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Efficient organic sensitizers containing benzo[*cd*]indole: Effect of molecular isomerization for photovoltaic properties

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ABSTRACT

Two isomeric organic dyes, **JK-51** and **JK-52** containing benzo[*cd*]indole were synthesized. Under standard global AM 1.5 solar condition, the **JK-51** sensitized cell gave a short circuit photocurrent density of 17.43 mA/cm^2, open circuit voltage of 0.680 V, and a fill factor of 0.71, corresponding to an overall conversion efficiency η of 8.42%. On the other hand, a solar-to-electric conversion efficiency of 6.88% was achieved with the isomeric dye **JK-52**. We found that the power conversion efficiency was shown to be quite sensitive to the isomeric configurations.

1. Introduction

Increasing energy demands and problems aroused by global warming have led to a greater interest on renewable energy sources in recent years [1]. Dye-sensitized solar cells (DSSCs) are attracting widespread interest for a new renewable energy source because of the low cost and high efficiency [2]. In these cells, dye is one of the key elements for high power conversion efficiencies. The most efficient metal complex sensitizers in DSSCs are Ru(II) polypyridyl complexes [3] because they have metal-to-ligand charge transfer (MLCT) transitions in the visible region and tune easily their spectral and photophysical properties by introducing an appropriate ligand in a controlled manner. Recently, several groups have developed metal free organic sensitizers to substitute the precious ruthenium metal complexes and obtained the impressive photovoltaic performance in the range of 6–9% [4–8]. A few simple methods for tuning the spectral properties of the sensitizers can be tested through the structural isomerization and geometrical isomerization (*cis*-to-*trans*) [9]. Several attempts have been made. The effect of changing the position of the bipyridyl substituents from 3,3′ to 4,4′ and 5,5′ in [Pt{X,X′-$(CO_2H)_2$-2,2′-bipyridyl}(dithiolate)] [10] and Ru{X,X′-$(CO_2H)_2$-2,2′-bipyridyl}$_2$ $(NCS)_2$ [11] (where $X = 3, 4, 5$) is discussed with reference to structural and electronic changes. The substituted positions of the COOH groups in the 2,2′-bipyridine were shown to have a profound influence on the photophysical and electro-optical properties of the Ru(II) and Pt(II) complexes. Systematic tuning of the LUMO and HOMO energy levels of the metal polypyridyl complexes are necessary to evaluate the optimal threshold band for maximum power conversion.

Very recently, we have designed and synthesized the novel organic dyes containing dimethylfluorenyl amine unit [12]. As an extension of our efforts to synthesize more efficient organic dyes, we are successful in preparing two isomeric organic dyes containing benzo[*cd*]indole (Fig. 1). Between two isomers, the **JK-51** dye has more impressive solar energy conversion efficiency than that of **JK-52**. We are interested in what effect the position of the dithiophene unit on the benzo[*cd*]indole has on the photophysical properties of the dye.

In this article, we report two isomeric organic dyes containing benzo[*cd*]indole as electron donor and cyano acrylic acid as electron acceptor bridged by a dithiophene unit. The solar conversion efficiency of two isomeric dyes is shown to be quite dependent of the substituted position on benzo[*cd*]indole.

2. Experimental

2.1. General methods

All reactions were carried out under an argon atmosphere. Solvents were distilled from appropriate reagents. All reagents were

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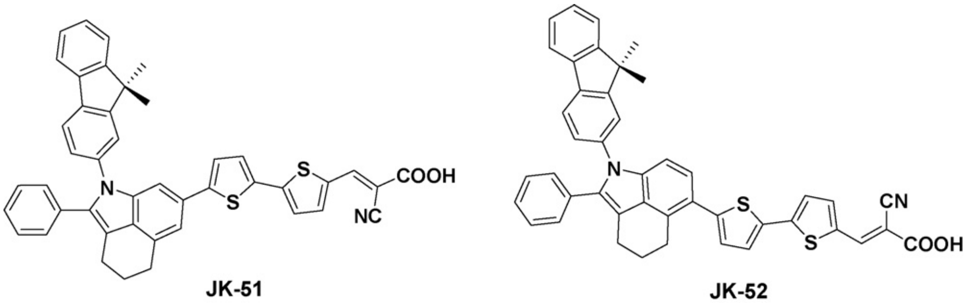


Fig. 1. Structures of the dyes of **JK-51** and **JK-52**.

purchased from Sigma–Aldrich. 2-Iodo-9,9-dimethylfluorene, [13] 4,4,5,5-tetramethyl-2-(5-(5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)thiophen-2-yl)-1,3,2-dioxaborolane (**5**) [14], tributyl(5-(thiophen-2-yl)thiophen-2-yl)stannane (**4**) [15] and 2,6,7,8-tetrahydro-1-phenylbenzo[*cd*]indole (**1**) [16] were synthesized using a modified procedure of previous references. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer. Elemental analyses were performed with a Carlo Elba 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.

2.2. Cyclovoltagram

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, a platinum wire electrode. Redox potential of dyes on TiO_2 were measured in CH_3CN with 0.1 M $(n\text{-}C_4H_9)_4N\text{-}PF_6$ with a scan rate of 50 mV s^{-1}.

2.3. Fabrication of DSSC

For the preparation of DSSC, a washed FTO (Pilkington, 8 Ω sq.$^{-1}$) glass plate was immerged in 40 mM $TiCl_4$ aqueous solution as reported by the Grätzel group. The first TiO_2 layer of 12 μm thickness was prepared by screen printing with transparent mesoporous TiO_2 paste (13 nm anatase, solaronix), and the second opaque layer of 4 μm thickness (400 nm, CCIC) was coated for the purpose of light scattering. The TiO_2 electrodes were immersed into the dyes (**JK-51** and **JK-52)** solution (0.3 mM in ethanol containing 1.0 mM 3a,7a-dihydroxy-5b-cholic acid) and kept at room temperature for 18 h. Counter electrodes were prepared by coating with a drop of H_2PtCl_6 solution (2 mg Pt in 1 mL ethanol) on a FTO plate. The electrolyte was then introduced into the cell, which was composed of 0.6 M 3-hexyl-1,2-dimethyl imidazolium iodide, 0.05 M iodine, 0.1 M LiI and 0.5 M 4-*tert*-butylpyridine in acetonitrile.

2.4. Characterization of DSSC

The cells were measured using 1000W xenon light source, whose power of an AM 1.5 Oriel solar simulator was calibrated by using KG5 filtered Si reference solar cell. The incident photon-to-current conversion efficiency (IPCE) spectra for the cells were measured on an IPCE measuring system (PV Measurements).

2.5. Measurements of electron lifetime and diffusion coefficient

Electron transport characteristics of the photoelectrodes adsorbing different dyes were evaluated via laser-induced photocurrent/photovoltage transient measurement using a diode laser source ($\lambda = 635$ nm) modulated with a function generator (UDP-303, PNCYS Co. Ltd., Korea) [17]. The transients of photocurrent and photovoltage were induced by the stepwise change of the laser intensity, which was controlled by a function generator. A set of ND filters was used to change the laser intensity. The effective cell area was 0.04 cm^2 and the TiO_2 film thickness was approximately 16 μm. All the cells were prepared with the same electrolyte described previously. The laser was operated at the voltage of 3.0 V and stepped down to 2.9 V for 5 s. Then the single shot of the time-profiles of the photocurrent and photovoltage was obtained from an oscilloscope (TDS 3052B, Tektronix) through a current amplifier (SR570, Stanford Research Systems) and a voltage amplifier (5307, NF electronic Instruments), respectively. Fig. 2 shows the simplified experimental set-up and more detailed information on the measurement has been reported by Nakade et al. [17a,b].

2.6. Synthesis

2.6.1. Bromination of **1**

To a solution of 2,6,7,8-tetrahydro-1-phenylbenzo[*cd*]indole **1** (3.65 g, 15.64 mmol) in $CHCl_3$ (100 mL) at 0 °C was added *N*-bromosuccinimide(NBS) (2.64 g, 14.88 mmol) over 30 min as a small potion. The mixture was stirred at same temperature for 4 h. After evaporating the solvent, the residue was extracted by dichloromethane (MC) and washed by H_2O. The organic layer was separated and dried in $MgSO_4$. The solvent was removed *in vacuo*. The pure product 4-bromo-2,6,7,8-tetrahydro-1-phenylbenzo[*cd*]indole **2** (eluent EA:Hx = 1:10, $R_f = 0.6$) and 5-bromo-2,6,7,8-tetrahydro-1-phenylbenzo[*cd*]indole **3** ($R_f = 0.4$) were obtained by silica gel chromatography as pale yellow solid in 56% and 41% yields, respectively. For **2**, Mp: 152 °C. ^{1}H NMR (Acetone-d$_6$): δ 10.36 (s, 1H), 7.74 (d, 2H, $J = 7.5$ Hz), 7.48 (t, 2H, $J = 7.5$ Hz), 7.40 (s, 1H), 7.32 (t, 1H, $J = 7.5$ Hz), 6.94 (s, 1H), 3.04 (t, 2H, $J = 6.3$ Hz), 2.90 (t, 2H, $J = 6.3$ Hz), 2.05 (q, 2H, $J = 6.3$ Hz). ^{13}C{^{1}H} NMR (Acetone-d$_6$): δ 136.1, 134.7, 133.9, 132.0, 129.6, 128.4, 127.5, 126.9, 119.6, 116.8, 111.8, 111.5, 27.7, 25.2, 23.7. MS: *m/z* 311 [M$^+$]. Anal. Calcd. for $C_{17}H_{14}BrN$: C, 65.40; H, 4.52. Found: C, 65.23; H, 4.45. For **3**, Mp: 155 °C. ^{1}H NMR ($CDCl_3$): δ 7.99 (s, 1H), 7.58 (d, 2H, $J = 7.2$ Hz), 7.47 (t, 2H, $J = 7.2$ Hz), 7.33 (t, 1H, $J = 7.2$ Hz), 7.27 (d, 1H, $J = 8.4$ Hz), 7.06 (d, 1H, $J = 8.4$ Hz), 3.02 (t, 2H, $J = 6.0$ Hz), 2.96 (t, 2H, $J = 6.0$ Hz), 2.11 (q, 2H, $J = 6.0$ Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 133.2, 133.0, 131.8, 131.4, 130.4, 129.1, 127.2, 126.3, 126.1, 111.5, 111.4, 109.7, 27.8, 24.4, 22.8. MS: *m/z* 311 [M$^+$]. Anal. Calcd. for $C_{17}H_{14}BrN$: C, 65.40; H, 4.52. Found: C, 65.20; H, 4.46.

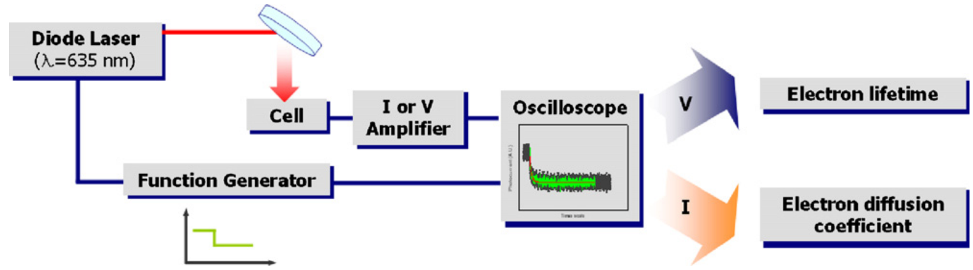


Fig. 2. Measurement set-up for photocurrent and photovoltage transients induced by stepwise light intensity.

2.6.2. 2,6,7,8-Tetrahydro-1-phenyl-4-(5-(thiophen-2-yl)thiophen-2-yl)benzo[cd] indole (6)

A mixture of **2** (0.6 g, 1.92 mmol), tributyl(5-(thiophen-2-yl)thiophen-2-yl)stannane **4** (0.88 g, 1.92 mmol), $Pd(PPh_3)_4$ (0.11 g, 0.096 mmol) and LiCl (0.41 g, 9.6 mmol) in dimethylformamide (DMF) (30 mL) was stirred at 100 °C for 12 h. After cooling the solution, H_2O (50 mL) was added to the solution and extracted by dichloromethane (50 mL 5×). The organic layer was separated and dried in $MgSO_4$. The solvent was removed *in vacuo*. The pure product **6** was obtained by silica gel chromatography (eluent MC:Hx = 1:3, $R_f = 0.3$) as a white solid in 88% yield. Mp: 122 °C. ^1H NMR (Acetone-d_6): δ 10.33 (s, 1H), 7.75 (d, 2H, $J = 7.5$ Hz), 7.48 (t, 2H, $J = 7.5$ Hz), 7.47 (d, 1H, $J = 4.2$ Hz), 7.40 (d, 1H, $J = 5.1$ Hz), 7.32 (t, 1H, $J = 7.5$ Hz), 7.31 (s, 1H), 7.28 (d, 1H, $J = 4.2$ Hz), 7.22 (d, 1H, $J = 3.6$ Hz), 7.12 (s, 1H), 7.08 (dd, 1H, $J = 3.6$ Hz, $J = 5.1$ Hz), 3.08 (t, 2H, $J = 6.0$ Hz), 2.96 (t, 2H, $J = 6.0$ Hz), 2.10 (q, 2H, $J = 6.0$ Hz). $^{13}C\{^1H\}$ NMR (Acetone-d_6): δ 146.7, 138.3, 135.9, 135.7, 134.2, 133.5, 132.7, 129.8, 129.7, 129.6, 128.9, 127.5, 126.9, 125.6, 125.2, 124.2, 123.6, 115.1, 112.0, 106.2, 27.4, 25.5, 24.0. MS: *m/z* 397 [M^+]. Anal. Calcd. for $C_{25}H_{19}NS_2$: C, 75.53; H, 4.82. Found: C, 75.34; H, 4.62.

*2.6.3. 2,6,7,8-Tetrahydro-2-(9,9-dimethyl-9H-fluoren-2-yl)-1-phenyl-4-(5-(thioph-en-2-yl)thiophen-2-yl)benzo[cd]indole (**8**)*

A stirred mixture of **6** (0.70 g, 1.76 mmol), 2-iodo-9,9-dimethylfluorene (0.84 g, 2.64 mmol), powdered anhydrous potassium carbonate (0.49 g, 3.52 mmol), copper bronze (0.11 g, 1.76 mmol) and 18-crown-6 (0.07 g, 0.26 mmol) in 1,2-dichlorobenzene (40 mL) was refluxed for 48 h. After cooling, the insoluble inorganic material was filtered off and washed with dichloromethane (3× 30 mL). The combined filtrate and organic phase was washed with dilute aqueous ammonia and water and dried with magnesium sulfate. The solvent was removed under reduced pressure. The pure product was obtained by silica gel chromatography (eluent MC:Hx = 1:3, $R_f = 0.6$) to afford **8** (0.87 g) in 84% yield. Mp: 129 °C. ^1H NMR ($CDCl_3$): δ 7.79 (d, 1H, $J = 8.1$ Hz), 7.75 (d, 1H, $J = 6.9$ Hz), 7.49 (s, 1H), 7.41 (t, 2H, $J = 6.6$ Hz), 7.38 (d, 1H, $J = 4.8$ Hz), 7.34 (t, 1H, $J = 7.2$ Hz), 7.25–7.15 (m, 9H), 7.12 (d, 1H, $J = 3.9$ Hz), 7.11 (s, 1H), 7.01 (dd, 1H, $J = 3.9$ Hz, $J = 4.8$ Hz), 3.05 (m, 4H), 2.16 (q, 2H, $J = 6.0$ Hz), 1.33 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 154.8, 153.9, 146.1, 145.8, 138.7, 138.0, 137.5, 136.5, 135.6, 134.2, 133.1, 132.2, 129.8, 129.7, 128.2, 128.0, 127.9, 127.4, 127.2, 126.9, 125.7, 124.7, 124.0, 123.3, 122.9, 122.8, 122.2, 120.6, 120.2, 115.9, 114.4, 105.4, 46.9, 27.8, 26.9, 24.7, 22.8. MS: *m/z* 589 [M^+]. Anal. Calcd. for $C_{40}H_{31}NS_2$: C, 81.45; H, 5.30. Found: C, 81.17; H, 5.22.

*2.6.4. 5-(5-(2,6,7,8-Tetrahydro-2-(9,9-dimethyl-9H-fluoren-2-yl)-1-phenylbenzo[cd] indol-4-yl)thiophen-2-yl) thiophene-2-carbaldehyde (**10**)*

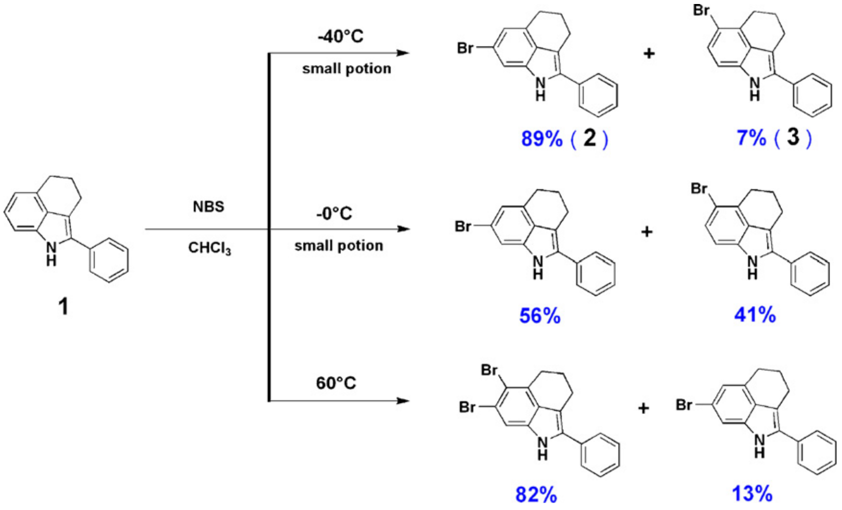
Compound **8** (0.47 g, 0.80 mmol) dissolved in tetrahydrofuran(THF) (30 mL) was cooled to −78 °C under N_2. *n*-Butyl lithium (1.25 mL, 1.6 M solution in hexane, 2.01 mmol) was added dropwise over 10 min with vigorous stirring. It was brought to 0 °C during 1 h and kept at this temperature for additional 1 h. Again the solution was cooled to -78 °C and dry DMF (1 mL) was added at once. The solution was warmed to room temperature and stirred overnight. The reaction was quenched by water (20 mL) and extracted with dichloromethane (3× 20 mL). The combined organic extract was dried over anhydrous $MgSO_4$ and filtered. The pure product **10** was obtained by silica gel chromatography (eluent MC:Hx = 1:1, $R_f = 0.3$) to afford **10** in 88% yield. Mp: 183 °C. ^1H NMR ($CDCl_3$): δ 9.86 (s, 1H), 7.82 (d, 1H, $J = 8.1$ Hz), 7.76 (d, 1H, $J = 6.9$ Hz), 7.67 (d, 1H, $J = 4.2$ Hz), 7.51 (s, 1H), 7.43 (t, 2H, $J = 8.1$ Hz), 7.41 (d, 1H, $J = 8.1$ Hz), 7.37 (t, 1H, $J = 6.9$ Hz), 7.34 (d, 1H, $J = 4.2$ Hz), 7.32–7.20 (m, 8H), 7.12 (s, 1H), 3.06 (m, 4H), 2.18 (q, 2H, $J = 6.0$ Hz), 1.35 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 182.5, 154.8, 153.9, 149.1, 147.9, 141.2, 138.6, 137.8, 137.6, 136.4, 134.7, 134.1, 133.9, 133.3, 132.1, 129.7, 129.0, 129.0, 128.4, 128.2, 127.5, 127.3, 127.0, 125.6, 123.6, 123.4, 122.8, 122.2, 120.7, 120.2, 115.9, 114.4, 105.7, 46.9, 27.8, 26.9, 24.7, 22.7. MS: *m/z* 617 [M^+]. Anal. Calcd. for $C_{41}H_{31}NOS_2$: C, 79.71; H, 5.06. Found: C, 79.49; H, 5.01.

*2.6.5. 2-Cyano-3-(5-(5-(2,6,7,8-tetrahydro-2-(9,9-dimethyl-9H-fluoren-2-yl)-1-phe-nylbenzo[cd]indol-4-yl)thiophen-2-yl)thiophen-2-yl)acrylic acid (**JK-51**)*

A mixture of **10** (0.29 g, 0.47 mmol) and cyanoacetic acid (0.060 g, 0.70 mmol) were vacuum-dried and added acetonitrile (20 mL) and piperidine (0.046 mL). The solution was refluxed for 6 h. After cooling the solution, the organic layer was removed *in vacuo*. The pure product was obtained by silica gel chromatography (eluent EA:MeOH = 10:1, $R_f = 0.2$) to afford **JK-51** (0.29 g) in 91% yield. Mp: 236 °C. ^1H NMR (DMSO-d_6): δ 8.08 (s, 1H), 7.94 (d, 1H, $J = 8.1$ Hz), 7.85 (d, 1H, $J = 6.9$ Hz), 7.63 (d, 1H, $J = 3.9$ Hz), 7.51 (d, 1H, $J = 6.6$ Hz), 7.42–7.19 (m, 14H), 2.95 (m, 4H), 2.03 (m, 2H), 1.27 (s, 6H). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 163.6, 154.3, 153.5, 146.3, 141.4, 140.2, 137.8, 137.2, 136.9, 136.3, 135.9, 135.4, 134.1, 133.5, 132.9, 131.3, 129.2, 128.4, 128.2, 127.6, 127.5, 127.2, 127.0, 126.8, 125.4, 124.0, 123.9, 122.8, 121.9, 121.1, 120.3, 119.3, 115.2, 113.9, 109.1, 104.6, 46.4, 27.0, 26.4, 24.0, 22.0. MS: *m/z* 684 [M^+]. Anal. Calcd. for $C_{44}H_{32}N_2O_2S_2$: C, 77.16; H, 4.71. Found: C, 76.92; H, 4.63.

*2.6.6. 2,6,7,8-Tetrahydro-5-(5-(5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)thio-phen-2-yl)-1-phenylbenzo[cd]indole (**7**)*

To a stirred solution of **3** (0.64 g, 2.05 mmol) and $Pd(PPh_3)_4$ (0.12 g, 0.103 mmol) in THF (10 mL) was added the THF (10 mL) solution of 4,4,5,5-tetramethyl-2-(5-(5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)thiophen-2-yl)-1,3,2-dioxaborolane (**5**) (1.00 g, 2.46 mmol), potassium carbonate (2.76 g, 20 mmol) and H_2O (20 mL) by cannula. The mixture was refluxed for 18 h. After cooling the solution, H_2O (30 mL) was added to the solution and extracted by dichloromethane (30 mL 3×). The organic layer was separated and dried in $MgSO_4$. The solvent was removed *in vacuo*. The pure product **7** was obtained by silica gel chromatography (elu-

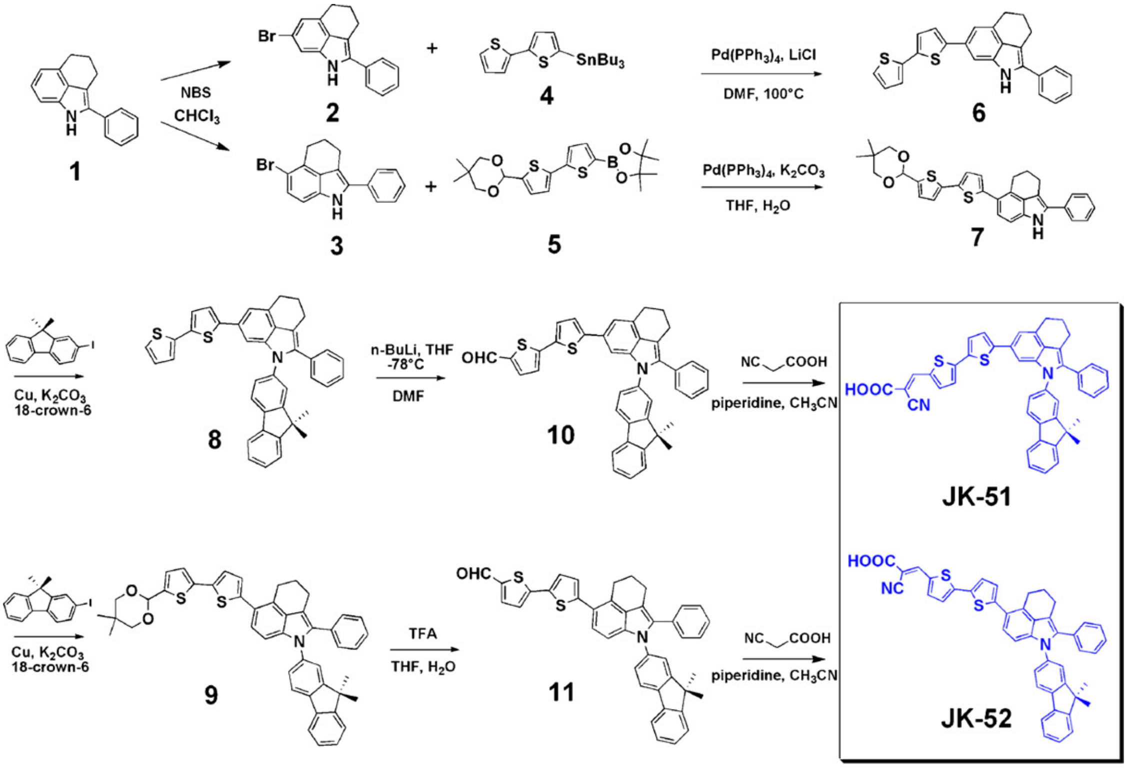


Scheme 1. Bromination of benzo[*cd*]indole.

ent MC:Hx = 1:1, $R_f = 0.2$) as a white solid in 90% yield. Mp: 131 °C. ^{1}H NMR (Acetone-d$_6$): δ 10.33 (s, 1H), 7.75 (d, 2H, J = 7.5 Hz), 7.48 (t, 2H, J = 7.5 Hz), 7.47 (d, 1H, J = 4.2 Hz), 7.33 (d, 1H, J = 8.1 Hz), 7.31 (t, 1H, J = 7.5 Hz), 7.25 (d, 1H, J = 4.2 Hz), 7.12 (d, 1H, J = 4.2 Hz), 7.07 (d, 1H, J = 8.1 Hz), 7.04 (d, 1H, J = 4.2 Hz), 5.66 (s, 1H), 3.69 (m, 4H), 3.07 (m, 4H), 2.04 (m, 2H), 1.20 (s, 3H), 0.79 (s, 3H). ^{13}C{^{1}H} NMR (Acetone-d$_6$): δ 144.2, 141.6, 138.3, 136.5, 135.4, 134.2, 132.2, 130.2, 129.7, 127.5, 127.1, 126.9, 126.7, 125.1, 125.0, 123.2, 122.3, 112.4, 109.7, 98.8, 77.8, 30.7, 27.5, 25.5, 23.7, 23.2, 21.8. MS: *m/z* 511 [M$^+$]. Anal. Calcd. for $C_{31}H_{29}NO_2S_2$: C, 72.76; H, 5.71. Found: C, 72.48; H, 5.66.

*2.6.7. 2,6,7,8-Tetrahydro-5-(5-(5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)thio-phen-2-yl)-2-(9,9-dimethyl-9H-fluoren-2-yl)-1-phenylbenzo[cd]indole (**9**)*

The product was synthesized according to the procedure as described above for synthesis of **8**, giving a yellow solid of the product **9** in 77% yield. Mp: 144 °C. ^{1}H NMR (CDCl$_3$): δ 7.75 (d, 1H, J = 7.8 Hz), 7.72 (d, 1H, J = 7.8 Hz), 7.43–7.17 (m, 12H), 7.09 (s, 1H), 7.06 (d, 1H, J = 5.1 Hz), 7.05 (d, 1H, J = 8.1 Hz), 7.02 (d, 1H, J = 3.3 Hz), 5.63 (s, 1H), 3.78 (d, 2H, J = 11.1 Hz), 3.65 (d, 2H, J = 11.1 Hz), 3.22 (m, 2H), 3.02 (m, 2H), 2.13 (m, 2H), 1.32 (s, 6H), 1.31 (s, 3H), 0.81 (s, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 154.8, 153.9, 143.2, 139.9, 138.7, 138.3,



Scheme 2. Synthesis of **JK-51** and **JK-52**.

137.9, 137.5, 136.3, 135.8, 134.0, 132.2, 130.1, 129.8, 128.2, 127.4, 127.2, 126.9, 126.3, 125.9, 125.7, 125.2, 124.2, 123.2, 122.8, 122.7, 122.2, 120.5, 120.2, 114.8, 108.4, 98.4, 77.7, 46.9, 30.4, 27.3, 26.9, 24.7, 23.1, 22.5, 22.0. MS: *m/z* 703 [M$^+$]. Anal. Calcd. for $C_{46}H_{41}NO_2S_2$: C, 78.48; H, 5.87. Found: C, 78.37; H, 5.79.

*2.6.8. 5-(5-(2,6,7,8-Tetrahydro-2-(9,9-dimethyl-9H-fluoren-2-yl)-1-phenylbenzo[cd]indol-5-yl)thiophen-2-yl)thiophene-2-carbaldehyde (**11**)*

THF (20 mL) and water (50 mL) were added to a flask containing acetal **9** (0.30 g, 0.43 mmol). Then, trifluoroacetic acid(TFA) (0.1 mL) was added to the solution. The resulting reaction mixture was stirred for 2 h at room temperature, quenched with saturated aqueous sodium bicarbonate, and extracted with dichloromethane. The combined organic phases were washed with aqueous sodium bicarbonate (2%, w/v), dried (Na_2SO_4), and evaporated *in vacuo*. The pure product **11** was obtained by silica gel chromatography (eluent MC:Hx = 1:1, $R_f = 0.4$) as a yellow solid in 96% yield. Mp: 181 °C. ^{1}H NMR ($CDCl_3$): δ 9.87 (s, 1H), 7.76 (d, 1H, $J = 8.1$ Hz), 7.73 (d, 1H, $J = 8.1$ Hz), 7.68 (d, 1H, $J = 3.9$ Hz), 7.42–7.20 (m, 13H), 7.10 (d, 1H, $J = 3.9$ Hz), 7.09 (s, 1H), 3.22 (m, 2H), 3.03 (m, 2H), 2.14 (m, 2H), 1.32 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 182.6, 154.8, 153.9, 147.9, 146.3, 141.3, 138.6, 137.8, 137.7, 137.6, 136.1, 134.8, 134.3, 132.1, 130.3, 129.8, 128.2, 127.5, 127.3, 127.0, 126.8, 126.7, 125.7, 125.0, 123.8, 123.8, 122.8, 122.1, 120.6, 120.2, 114.7, 108.5, 46.9, 27.3, 26.9, 24.7, 22.5. MS: *m/z* 617 [M$^+$]. Anal. Calcd. for $C_{41}H_{31}NOS_2$: C, 79.71; H, 5.06. Found: C, 79.46; H, 4.92.

*2.6.9. 2-Cyano-3-(5-(5-(2,6,7,8-tetrahydro-2-(9,9-dimethyl-9H-fluoren-2-yl)-1-phe-nylbenzo[cd]indol-5-yl)thiophen-2-yl)thiophen-2-yl)acrylic acid (**JK-52**)*

The product was synthesized according to the procedure as described above for synthesis of **JK-51**, giving a red solid of the product **JK-52** in 94% yield. Mp: 251 °C. ^{1}H NMR (DMSO-d_6): δ 8.09 (s. 1H), 7.88 (d, 1H, $J = 8.1$ Hz), 7.82 (d, 1H, $J = 8.1$ Hz), 7.66 (d, 1H, $J = 3.9$ Hz), 7.50–7.15 (m, 15H), 3.13 (m, 2H), 2.91 (m, 2H), 2.01 (m, 2H), 1.25 (s, 6H). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 163.4, 154.3, 153.4, 143.7, 141.3, 140.0, 137.8, 137.1, 137.0, 136.1, 135.9, 135.6, 135.4, 134.4, 133.6, 131.3, 129.4, 129.3, 128.1, 127.6, 127.5, 127.2, 126.9, 126.1, 125.5, 124.6, 124.0, 122.8, 122.0, 121.9, 120.9, 120.3, 119.4, 114.1, 109.5, 108.4, 46.4, 27.1, 26.4, 24.1, 21.7. MS: *m/z* 684 [M$^+$]. Anal. Calcd. for $C_{44}H_{32}N_2O_2S_2$: C, 77.16; H, 4.71. Found: C, 76.91; H, 4.62.

3. Results and discussion

3.1. Synthesis

Schemes 1 and 2 illustrate the synthetic protocol of organic dyes **JK-51** and **JK-52** starting from 2,6,7,8-tetrahydro-1-phenylbenzo[*cd*]indole **1** [16]. We started with the bromination reaction of **1**. When the bromination reaction of **1** using NBS at 0 °C was carried out, two isomeric products **2** and **3** were formed in 56% and 41%, respectively (Scheme 1). We found that the bromination reaction was quite sensitive to the reaction temperature. At low temperature (ca. −40 °C) the 4-bromobenzo[*cd*]indole **2** predominates. On the other hand, at high temperature (ca. 60 °C) the dibromobenzo-[*cd*]indole is predominantly formed (Scheme 1). All the spectral data of **2** and **3** are consistent with the proposed formulation. A key feature in the ^{1}H NMR spectrum of **3** includes two doublets at δ 7.27 and 7.06 assigned to the benzo[*cd*]indole hydrogens. Due to two possibilities of *N*-arylation in bromobenzo[*cd*]indole, first we blocked the bromobenzo position by dithiophene moiety. The indole bithiophene **6** was synthesized by the coupling reaction of **2** with stannylthiophene unit in the presence of tetrakis(triphenylphosphine)palladium(0) and lithium chloride according to the Stille reaction [18]. The indole bithiophene **7** was not formed under the same reaction condition of **6**. Instead, the compound **7** was obtained by Suzuki coupling reaction (Scheme 2) [19]. Fluorene substituted indole bithiophene derivatives **8** and **9** were readily synthesized by Ullmann-type coupling reaction [20] involving copper bronze, potassium carbonate and 18-crown-6. These bithiophene derivatives were converted into their corresponding bithiophene aldehydes **10** and **11** by lithiation with 2.5 equiv. *n*-butyl lithium followed by subsequent quenching with dimethylformamide and cleavage of the 1,3-dioxalane protecting group in aqueous acid, respectively. An acetonitrile solution of bithiophene aldehyde derivatives and cyanoacetic acid was refluxed in the presence of piperidine for 6 h. Solvent removal followed by purification by silica gel column chromatography yielded **JK-51** and **JK-52** as a red solid.

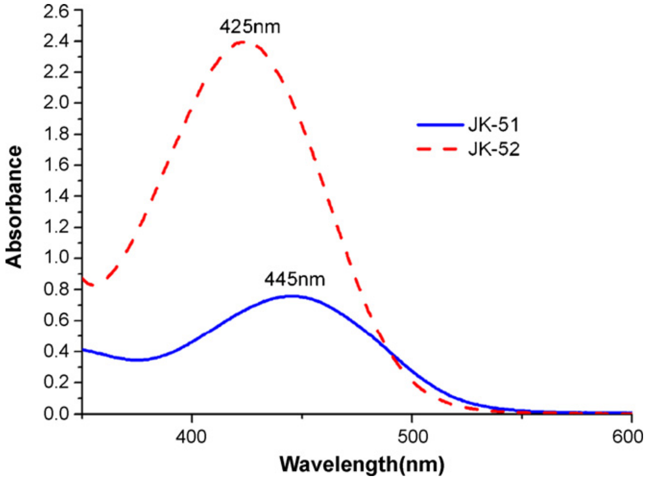


Fig. 3. Absorption spectra of **JK-51** (blue, solid line), **JK-52** (red, dashed line) in ethanol.

3.2. Spectroscopic studies

Fig. 3 shows the UV/vis spectra of the **JK-51** and **JK-52** sensitizers measured in ethanol. The absorption spectrum of the **JK-51** sensitizer exhibits one absorption maximum at 445 nm ($\varepsilon = 15{,}188$ dm^3 mol^{-1} cm^{-1}) which is attributable to the π–π^* transitions of the conjugated molecule. Under same conditions, the **JK-52** sensitizer exhibits absorption band at 425 nm ($\varepsilon = 48140$ dm^3 mol^{-1} cm^{-1}) that is blue-shifted compared to the **JK-51** sensitizer. A blue shift of **JK-52** can be understood from modeling studies of the two dyes. The ground state structure of **JK-51** possesses a 27.2° twist between the benzo[*cd*]indole and the thienyl unit (Fig. 4). For **JK-52**, the dihedral angle between the benzo[*cd*]indole and the thienyl unit is 54.8°, giving more twisted than that of **JK-51**. Therefore, a significant red shift of **JK-51** relative to **JK-52** derives from more delocalization over an entire conjugated system in **JK-51**. When the **JK-52** sensitizer was absorbed on TiO_2 electrode, a slight blue shift from 425 to 414 nm was found probably due to the H-aggregation (Fig. 5). The absorption spectra of **JK-51** and **JK-52** on TiO_2 electrode are broadened. Such broadening of the absorption spectra is due to an interaction between the dyes and TiO_2. [21] When the **JK-51** and **JK-52** sensitizers are excited within their π–π^* bands in an air-equilibrated solution and at 298 K, they exhibit strong luminescence maximum at 602 nm. No emission signal was observed for the two dyes on TiO_2 films, suggesting that the injection of the excited electron from the excited dye to the TiO_2 electrode is efficient.

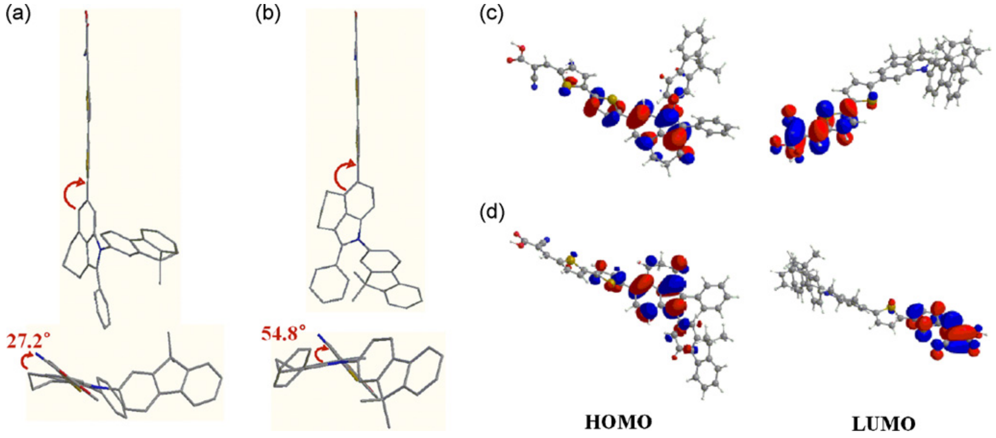


Fig. 4. The optimized structure of **JK-51** (a), **JK-52** (b) and the frontier molecular orbitals of the HOMO and LUMO of **JK-51** (c), **JK-52** (d) calculated with TD-DFT on B3LYP/3-21G*.

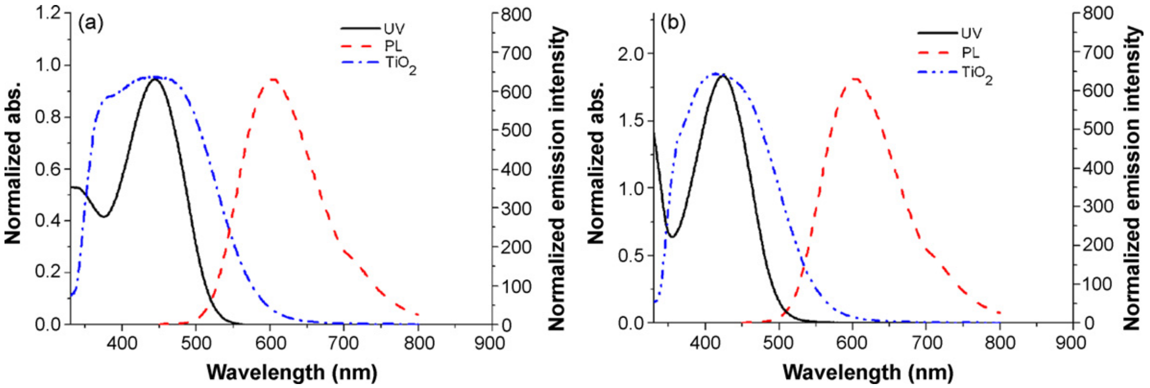


Fig. 5. Absorption (black, solid line) and emission (red, dashed line) spectra in ethanol, and absorption spectra on TiO_2 film (blue, dashed dot line) of **JK-51** (a) and **JK-52** (b).

3.3. *Redox behavior of benzo[cd]indole dyes*

Electrochemical properties of the **JK-51** and **JK-52** sensitizers were scrutinized by cyclic voltammetry in acetonitrile containing tetrabutylammonium hexafluorophosphate. TiO_2 films stained with sensitizer were used as working electrodes. The two organic dyes **JK-51** and **JK-52** absorbed on TiO_2 films show quasi-reversible couples. The oxidation potential of **JK-51** was measured to be 1.30 V vs NHE with a separation of 0.14 V between anodic-to-cathodic peak, which is due to the oxidation of [(9,9-dimethyl-9*H*-fluoren-2-yl)-1-phenylbenzo[*cd*]indol-4-yl] group. Under same conditions, the redox couple of **JK-52** dye was located at 1.53 V vs NHE. The oxidation potential of both sensitizers is energetically favorable for iodide oxidation. The oxidation potential of dye **JK-52** is more positive than that of dye **JK-51**. This reflects the decreased electron-donating ability compared to that of **JK-51** due to the localization on the benzo[*cd*]indole unit. The reduction potentials of the two dyes calculated from the oxidation potentials and the E_{0-0} determined from the intersection of absorption and emission spectra were listed in Table 1 [6b,c]. The excited-state oxidation potential ($E^{*}_{\rm ox}$) of the dyes (**JK-51**: −1.08 V vs NHE; **JK-52**: −0.91 V vs NHE) are more negative than the conduction level of TiO_2 at approximately −0.5 V vs NHE. [22] The LUMO of **JK-51** is more negative (about 0.17 V) than one of **JK-52**, increasing the driving force for electron injection to the TiO_2 surface (Table 1).

3.4. *Theoretical calculations of geometrical and electronic properties*

In order to obtain the geometrical configuration and the electronic structure of both organic dyes, molecular orbital calculations of the **JK-51** and **JK-52** sensitizers were performed with the TD-DFT on B3LYP/3-21G* [23]. The dihedral angle formed between the benzo[*cd*]indole and the thiophene plane is calculated to be

Table 1
Optical and electrochemical properties of **JK-51** and **JK-52**.

Dye	$\lambda_{\rm abs}{}^{a}$/nm (ε/M^{-1} cm^{-1})	$\lambda_{\rm abs}{}^{b}$/nm	$\lambda_{\rm em}{}^{c}$/nm	$E_{\rm ox}{}^{d}$ ($\Delta E_{\rm p}$)/V	$E_{0-0}{}^{e}$/V	$E_{\rm LUMO}{}^{f}$/V vs NHE
JK-51	445 (15188)	443	602	1.30 (0.27)	2.38	−1.08
JK-52	425 (48140)	414	602	1.53 (0.39)	2.44	−0.91

[a] Absorption spectra were measured in ethanol.
[b] Absorption spectra were measured on TiO_2 film.
[c] Emission spectra were measured in ethanol.
[d] 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}.
[e] E_{0-0} was determined from intersection of absorption and emission spectra in ethanol.
[f] $E_{\rm LUMO}$ was calculated by $E_{\rm ox}$–E_{0-0}.

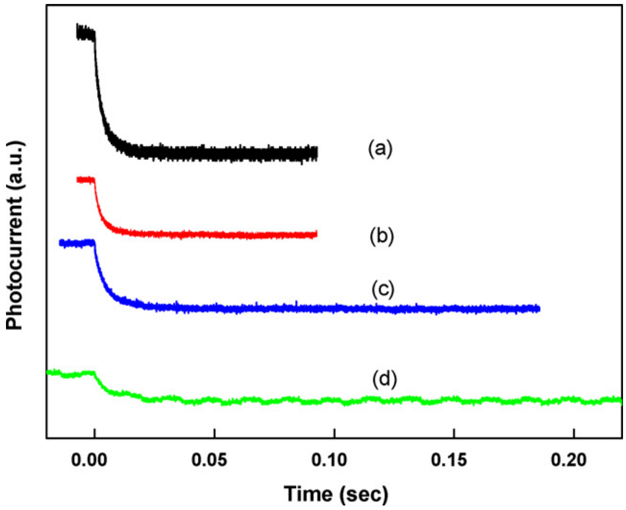


Fig. 6. Typical photocurrent profiles of the cell (**JK-51**) measured at the different stepped laser intensities. Initial short-circuit currents were (a) 350 μA, (b) 298 μA, (c) 164 μA, and (d) 38 μA.

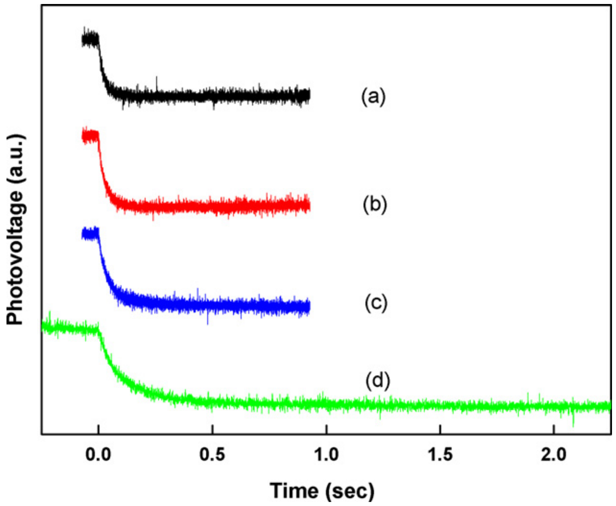


Fig. 7. Typical photovoltage profiles of the cell (**JK-51**) measured at the different stepped laser intensities. Initial open-circuit voltages were (a) 581 mV, (b) 575 mV, (c) 554 mV, and (d) 500 mV.

27.2° and 54.8° in **JK-51** and **JK-52** dyes, respectively, while the cyanoacrylic acid group was found to be almost coplanar with respect to the thiophene unit, reflecting the entire conjugation through the thiophene–cyanoacrylate groups. Fig. 4 shows the iso-density plots of the frontier molecular orbitals of **JK-51** and **JK-52**. The highest occupied molecular orbital (HOMO) of **JK-51** is delocalized over the thiophene ligand, with maximum components arising from the π-orbital of the nitrogen atom and the π-framework of benzo[*cd*]indole. On the other hand, the HOMO of **JK-52** is localized over the benzo[*cd*]indole due to the more twisted configuration between the benzo[*cd*]indole and thiophene unit. The LUMO of both dyes is delocalized over the cyanoacrylic unit and thiophene ligand, with sizable contribution from the cyano- and carboxylic moieties. Examination of the HOMO and LUMO of two dyes indicates that HOMO–LUMO excitation moved the electron distribution from the benzo[*cd*]indole unit to the cyanoacrylic acid moiety and the photo-induced electron transfer from the dyes to TiO_2 electrode can be efficiently occurred by the HOMO–LUMO transition.

3.5. *Laser-induced transient photocurrent and photovoltage measurements*

Electron transport in DSSCs can be characterized by two major parameters of electron diffusion coefficient (D_e) and electron lifetime (τ_e). D_e was derived by a time constant (τ_c) determined by fitting the decay of the photocurrent transients with a single exponential and the TiO_2 film thickness by $D_e = w^2/2.77\tau_c$ (here, w is the film thickness). [17a] Moreover, τ_e is the parameter related to the electron recombination and the dark current. This parameter can also be determined by fitting the decay of the photovoltage transients with a single exponential (*i.e.* $\exp(-t/\tau_e)$) [17a]. The typical photocurrent and the photovoltage time-profiles measured at the different stepped laser intensities are shown in Figs. 6 and 7, respectively (dye: **JK-51**). Fig. 8 shows the D_e (a) and τ_e (b) values versus short-circuit currents in the photoanodes adsorbing two isomeric dyes (*i.e.* **JK-51** and **JK-52**). 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 organic dyes are shown to be very similar each other at the identical short-circuit current conditions. This result indicates that the D_e values are hardly affected by the kind of dye molecules, showing the similar trend to those of coumarin

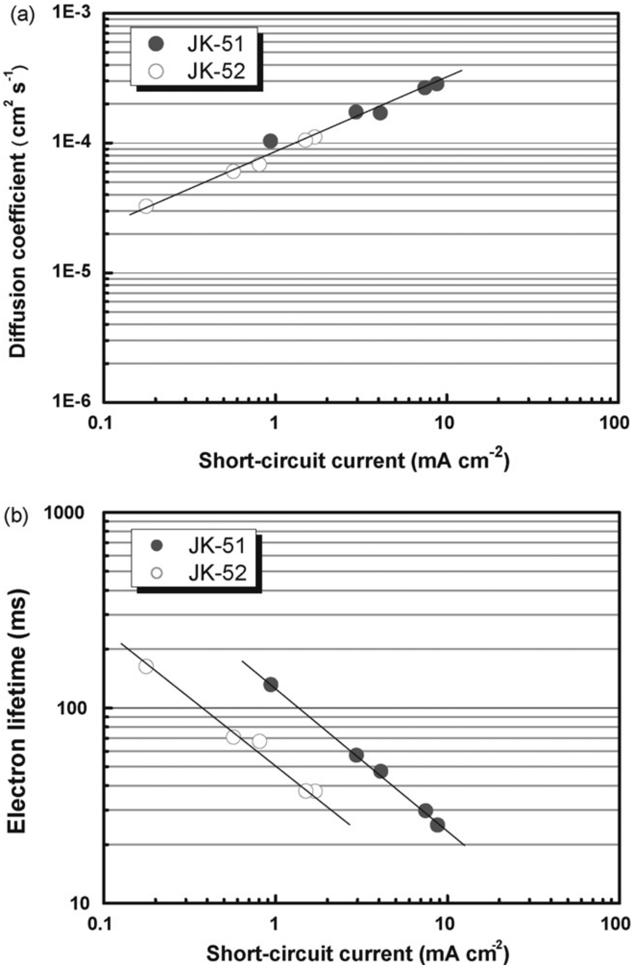


Fig. 8. Electron diffusion coefficients (a) and lifetimes (b) in the photoelectrodes adsorbing the dyes of **JK-51** and **JK-52**.

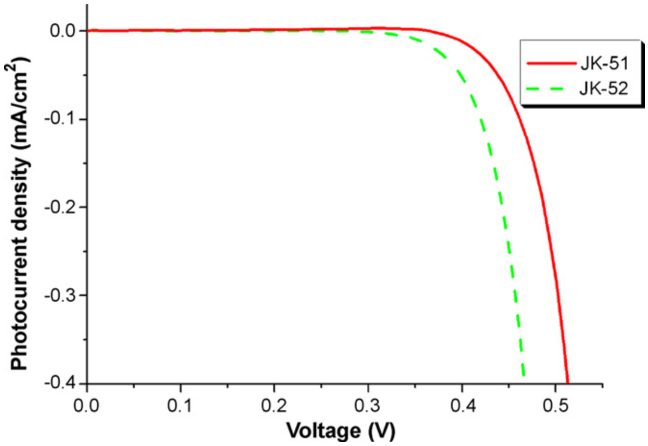


Fig. 9. The plot of dark current density versus negative bias potential for **JK-51** and **JK-52** dye-sensitized solar cells. The electrolyte used was 0.6 M 3-hexyl-1,2-dimethyl imidazolium iodide, 0.05 M I_2, 0.1 M LiI and 0.5 M *tert*-butylpyridine in acetonitrile.

dyes [24]. Meanwhile, the τ_e values of the photoelectrode with the **JK-52** dye were much smaller than those of the **JK-51** dye as shown in Fig. 8(b). Dark current properties for DSSCs based on these two dyes are also characterized and are shown in Fig. 9. The onset of dark current for a DSSC based on a **JK-51** dye is shifted negatively compared to the onset for a DSSC based on a **JK-52** dye, which indicates that dark current is suppressed in DSSCs based on a **JK-51** dye. Therefore, It is also evidenced that the τ_e values of the photoelectrode with the **JK-51** dye were much larger than those of the **JK-52** dye. It is believed that the dark current occurred more significantly in the electrode adsorbing the **JK-52** dye due to the relatively large TiO_2 surface area unoccupied by dye molecules.

3.6. Photovoltaic performance

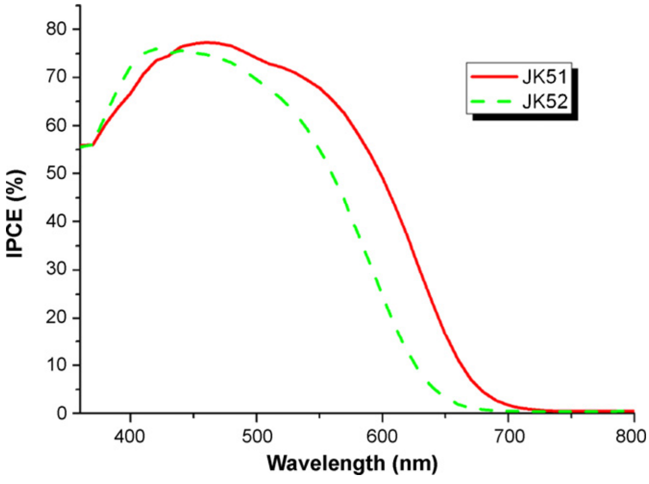


Fig. 10. Spectra of monochromatic incident photon-to-current conversion efficiencies (IPCEs) for DSSC: **JK-51** (red, solid line), **JK-52** (green, dashed line).

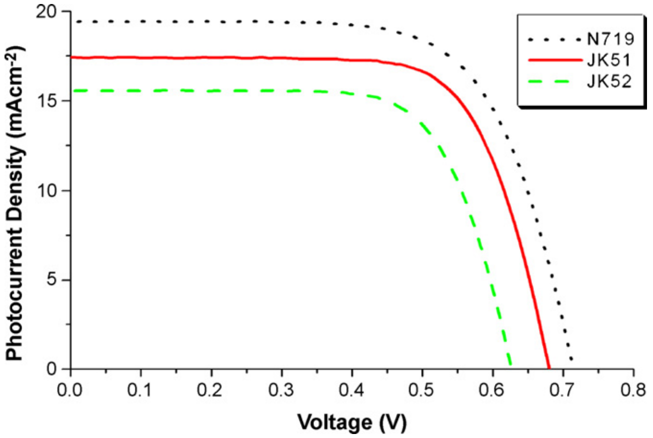


Fig. 11. Photocurrent density–voltage characteristics of DSSCs with **N-719** (black, dot line), **JK-51** (red, solid line) and **JK-52** (green, dashed line) at AM 1.5 illumination.

Table 2
DSSC performance parameters of dyes[a].

Dye	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
N719	19.42	0.714	0.68	9.42
JK-51	17.43	0.680	0.71	8.42
JK-52	15.56	0.626	0.70	6.88

[a] Performances of DSSCs were measured with 0.18 cm^2 working area.

Fig. 10 shows the incident monochromatic photon-to-current conversion efficiency (IPCE) for a sand with cell based on **JK-51** and **JK-52** (electrolyte: 0.6 M 3-hexyl-1,2-dimethyl imidazolium iodide, 0.04 M I_2, 0.025 M LiI and 0.28 M *tert*-butylpyridine in acetonitrile). The IPCE for dye **JK-52** exhibits a high peak about 76% at 422 nm and the IPCE of **JK-51** exhibits a maximum value about 77% at 460 nm. The **JK-51** sensitizer IPCE spectrum is red-shifted by 50 nm as compared to the **JK-52** as a result of extended π-conjugation, which is consistent with the absorption spectra of the **JK-51** and **JK-52** dyes. Under standard global AM 1.5 solar condition, the **JK-51** sensitized cell gave the short circuit photocurrent density (J_{sc}) of 17.43 mA/cm^2, and an open circuit voltage (V_{oc}) of 0.680 V and a fill factor (FF) of 0.71, corresponding to an overall conversion efficiency of 8.42% (Fig. 11). In the same condition, The **JK-52** sensitized cell gave a short circuit photocurrent density of 15.56 mA/cm^2, an open circuit voltage of 0.626 V and a fill factor of 0.70, corresponding to an overall conversion efficiency, η, of 6.88% (Table 2). From these results, we have observed the J_{sc} of dye **JK-51** was higher than that of dye **JK-52** even though the dye **JK-52** exhibited a high molar absorption coefficient. To explain this result, we measured the amounts of **JK-51** and **JK-52** absorbed on TiO_2 film. As the absorbed amount of **JK-51** (5.8×10^{-7} mol/cm^2) was larger than that of **JK-52** (7.7×10^{-8} mol/cm^2), the **JK-51** sensitizer showed more higher J_{sc} than the **JK-52**. In addition, the larger absorbed amount of **JK-51** also contributes higher V_{oc} due to the decrease of the dark current. Meanwhile, we consider that IPCE in the region of 440–700 nm for the **JK-51** sensitized solar cell is higher than that for **JK-52** due to a red-shift of **JK-51**, resulting in larger J_{sc} compared to that for **JK-52**. Finally, a small energy difference between the LUMO of **JK-52** and the conduction band of TiO_2 as compared with the **JK-51**, suppressing electron injection, may be a factor contributing to lower photocurrent performance of the **JK-52** sensitizer solar cell.

4. Conclusions

In summary, we have molecularly engineered a highly efficient novel type of two isomeric organic sensitizers. The organic sensitizer **JK-51** containing dimethylfluorenyl benzo[*cd*]indole moiety is very efficient dye for dye-sensitized solar cells, yielding 77% IPCE and 8.42% power conversion efficiency under standard AM 1.5 solar condition. We believe that the development of alternative efficient organic dyes to precious ruthenium complexes can be possible through the more sophisticated structural modifications, and these works are now in progress.

Acknowledgments

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