analyzer. Mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer. The absorption and photoluminescence spectra were recorded on a PerkinElmer Lambda 2S UV-visible spectrometer and a Perkin LS fluorescence spectrometer, respectively. ATR-FTIR spectra were measured using a Nicolet 5700 spectrometer. These spectra were measured with the use of a Smart Orbit diamond ATR accessory. Each sample was subjected

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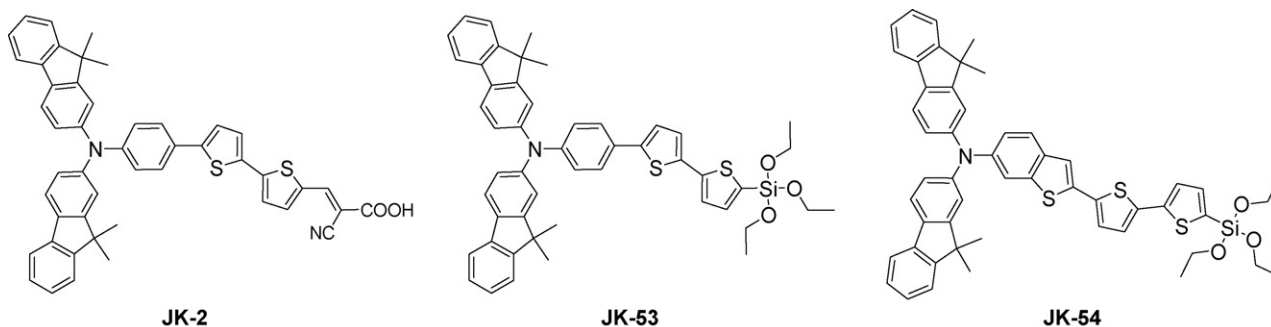


Fig. 1. Structures of the JK-2, JK-53, and JK-54 dyes.

to the same mechanical force using the instrument's pressure arm. This was done in order to establish good (and consistent) contact between each sample and the diamond and thereby improve the quality of the resulting spectra. No ATR correction was applied to the data.

2.1.1. Electrochemical measurements

Cyclic voltammetry was carried out using a BAS 100B (Bioanalytical Systems, Inc.). A three-electrode system consisting of a gold disk, a working electrode, and a platinum wire electrode was used. The redox potentials of the dyes (**JK-2**, **JK-53**, and **JK-54**) on TiO₂ were measured in CH₃CN with 0.1 M (*n*-C₄H₉)₄N-PF₆ at a scan rate of 50 mV s⁻¹ (vs. Fc/Fc⁺) (Table 1).

2.1.2. Device fabrication [23]

Fluorine-doped tin oxide (FTO) glass plates (Pilkington, 8 Ω sq⁻¹, 2.3 mm thick) were cleaned for 15 min in a detergent solution using an ultrasonic bath and then rinsed with water and ethanol. The FTO glass plates were immersed in 40 mM of TiCl₄ (aqueous) at 70 °C for 30 min and then washed with water and ethanol. A TiO₂ paste (Solaronix, Ti-Nanoxide T/SP) and a scattering layer paste (CCIC, PST-400C) were deposited on each glass plate by doctor blade printing. The resulting sintered layer was composed of a 10-μm-thick transparent layer and a 4-μm-thick scattering layer. The TiO₂ electrodes were treated with TiCl₄ again and then sintered at 500 °C for 30 min. Subsequently, the TiO₂ electrodes were immersed in a dye solution of **JK-2**, **JK-53**, or **JK-54** (0.5 mM in THF) contained in a pressure tube maintained at 80 °C in a nitrogen atmosphere in the dark. The electrodes remained under these conditions for 24 h. Counter electrodes were prepared by coating FTO plates with H₂PtCl₆ solution (2 mg of H₂PtCl₆ in 1 mL of ethanol per plate) and then heating them at 400 °C for 15 min. The dye-containing TiO₂ electrodes and Pt-counter electrodes were assembled into sealed sandwich-type cells. In each case, this was achieved by heating the two electrodes with a hot-melt polymer film (Surllyn 1702, DuPont), which served as a spacer between the electrodes. A drop of electrolyte solution (electrolyte of 0.6 M 1-hexyl-2,3-dimethyl-imidazolium iodide, 0.05 M iodine, 0.1 M LiI, and 0.5 M *tert*-butylpyridine in acetonitrile) was placed on the drilled hole in the counter electrode of the assembled cell and then driven into the cell by vacuum backfilling. Finally, the hole was sealed using Surllyn and a cover glass (0.1 mm thick).

2.1.3. Measuring the electron lifetime and diffusion coefficient

The electron transport characteristics of the photoelectrodes with different adsorbed dyes were evaluated via laser-induced photocurrent/photovoltage transient measurements using a diode laser source (Coherent, LabLaser, λ = 635 nm) modulated with a function generator. The photocurrent and photovoltage transients were induced by a stepwise change in the laser intensity, which

was controlled by a function generator. A set of ND filters with different optical densities were used to change the laser intensity. The principle and the experimental details of the measurements have been described previously by Nakade *et al.* [27].

2.1.4. Measurements of long-term stability of DSSCs

The long-term stability of the DSSCs employing the organic dyes (*i.e.* **JK-2**, **JK-53**, and **JK-54**) was evaluated by measuring the photovoltaic performances during accelerated aging of the DSSCs employing a polymer electrolyte at AM 1.5G and 60 °C (85% RH). The polymer electrolyte employed in DSSCs was prepared by dissolving polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP, 5 wt.%), 1,2-dimethyl-3-*n*-propylimidazolium iodide (DMPImI, 0.6 M), I₂ (0.1 M), and *N*-methylbenzimidazole (NMBI, 0.5 M) in 3-methoxypropionitrile (MPN) solvent. A 420-nm cut-off filter was placed on the cell surface during illumination.

2.2. Synthesis

2.2.1. 5'-[*N,N*-bis(9,9-dimethylfluoren-2-yl)phenyl]-5-iodo-2,2'-bithiophene (**2**)

n-BuLi (0.3 mL, 1.6 M solution in hexane, 0.48 mmol) was added to a stirred Et₂O solution (50 mL) of 5'-[*N,N*-bis(9,9-dimethylfluoren-2-yl)phenyl]-2,2'-bithiophene (**1**) (0.3 g, 0.47 mmol) at -78 °C under nitrogen atmosphere. The solution was warmed to 0 °C and then stirred at this temperature for 1 h. It was subsequently re-chilled to -78 °C, after which I₂ (0.13 g, 0.53 mmol) was added. The solution was slowly warmed to room temperature and then stirred overnight. H₂O and brine were then added. The product was extracted. The pure product was isolated by chromatography to afford **2** (0.26 g, 74%). MP: 237 °C. ¹H NMR (CHCl₃): δ 7.68 (d, 2H, *J* = 7.2 Hz), 7.61 (d, 2H, *J* = 8.1 Hz), 7.48 (d, 2H, *J* = 8.1 Hz), 7.40–7.24 (m, 6H), 7.20–7.07 (m, 9H), 6.85 (d, 1H, *J* = 3.9 Hz), 1.42 (s, 12H). ¹³C{¹H} NMR (CDCl₃): δ 155.3, 153.7, 147.8, 147.1, 143.8, 143.7, 139.0, 137.8, 134.6, 127.9, 127.3, 127.2, 126.7, 126.6, 125.2, 124.8, 123.8, 123.5, 122.9, 122.6, 120.8, 119.6, 119.0, 47.0, 27.2. MS: *m/z* 767. [M⁺]. Anal. Calcd. for C₄₄H₃₄IN₂: C, 68.83; H, 4.46. Found: C, 68.64; H, 4.41.

2.2.2. 5'-[*N,N*-bis(9,9-dimethylfluoren-2-yl)phenyl]-5-(triethoxysilyl)-2,2'-bithiophene (**JK-53**)

5'-[*N,N*-bis(9,9-dimethylfluoren-2-yl)phenyl]-5-iodo-2,2'-bithiophene (**2**) (0.25 g, 0.36 mmol), NEt₃ (72 mg, 0.72 mmol), and triethoxysilane (0.11 mL, 0.62 mmol) were added to a solution of Pd₂(dba)₃·CHCl₃ (5 mg, 0.005 mmol) and P(*o*-tol)₃ (0.006 g, 0.019 mmol) in NMP (10 mL). The mixture was stirred for 1 h at room temperature and then extracted with benzene. The extract was first washed three times with water to remove the NMP and

then dried over MgSO_4 . The mixture was precipitated by adding it to MeOH. The resulting yellow solid was collected and reprecipitated from Et_2O into MeOH. The yellow solid was collected and dried under vacuum to afford **JK-53** (0.23 g, 80%). MP: 135°C (dec). ^1H NMR (CHCl_3): δ 7.66 (d, 2H, $J=7.2$ Hz), 7.61 (d, 2H, $J=8.1$ Hz), 7.50 (d, 2H, $J=8.1$ Hz), 7.41–7.25 (m, 10H), 7.21–7.10 (m, 6H), 3.91 (q, 6H, $J=6.9$ Hz), 1.42 (s, 12H), 1.28 (t, 9H, $J=6.9$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 155.2, 153.6, 147.7, 147.1, 144.2, 143.6, 139.0, 137.9, 135.5, 134.5, 128.2, 128.1, 127.1, 126.7, 126.5, 125.3, 124.7, 123.9, 123.4, 123.0, 122.6, 120.8, 119.6, 118.9, 59.2, 49.9, 27.2, 18.3. MS: m/z 804 $[\text{M}^+]$. Anal. Calcd. for $\text{C}_{50}\text{H}_{49}\text{NO}_3\text{S}_2\text{Si}$: C, 74.68; H, 6.14. Found: C, 74.49; H, 6.01.

2.2.3. 6-[*N,N*-(9,9-dimethylfluoren-2-yl)amino]-2-iodo benzo[*b*]thiophene (**4**)

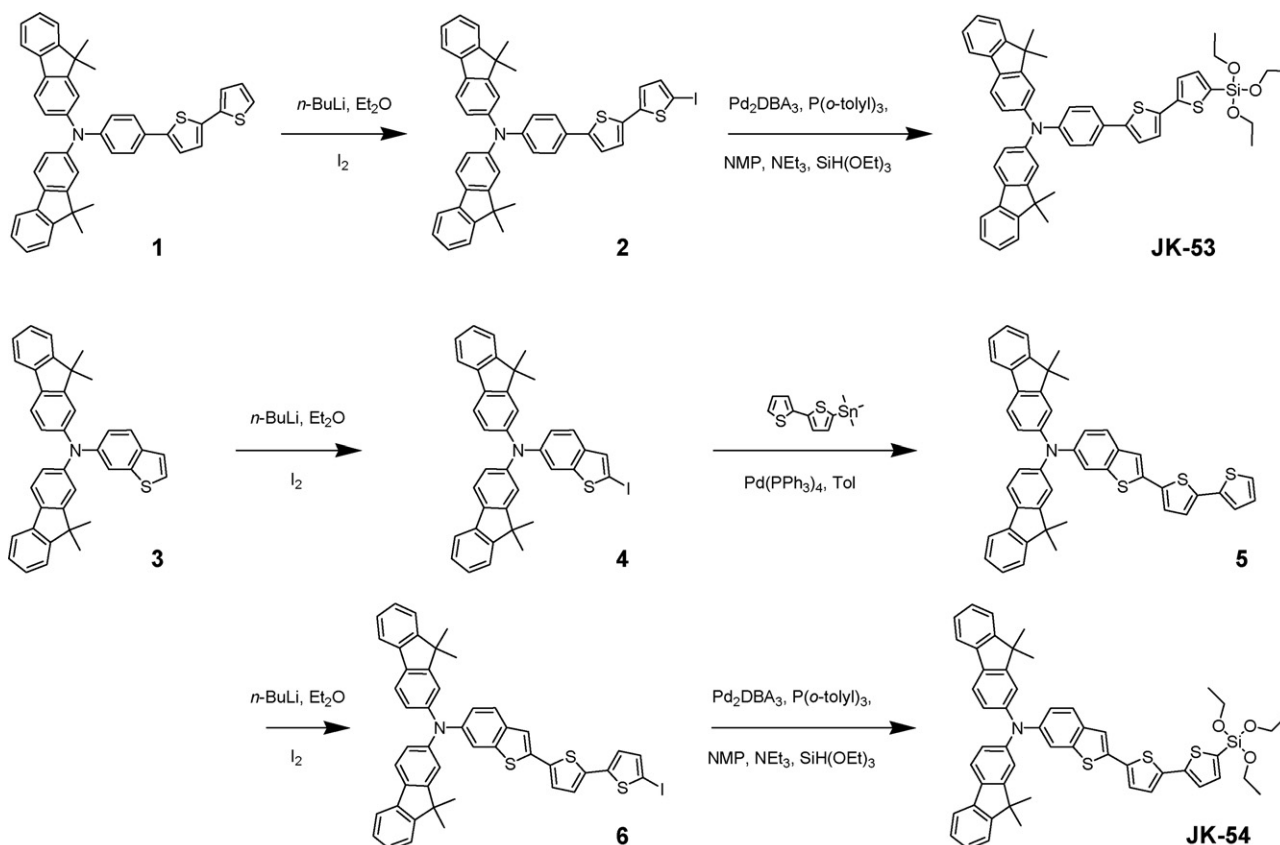
n-BuLi (0.51 mL, 1.6 M solution in hexane, 0.82 mmol) was added to a stirred Et_2O solution (50 mL) of 6-amino benzo[*b*]thiophene (**3**) (0.4 g, 0.75 mmol) at -78°C under nitrogen atmosphere. The solution was warmed to 0°C and then stirred at this temperature for 1 h. The solution was rechilled to -78°C , after which I_2 (0.21 g, 0.82 mmol) was added. The solution was slowly warmed to room temperature and then stirred overnight. H_2O and brine were then added. The product was extracted. The pure product was isolated by chromatography to afford **4** (0.39 g, 82%). MP: 198°C . ^1H NMR (CHCl_3): δ 7.64 (d, 2H, $J=7.2$ Hz), 7.59 (d, 2H, $J=8.1$ Hz), 7.58 (td, 2H, $J=8.1$ Hz, 1.8 Hz), 7.47 (s, 1H), 7.39 (d, 2H, $J=8.1$ Hz), 7.35–7.18 (m, 7H), 7.08 (dd, 2H, $J=8.1$ Hz, 1.8 Hz), 1.41 (s, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 155.2, 153.6, 147.5, 145.6, 145.3, 139.0, 136.6, 134.4, 133.5, 127.1, 126.7, 123.2, 122.7, 122.6, 122.4, 120.8, 119.6, 118.6, 116.3, 47.0, 27.2. MS: m/z 659 $[\text{M}^+]$. Anal. Calcd. for $\text{C}_{38}\text{H}_{30}\text{INS}$: C, 69.19; H, 4.58. Found: C, 59.97; H, 4.34.

2.2.4. 6-[*N,N*-bis(9,9-dimethylfluoren-2-yl)amino]-2-(2,2'-bithiophen-5-yl) benzo[*b*]thiophene (**5**)

A stirred mixture of 6-[*N,N*-(9,9-dimethylfluoren-2-yl)amino]-2-iodo benzo[*b*]thiophene (**4**) (0.3 g, 0.45 mmol), trimethyl 5-(2,2'-thiophen-2-yl)stannane (0.2 g, 0.6 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (0.025 g, 0.022 mmol) in toluene (30 mL) was refluxed for 12 h. After cooling the solution, H_2O and brine were added. The organic layer was separated and dried over MgSO_4 . The solvent was removed *in vacuo*. The product was isolated by chromatography to afford pure **5** (0.23 g, 73%). MP: 229°C . ^1H NMR (CHCl_3): δ 7.66 (d, 2H, $J=7.2$ Hz), 7.62 (td, 2H, $J=8.1$ Hz, 1.8 Hz), 7.61 (d, 2H, $J=8.1$ Hz), 7.40 (d, 2H, $J=8.1$ Hz), 7.38 (s, 1H), 7.35–7.20 (m, 8H), 7.15–7.09 (m, 5H), 7.04 (dd, 1H, $J=5.1$ Hz, 3.6 Hz), 1.42 (s, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 115.2, 153.6, 149.7, 147.5, 145.5, 143.0, 140.5, 139.1, 137.1, 136.4, 136.6, 135.7, 135.3, 134.3, 128.1, 127.6, 127.1, 126.6, 124.8, 124.5, 124.0, 123.2, 122.6, 122.8, 120.8, 119.6, 118.6, 117.3, 47.0, 27.2. MS: m/z 697 $[\text{M}^+]$. Anal. Calcd. for $\text{C}_{46}\text{H}_{35}\text{NS}_3$: C, 79.16; H, 5.05. Found: C, 78.94; H, 4.86.

2.2.5. 6-[*N,N*-bis(9,9-dimethylfluoren-2-yl)amino]-2-(5'-iodo-2,2'-bithiophen-5-yl) benzo[*b*]thiophene (**6**)

n-BuLi (0.2 mL, 1.6 M solution in hexane, 0.31 mmol) was added to a stirred Et_2O solution (50 mL) of 6-[*N,N*-bis(9,9-dimethylfluoren-2-yl)amino]-2-(2,2'-bithiophen-5-yl) benzo[*b*]thiophene (**5**) (0.2 g, 0.29 mmol) at -78°C under nitrogen atmosphere. The solution was warmed to 0°C and then stirred at this temperature for 1 h. After rechilling the solution to -78°C , I_2 (0.078 g, 0.31 mmol) was added. The solution was slowly warmed to room temperature and then stirred overnight. H_2O and brine



Scheme 1. Schematic diagram for the syntheses of the organic dyes **JK-53** and **JK-54**.

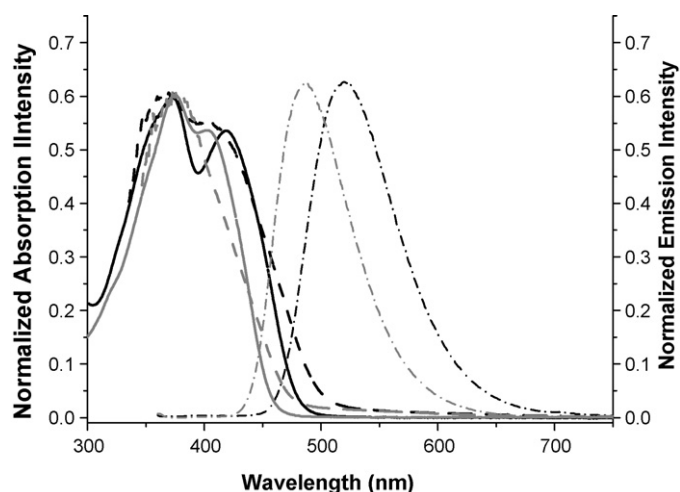


Fig. 2. Absorption (solid lines) and emission (dashed lines) spectra of the dyes in THF and absorption spectra of the dyes on TiO₂ films (dashed-dotted lines). The gray lines are for the JK-53 dye and the black lines are for the JK-54 dye.

were then added to the solution. The product was extracted. The pure product was isolated by chromatography to afford **6** (0.19 g, 78%). MP: 242 °C. ¹H NMR (CHCl₃): δ 7.66 (d, 2H, *J* = 7.2 Hz), 7.62 (td, 2H, *J* = 8.1 Hz, 1.8 Hz), 7.61 (d, 2H, *J* = 8.1 Hz), 7.40 (d, 2H, *J* = 8.1 Hz), 7.38 (s, 1H), 7.35–7.20 (m, 6H), 7.17 (d, 1H, *J* = 3.6 Hz), 7.14–7.09 (m, 4H), 7.05 (d, 1H, *J* = 3.9 Hz), 6.86 (d, 1H, *J* = 3.9 Hz), 1.42 (s, 12H). ¹³C{¹H} NMR (CDCl₃): δ 155.2, 153.6, 147.5, 145.6, 143.0, 140.6, 139.1, 137.9, 136.1, 136.0, 135.7, 135.4, 134.4, 127.1, 126.6, 125.3, 125.3, 124.9, 124.0, 123.2, 122.8, 122.6, 120.8, 119.8, 119.6, 118.6, 117.1, 46.9, 27.2. MS: *m/z* 823 [M⁺]. Anal. Calcd. for C₄₆H₃₄INS₃: C, 67.06; H, 4.16. Found: C 68.87; H, 4.01.

2.2.6.

6-[*N,N*-bis(9,9-dimethylfluoren-2-yl)amino]-2-(5'-triethoxysilyl-2,2'-bithiophen-5-yl)benzo[*b*]thiophene (**JK-54**)

6-[*N,N*-bis(9,9-dimethylfluoren-2-yl)amino]-2-(5'-iodo-2,2'-bithiophen-5-yl)benzo[*b*]thiophene (**6**) (0.18 g, 0.21 mmol), NEt₃ (42 mg, 0.42 mmol), and triethoxysilane (0.65 mL, 0.38 mmol) were added to a solution of Pd₂(dba)₃·CHCl₃ (3 mg, 0.003 mmol) and P(*o*-tol)₃ (0.004 g, 0.012 mmol) in NMP (10 mL). The mixture was stirred for 1 h at room temperature and then extracted with benzene. The extract was first washed three times with water in order to remove the NMP and subsequently dried over MgSO₄. The mixture was precipitated by adding it to MeOH. The resulting yellow solid was collected and reprecipitated from Et₂O into MeOH. The yellow solid was collected and dried under vacuum to afford **JK-53** (0.14 g, 80%). MP: 146 °C (dec). ¹H NMR (CHCl₃): δ 7.66 (d,

2H, *J* = 7.2 Hz), 7.62 (td, 2H, *J* = 8.1 Hz, 1.8 Hz), 7.61 (d, 2H, *J* = 8.1 Hz), 7.41–7.20 (m, 10H), 7.16–7.09 (m, 6H), 3.91 (q, 6H, *J* = 6.9 Hz), 1.42 (s, 12H), 1.28 (t, 9H, *J* = 6.9 Hz). ¹³C{¹H} NMR (CDCl₃): δ 155.2, 153.6, 147.5, 145.5, 143.5, 140.5, 139.1, 137.9, 136.8, 136.6, 136.0, 135.6, 134.3, 129.0, 127.1, 126.6, 125.4, 125.2, 125.1, 124.0, 123.2, 122.8, 122.6, 120.8, 119.6, 119.5, 118.6, 117.2, 59.2, 47.0, 27.2, 18.35. MS: *m/z* 859 [M⁺]. Anal. Calcd. for C₅₂H₄₉NO₃S₃Si: C, 72.60; H, 5.74. Found: C, 72.36; H, 5.47.

3. Results and discussion

The dyes **JK-53** and **JK-54** were prepared by the stepwise synthetic protocol illustrated in Scheme 1. The iodo-derivatives **2**, **4**, and **6** were synthesized by *n*-butyllithium and I₂ iodination of **1** [18,19], **3** [20–22], and **5**, respectively. The silylation of **2** and **6** with triethoxysilane afforded the silane compounds **JK-53** and **JK-54**, respectively. For the fabrication of each DSSC, an FTO glass plate (Pilkington, 8 Ω sq⁻¹) was cleaned for 15 min in a detergent solution using an ultrasonic bath and then rinsed with water and ethanol. The glass plate was then immersed in 40 mM of TiCl₄ aqueous solution at 70 °C for 30 min, as reported by the Grätzel group. A 12-μm-thick TiO₂ paste (Solaronix, Ti-Nanoxide T/SP) and a 4-μm-thick scattering layer paste (CCIC, PST-400C) were coated onto the glass by a doctor blade technique. The TiO₂ electrode was treated with TiCl₄ again and then sintered at 500 °C for 30 min. Subsequently, the TiO₂ electrode was immersed in a dye solution of **JK-2**, **JK-53**, or **JK-54** (0.5 mM in THF) contained in a pressure tube maintained at 80 °C in a nitrogen atmosphere in the dark. The electrode remained under these conditions for 24 h. The color of the TiO₂ surface layer gradually changed from white to green to light orange. The colored layer did not show any decoloration when immersed in any solvents, such as THF, ethanol, ethanol containing NaOH (0.1 mol/L), acetonitrile, and DMF. The dye-containing TiO₂ electrode and Pt-counter electrode were assembled into a sealed sandwich-type cell. An electrolyte consisting of 0.6 M 1-hexyl-2,3-dimethylimidazolium iodide, 0.05 M I₂, 0.1 M LiI, and 0.5 M *tert*-butylpyridine in CH₃CN was driven into the cell via vacuum backfilling. ATR-FTIR spectroscopy was used to determine how the dye anchors to the TiO₂ film. The absorptions at 937 cm⁻¹ and 931 cm⁻¹ for the **JK-53** and **JK-54** dyes, respectively, are both attributed to the presence of a Ti–O–Si moiety. These results indicate that these dyes adsorb onto the TiO₂ through their silyl trioxo group.

The UV–vis absorption and emission spectra of the dyes in THF are shown in Fig. 2. The data extracted from these spectra are listed in Table 1. Both dyes exhibited two narrow absorption bands, but the spectrum of **JK-54** were slightly red-shifted compared to those of the **JK-53** sensitizer. The absorption peaks of the two dyes adsorbed on the TiO₂ films are broadened compared to

Table 1
Optical, redox, and DSSC performance parameters of **JK-53**, **JK-54**, and **JK-2**.

| Dye | λ_{abs} (nm) ^a ($\epsilon/\text{dm}^3 \text{M}^{-1} \text{cm}^{-1}$) | E_{ox}^b (ΔE_p)/V vs. NHE | E_{0-0}^c /V vs. NHE | E_{LUMO}^d /V vs. NHE | L_d^e (μm) | J_{sc} (mA cm ⁻²) | V_{oc} (V) | FF | η (%) |
|--------------|--|--|------------------------|--------------------------------|---------------------------|--|---------------------|------|------------|
| JK-53 | 374 (60,000) | 1.59 (0.17) | 2.77 | −1.18 | 17.95 | 6.37 | 0.70 | 0.74 | 3.31 |
| | 402 (53,600) | | | | | | | | |
| JK-54 | 373 (62,800) | 1.54 (0.27) | 2.63 | −1.09 | 24.48 | 7.52 | 0.71 | 0.75 | 4.01 |
| | 419 (56,300) | | | | | | | | |
| JK-2 | 364 (44,000) | 1.01 (0.21) | 2.37 | −1.36 | 7.86 | 14.0 | 0.75 | 0.77 | 8.01 |
| | 452 (39,000) | | | | | | | | |

^a Absorption spectra were measured in THF.

^b The electrochemical experiments of the dyes on 10 μm TiO₂ were carried out in 0.1 M [*n*-Bu₄N]PF₆/MeCN.

^c E_{0-0} was determined from the intersection of the absorption and emission spectra in THF.

^d $E_{\text{LUMO}} = E_{\text{ox}} - E_{0-0}$. The performances of the DSSCs were measured under 100 mW/cm². ϵ : Absorption coefficient; E_{ox} : oxidation potential; J_{sc} : short-circuit photocurrent density; V_{oc} : open-circuit photovoltage; FF : fill factor; η : total power conversion efficiency.

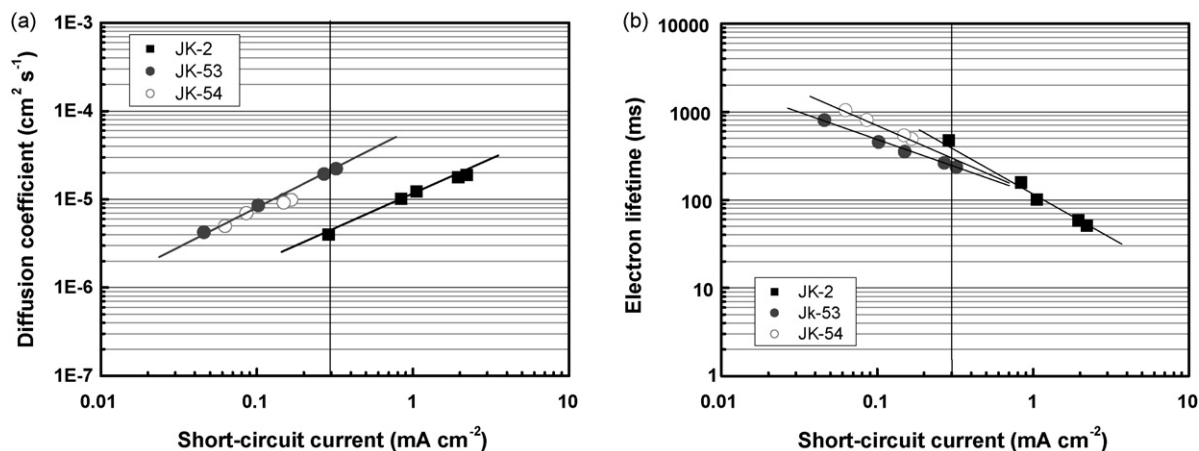


Fig. 3. Electron diffusion coefficients D_e (a) and electron lifetime values τ_e (b) in the photoelectrodes with different adsorbed dyes (i.e., JK-2, JK-53, and JK-54).

those obtained for the dyes in THF. This broadening is favorable for harvesting solar light [23–26]. When the JK-53 and JK-54 sensitizers are excited within their $\pi-\pi^*$ bands in an air-equilibrated solution at 298 K, they exhibit strong luminescence maxima at 489 and 523 nm, respectively. No emission signal was observed for the dyes adsorbed on the TiO_2 films, suggesting that the injection of the excited electron from the excited dye to the TiO_2 electrode is efficient.

To thermodynamically evaluate the possibility of electron transfer from the excited state of the dye to the conduction band of the TiO_2 electrode, cyclic voltammograms were performed in order to determine the redox potentials. The organic dyes adsorbed on the TiO_2 films both showed quasi-reversible oxidation potentials (JK-53: 1.59 V vs. NHE; JK-54: 1.54 V vs. NHE). The reduction potential of each dye was calculated using the oxidation potential and the E_{0-0} energy, the latter of which was determined from the intersection of the absorption and emission spectra. The excited-state oxidation potentials (E_{OX}^*) of the dyes (JK-53: -1.18 V vs. NHE; JK-54: -1.09 V vs. NHE) are much more negative than the conduction band potential of the TiO_2 (approximately -0.5 V vs. NHE).

Electron transport in DSSCs can be characterized by two major parameters: the electron diffusion coefficient (D_e) and the electron lifetime (τ_e). Fig. 3 shows the D_e (a) and τ_e (b) values versus the short-circuit currents in the photoanodes with the different adsorbed dyes (i.e., JK-53, JK-54, and JK-2) [27–29]. Note that we considered a similar structured organic dye with a carboxylic anchoring group (labelled JK-2) for comparison. The J_{sc} values in the x -axis increased with an increase in the initial laser intensity. The D_e values of the photoanodes with the SiO_3 -containing organic dyes (JK-53 and JK-54) are shown to be very similar to each other but are much larger than that of the photoanode with the COO-containing dye (JK-2) for the same J_{sc} value (0.3 mA cm^{-2}). These findings might have resulted from the different anchoring groups affecting the abilities of the dyes to adsorb on the TiO_2 surface. To investigate this further, we measured the amount of dye adsorbed on the TiO_2 surfaces. The amounts of the dye molecules adsorbed on the TiO_2 electrodes were shown to be 6.3×10^{-8} , 7.2×10^{-8} , and $2.12 \times 10^{-7} \text{ mol cm}^{-2}$ for JK-53, JK-54, and JK-2, respectively. The low loading of the SiO_3 -containing dyes might provide an enlarged vacant surface (unoccupied by dye molecules) on the TiO_2 electrode that enables the adsorption of cations, thereby leading to the promotion of electron diffusion in the TiO_2 electrode. This is rationalized by ambipolar diffusion [30]. Moreover, the J_{sc} levels of the cells with the JK-53 and JK-54 dyes are shown to be lower than that of the cell incorporating the JK-2 dye. This is due to the adsorption

of relatively small amounts of the JK-53 and JK-54 dyes compared to the JK-2 dye.

Meanwhile, the τ_e values of the cell with the JK-53 and JK-54 dyes are slightly lower than that of the cell containing the JK-2 dye, as shown in Fig. 3(b). It is believed that the electron recombination occurred to a greater extent in the photoelectrodes with the SiO_3 -containing dyes. This is thought to be due to the relatively large extents of their TiO_2 surfaces being unoccupied by dye molecules (as described above). This results in their decreased τ_e values. In addition, the electron lifetime results are in good agreement with those of the open-circuit voltage (V_{oc}) shown in Table 1. The conflicting contribution of diffusion coefficient and lifetime can be combined and expressed by means of the diffusion length (L_d). Diffusion length of electrons is denoted as $L_d = (D_e \cdot \tau_e)^{0.5}$ [31]. The diffusion length was shown to increase in the order of JK-54 > JK-53 > JK-2 as listed in Table 1. This result indicates that the new dyes with SiO_3 anchoring groups have potentialities for the DSSC application. However, the amount of dyes adsorbed onto TiO_2 should be enhanced to achieve high performance of DSSC employing them.

The J - V curves of the JK-53- and JK-54-sensitized cells are shown in Fig. 4. Under standard global AM 1.5 solar conditions, the JK-54-sensitized cell gave a short-circuit photocurrent density (J_{sc}) of 7.52 mA cm^{-2} , a V_{oc} of 0.71 V, and a fill factor (FF) of 0.75. These

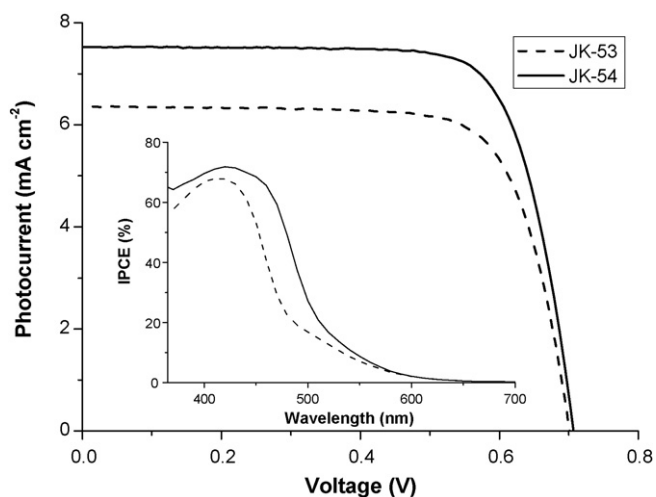


Fig. 4. J - V curves and IPCE spectra (inset) of JK-53 (dashed lines) and JK-54 (solid lines). The light intensity was 100 mW/cm^{-2} .

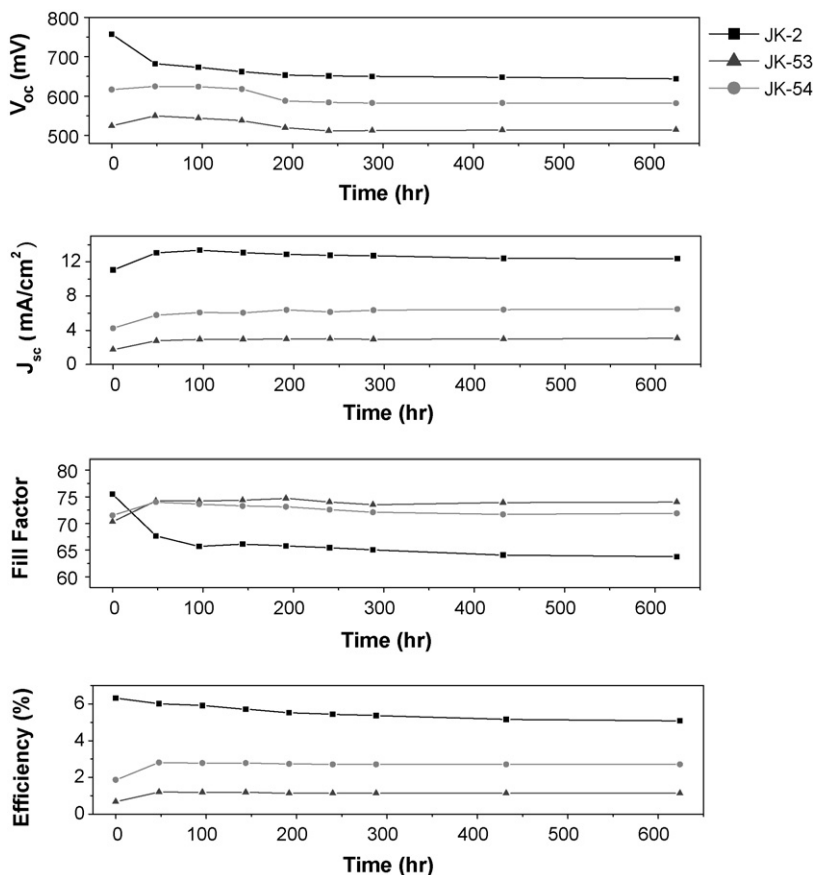


Fig. 5. Evolution of the photovoltaic parameters with JK-2 (■), JK-53 (▲), and JK-54 (●) during visible-light soaking (AM 1.5G, 100 mW cm^{-2}) at 60°C . A 420-nm cut-off filter was placed on the cell surface during illumination.

correspond to an overall conversion efficiency of 4.01% (calculated from the equation: $\eta = J_{sc} V_{oc} FF / \text{light intensity}$). The incident monochromatic photon-to-current conversion efficiencies (IPCEs) of the JK-53 and JK-54-sensitized cells are also shown in Fig. 4. The onsets of the IPCE spectra of the JK-53- and JK-54-sensitized cells were both at 650 nm, and the maximum IPCE values of both the JK-53- and JK-54-sensitized cells were observed at 420 (66%) and 430 nm (72%), respectively. In the long wavelength region, the difference is even more pronounced. Thus, at 470 nm, the IPCE value for the JK-54 cell is twice as high as that for the JK-53 cell. Consequently, the short-circuit photocurrent of the JK-54 cell is about 20% higher than that of the JK-53 cell.

Moreover, we have measured the long-term stability of the DSSCs employing the organic dyes (i.e. JK-2, JK-53, and JK-54). Fig. 5 shows the photovoltaic performances during long-term accelerated aging of the DSSCs employing MPN-based polymer electrolyte at AM 1.5G and 60°C (85% RH). The values of J_{sc} , V_{oc} , FF, and the overall efficiency (η) were recorded over a period of 600 h. During the long-term stability test, the new dyes with SiO_3 anchoring groups showed more stable photovoltaic performances compared to those of JK-2 with COOH anchoring group.

4. Conclusion

In summary, we have designed and synthesized two novel organic sensitizers (JK-53 and JK-54) that both contain the trialkoxysilyl anchoring group, which has been shown to be an efficient immobilization group for TiO_2 . Under AM 1.5 sunlight, the JK-54-sensitized cell resulted in a J_{sc} of 7.52 mA cm^{-2} , a V_{oc} of 0.71 V, and a fill factor of 0.75. These values correspond to an

overall conversion efficiency of 4.01%. Moreover, the dyes with the trialkoxysilyl anchoring group were shown to provide stronger binding property compared with those containing the carboxylate anchoring group, improving the durability of the DSSCs.

Acknowledgements

This work was supported by the Korea Science and Engineering Foundation (KOSEF) through the National Research Laboratory Program, which was funded both by the Ministry of Science and Technology (No. M10500000034-06J0000-03410), ITRC Program (IITA 2008 C1090 0904 0013), MEST Program (R11-2008-088-02001-0) and BK 21 (2006).

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