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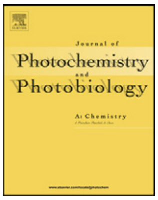

Molecular engineering of thia-bridged triphenylamine heterohelicenes as novel organic dyes for dye-sensitized solar cells

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ABSTRACT

Three organic sensitizers incorporating thia-bridged heterohelicene unit, thiophene-conjugate bridge, and cyanoacrylic acid were synthesized. The power conversion efficiency was quite sensitive to the substituents on heterohelicene donor group. Under standard global AM 1.5 solar conditions, the **JK-206**-sensitized cell gave a short-circuit photocurrent density (J_{sc}) of 13.44 mA cm^{-2}, an open-circuit voltage (V_{oc}) of 0.71 V, and a fill factor of 0.74, corresponding to an overall conversion efficiency of 7.08%. The device based on the **JK-206** with an ionic liquid electrolyte showed an excellent long-term stability. The initial efficiency of 5.6% for **JK-206** slightly decreased to only 5.4% after the 1000 h light soaking at 60 °C.

1. Introduction

Photovoltaic solar energy conversion represents a promising candidate to renewable resource [1]. Despite its advantages and continuing advances, photovoltaic technology still remains non cost-effective against traditional fossil fuels. For this purpose, the development of dye-sensitized solar cells (DSSCs) has received a great deal of attention from both academic and industrial fields owing to their low cost and high efficiency [2,3]. In these cells, dye is one of the key components for high power conversion efficiencies. Although some Ru^{II} polypyridyl sensitizers have achieved impressive efficiencies above 11% [4–7], they have some limitations to be addressed owing to the precious metal and difficult synthetic procedures. In this regard, organic sensitizers might be considered as an alternative to ruthenium sensitizers. However, the efficiency is still low compared with that of the ruthenium sensitizer. The main factors for the low efficiency of organic dyes are the formation of dye aggregate on the semiconductor surface [8–14], the interfacial recombination dynamics [15–17], and the short lifetime [18–20]. Our concept toward the high photovoltaic performance of organic-dye-sensitized solar cell is based on the structural modification of the dye to prevent the aggregation of dye and to diminish the charge recombination between the electrons and acceptors as well as to increase the lifetime of cation species. Organic dyes are composed of three components, donor, spacer and anchoring group. Triarylamine derivatives are electron donors in most of organic dyes [21–23]. The unsubstituted triphenylamine cations formed by the injection of electron to conduction band of TiO_2 are generally unstable. Accordingly, flattening the structure and introducing the *para* substituent on the phenyl unit would increase the stability and induce a red shift of the absorption spectrum as well as increase the electron lifetimes (τ_e) of the dye by the delocalization of the resulting cation on a flattened configuration [24,25]. In order to obtain insight into the structure–photophysical relationships on this system, we have investigated a bridged triarylamine heterohelicene, 2,2′:6′,2″-dithiatriphenylamine and its bulky substituents [26,27]. As part of our continuing efforts to develop novel organic dyes, we set out to synthesize organic sensitizers, coded as **JK-205**, **JK-206** and **JK-207**, which incorporate thia-bridged triarylamines as the electron donor and a cyano acrylic acid as the electron acceptor bridged by the oligothiophene.

In this article, as part of our efforts to develop novel organic dyes, we report new type of organic dyes (**JK-205**, **JK-206**, and **JK-207**) containing a flattened thia-bridged heterohelicene moiety as the electron donor and cyanoacrylic acid as the electron acceptor bridged by a variety of linkers (Structure 1).

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2. Experimental

2.1. General methods

All reactions were carried out under an argon atmosphere. Solvents were distilled from appropriate reagents. *p*-Bromo-*N*,*N*-diphenylaniline (**1**) [42], phthalimide-*N*-sulfenyl chloride (**4**) [32], 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-dioxaborolan (**7**) [43], 2,2′:6′,2″-dithiatriphenylamine (DTTPA) (**10**) [26,27], were synthesized using a modified procedure of previous references.

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 and a platinum wire electrode. Redox potential of dyes on TiO_2 was 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. Electron transport measurements

The electron diffusion coefficient (D_e) and lifetimes (τ_e) on TiO_2 photoelectrode were measured by the stepped light-induced transient measurements of photocurrent and voltage (SLIM-PCV) [44–47]. The transients were induced by a stepwise change in the laser intensity. A diode laser (λ = 635 nm) as a light source was modulated using a function generator. The initial laser intensity was a constant $90\,mW\,cm^{-2}$ and was attenuated up to approximately $10\,mW\,cm^{-2}$ using a ND filter which was positioned at the front side of the fabricated samples (TiO_2 film thickness = ca. 10 μm; active area = $0.04\,cm^2$). The photocurrent and photovoltage transients were monitored using a digital oscilloscope through an amplifier. The D_e value was obtained by a time constant (τ_c) determined by fitting a decay of the photocurrent transient with $\exp(-t/\tau_c)$ and the TiO_2 film thickness (ω) using the equation, $D_e = \omega^2/(2.77\tau_c)$. The τ_e value was also determined by fitting a decay of photovoltage transient with $\exp(-t/\tau_e)$. All experiments were carried out at room temperature.

2.4. Characterization of DSSC

The cells were measured using 1000 W 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. Synthesis

2.5.1. 7-Bromo(DTTPA) (1)

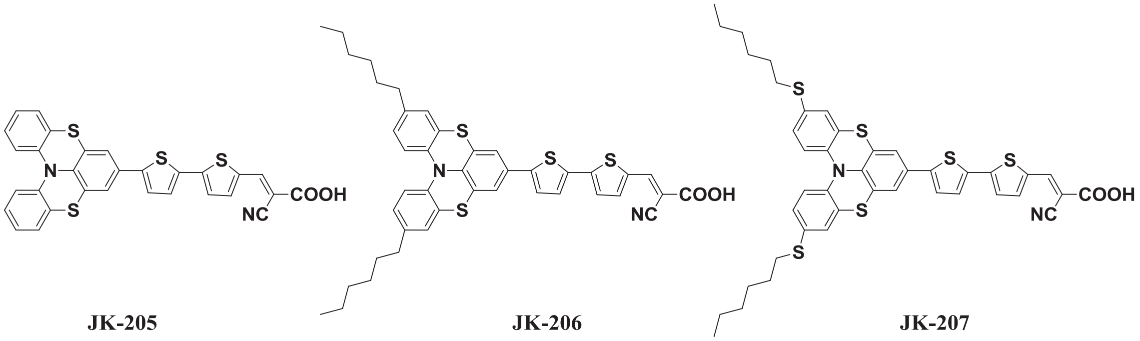
A stirred solution of thia-bridged triarylamine heterohelicene (1.36 g, 4.45 mmol) in acetic acid (60 mL) was flushed with nitrogen for 5 min, then bromine (0.25 mL, 4.90 mmol) was added dropwise, and stirring was continued for 8 h. The solution turned pink immediately, then changed gradually to deep red, next to green, and finally to black with the evolution of hydrogen bromide. The solvent was evaporated *in vacuo* to yield a black powdery material which was redissolved in aqueous sodium bicarbonate (30 mL). The resulting mixture was extracted with five 20-mL portions of benzene. The orange extracts were combined, dried over anhydrous Na_2SO_4, filtered and evaporated to yield an oily material. The pure product was obtained by silica gel chromatography using a mixture of methylene chloride and hexane (1:3) as an eluent (yield: 60%). Mp: 117 °C. ^1H NMR ($CDCl_3$): δ 7.33 (s, 2H), 7.24 (m, 4H), 7.02 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.2, 139.4, 130.6, 128.1, 127.7, 126.0, 125.1, 121.8, 120.6, 116.9. MS: *m*/*z* 384 [M$^+$]. Anal. Calcd. for $C_{18}H_{10}BrNS_2$: C, 56.25; H, 2.62. Found: C, 56.04; H, 2.48.

2.5.2. 2-(5-(5-(DTTPA-2)thiophen-2yl)thiophen-2-yl)-5,5-dimethyl-1,3-dioxane (3)

To a stirred solution of **1** (1.1 g, 1.98 mmol) and $Pd(PPh_3)_4$ (0.12 g, 0.099 mmol) in tetrahydrofuran (50 mL) was added 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 (**2**) (0.7 g, 2.37 mmol), potassium carbonate (1.64 g, 11.9 mmol) in THF (20 mL) and H_2O (5.9 mL). 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 **3** was obtained by silica gel chromatography using a mixture of methylene chloride and *n*-hexane (1:2) as an eluent (yield: 70%). Mp: 155 °C. ^1H NMR ($CDCl_3$): δ 7.42 (s, 2H), 7.33 (d, 2H, *J* = 8.1 Hz), 7.23–6.94 (m, 10H), 5.62 (S, 1H), 3.79 (d, 2H, *J* = 11.1 Hz), 3.66 (d, 2H, *J* = 11.1 Hz), 1.29 (S, 3H), 0.81 (S, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.4, 141.9, 141.6, 140.4, 137.7, 136.6, 132.3, 130.9, 128.1, 127.9, 127.6, 127.3, 127.2, 126.0, 125.5, 124.9, 123.7, 120.9, 98.2, 77.6, 23.1, 21.9. MS: *m*/*z* 583 [M$^+$]. Anal. Calcd. for $C_{32}H_{25}NO_2S_4$: C, 65.83; H, 4.32. Found: C, 65.72; H, 4.11.

2.5.3. 5-(5-(DTTPA-2-yl)thiophen-2-yl)thiophen-2-carbaldehyde (4)

THF (30 mL) and water (10 mL) were added to a flask containing acetal **3** (0.20 g, 0.37 mmol). Then, TFA (5 mL) was added to the solution. The resulting reaction mixture was stirred for 6 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),



JK-205 **JK-206** **JK-207**

Structure 1. The structure of **JK-205**, **JK-206**, and **JK-207**.

dried (Na_2SO_4), and evaporated *in vacuo*. The pure product **4** was obtained by silica gel chromatography using a mixture of methylene chloride and *n*-hexane (1:2) as an eluent (yield: 90%). Mp: 178 °C. ^{1}H NMR ($CDCl_3$): δ 9.87 (s, 1H), 7.68 (d, 2H, J = 8.1 Hz), 7.45 (s, 2H), 7.34 (m, 3H), 7.23 (m, 4H), 7.02 (m, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 182.6, 147.1, 145.7, 144.8, 142.7, 142.2, 139.3, 137.5, 135.2, 133.8, 130.5, 130.2, 129.6, 128.1, 127.3, 126.0, 125.4, 124.2, 120.9. MS: *m*/*z* 497 [M$^+$]. Anal. Calcd. for $C_{27}H_{15}NOS_4$: C, 65.16; H, 3.04. Found: C, 64.91; H, 2.90.

*2.5.4. 2-Cyano-3-(-5-(5-(DTTPA-2-yl)thiophen-2-yl)thiophen-2-yl)acrylic acid (**JK-205**)*

A mixture of **4** (0.17 g, 0.35 mmol) and cyanoacetic acid (0.04 g, 0.45 mmol) was vacuum-dried and added acetonitrile (20 mL), chloroform (20 mL) and piperidine (0.02 mL). The solution was refluxed for 6 h. After cooling the solution, the organic layer was removed *in vacuo*. The pure product of **JK-205** was obtained by silica gel chromatography using a mixture of methylene chloride and methanol (9:1) as an eluent (yield: 80%). Mp: 238 °C. ^{1}H NMR (DMSO): δ 8.00 (s, 1H), 7.73 (s, 2H), 7.64 (d, 2H, J = 6.9 Hz), 7.57 (d, 1H, J = 7.5 Hz), 7.49 (d, 1H, J = 6.3 Hz), 7.46 (d, 1H, J = 6.9 Hz), 7.38 (d, 2H, J = 7.5 Hz), 7.19 (m, 5H). ^{13}C{^{1}H} NMR (DMSO): δ 163.1, 145.1, 144.5, 143.5, 141.3, 140.7, 137.8, 136.8, 134.7, 132.9, 129.8, 128.7, 128.0, 127.1, 126.4, 125.2, 124.4, 123.1, 122.1, 118.1. MS: *m*/*z* 564 [M$^+$]. Anal. Calcd. for $C_{30}H_{16}N_2O_2S_4$: C, 63.81; H, 2.86; N, 4.96. Found: C, 63.57; H, 2.69; N, 4.78.

*2.5.5. 1,1′-(4,4′-(4-Bromophenylazanediyl)bis(4,1-phenylene)) dihexan-1-one (**5**)*

Anhydrous $AlCl_3$ (2.3 g, 17.2 mmol) was suspended in excess dry methylene chloride (30 mL) and kept at 0 °C with stirring. To this stirred suspension, hexanoyl chloride (1.74 g, 12.4 mmol) was added slowly for a period of 30 min, keeping the temperature at 0 °C during the addition. The reaction mixture was thawed to room temperature and stirring was continued at room temperature for an additional 30 min. To a stirred solution of anhydrous $AlCl_3$ and hexanoyl chloride in methylene chloride was added **1** (2 g, 6.17 mmol) in methylene chloride (20 mL). The reaction mixture was stirred at 60 °C for an additional 10 h. The $AlCl_3$-complex was then quenched by pouring the reaction mixture into crushed ice and cold 10% HCl. After cooling the solution, H_2O (30 mL) was added to the solution and extracted by methylene chloride (30 mL × 3). The organic layer was separated and dried in $MgSO_4$. The solvent was removed *in vacuo*. The pure product **5** was obtained by silica gel chromatography using a mixture of ethyl acetate and *n*-hexane (1:10) as an eluent (yield: 87%). Mp: 247 °C. ^{1}H NMR ($CDCl_3$): δ 7.88 (d, 4H, J = 9 Hz), 7.47 (d, 2H, J = 8.4 Hz), 7.10 (d, 4H, J = 9 Hz), 7.04 (d, 2H, J = 8.4 Hz), 2.89 (t, 4H, J = 7.2 Hz), 1.733 (m, 4H), 1.35 (m, 8H), 0.91 (t, 6H, J = 5.1 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 199.2, 150.6, 145.2, 133.1, 132.1, 129.9, 127.9, 122.8, 118.4, 38.5, 31.7, 24.4, 24.3, 22.7, 14.1. MS: *m*/*z* 521 [M$^+$]. Anal. Calcd. for $C_{30}H_{34}BrNO_2$: C, 69.23; H, 6.58. Found: C, 69.01; H, 6.39.

*2.5.6. 4-Bromo-N,N-bis(4-hexylphenyl)aniline (**6**)*

The product **5** (2.7 g, 5.23 mmol) was then subjected to reduction using hydrazine hydrate (1 mL, 31.4 mmol), KOH (1 g, 17.3 mmol) in ethylene glycol (50 mL) under reflux at 195 °C for 6 h. Ethylene glycol was then removed by distillation and the reaction mixture was poured to crushed ice and neutralized with 1 M HCl (10 mL) and extracted with dichloromethane. The combined dichloromethane phases were then washed with H_2O and dried with $MgSO_4$. The organic layer was removed *in vacuo*. The pure product **3** was obtained by silica gel chromatography using a hexane as an eluent (yield: 70%). Mp: 240 °C. ^{1}H NMR ($CDCl_3$): δ 7.29 (d, 2H, J = 8.7 Hz), 7.08 (d, 4H, J = 8.1 Hz), 7.00 (d, 4H, J = 8.7 Hz), 6.91 (d, 2H, J = 8.1 Hz), 2.57 (t, 4H, J = 7.8 Hz), 1.60 (m, 4H), 1.32 (m, 12H), 0.91 (t, 6H, J = 5.1 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 147.6, 145.1, 138.1, 132.0, 129.4, 124.7, 124.2, 113.8, 35.5, 31.9, 31.6, 29.2, 22.8, 14.2. MS: *m*/*z* 491 [M$^+$]. Anal. Calcd. for $C_{30}H_{38}BrN$: C, 73.16; H, 7.78. Found: C, 73.00; H, 7.62.

*2.5.7. 2,2′-((((4-Bromophenyl)azanediyl)bis(3-hexyl-6,1-phenylene))bis(sulfanediyl))bis(isoindoline-1,3-dione) (**7**)*

To a solution of **6** (1.15 g, 2.33 mmol) in dry $CHCl_3$ (60 mL) was added phthalimidesulfenyl chloride (PhtNSCl) (1.14 g, 5.36 mmol) under a nitrogen atmosphere. After stirring at 60 °C for 24 h, the reaction mixture was diluted with CH_2Cl_2 (10 mL), and washed with a saturated $NaHCO_3$ solution (2 × 30 mL) and water (2 × 30 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude material was purified by flash chromatography (CH_2Cl_2: hexane = 4:1) to provide **7** as a yellow solid (83% yield). ^{1}H NMR ($CDCl_3$): δ 7.92 (m, 4H), 7.75 (m, 4 H), 7.68 (d, 2H, J = 8.1 Hz), 7.28 (d, 2H, J = 7.5 Hz), 7.12 (d, 2H, J = 8.1 Hz), 6.91 (s, 2H), 6.61 (d, 2H, J = 7.5 Hz), 2.46 (t, 4H, J = 7.2 Hz), 1.48 (m, 4H), 1.16 (m, 12H), 0.81 (t, 6H, J = 5.1 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 168.3, 146.9, 142.4, 136.7, 134.4, 133.8, 132.4, 130.7, 130.4, 129.1, 128.2, 126.8, 124.2, 118.9, 35.5, 32.1, 31.8, 29.7, 23.0, 14.8. MS: *m*/*z* 847 [M$^+$]. Anal. Calcd. for $C_{46}H_{44}BrN_3O_4S_2$: C, 65.24; H, 5.24. Found: C, 64.88; H, 5.02.

*2.5.8. 4-Bromo(bis(3-hexyl-6,1-phenylene))-DTTPA (**8**)*

To a solution of compound **7** (1 g, 1.2 mmol) in dry CH_2Cl_2 (50 mL) was added $BF_3{\cdot}Et_2O$ (6 mL, 47 mmol) under a nitrogen atmosphere. After the mixture had been stirred for 3 h at room temperature, the mixture was diluted with CH_2Cl_2 (15 mL) and washed with a saturated Na_2CO_3 solution (100 mL × 2) and a saturated NaF solution (100 mL × 2). The organic layer was dried over $MgSO_4$. Evaporation of the solvent gave a crude product that was purified by flash chromatography using a mixture of petroleum ether and methylene chloride (1:1) as an eluent. The compound was further purified by recrystallization from $CHCl_3$ (yield: 60%). Mp: 169 °C. ^{1}H NMR ($CDCl_3$): δ 7.65 (d, 2H, J = 8.4 Hz), 7.25 (s, 2H), 7.21 (d, 2H, J = 8.4 Hz), 6.90 (s, 2H), 2.45 (t, 4H, J = 7.8 Hz), 1.55 (m, 4H), 1.27 (m, 12H), 0.87 (t, 6H, J = 5.1 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 141.4, 137.9, 137.7, 134.3, 133.7, 130.6, 127.6, 126.9, 125.6, 122.2, 34.9, 31.8, 31.5, 29.0, 22.7, 14.2. MS: *m*/*z* 553 [M$^+$]. Anal. Calcd. for $C_{30}H_{38}BrN$: C, 65.20; H, 6.20. Found: C, 65.03; H, 5.99.

*2.5.9. 2-((Bis(3-hexyl-6,1-phenylene)5-(5-(DTTPA-2)thiophen-2yl)thiophen-2-yl)-5,5-dimethyl-1,3-dioxane) (**9**)*

To a stirred solution of **8** (0.2 g, 0.36 mmol) and $Pd(PPh_3)_4$ (20 mg, 0.02 mmol) in tetrahydrofuran (20 mL) was added 4,4,5,5-tetramethyl-2-(5-(5-(5,5-dimethyl-1,3-dioxa n-2-yl)thiophen-2-yl) thiophen-2-yl)-1,3,2-dioxaborolane **2** (0.22 g, 0.54 mmol), potassium carbonate (0.2 g, 1.48 mmol) in THF (20 mL) and H_2O (0.8 mL). 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 **9** was obtained by silica gel chromatography using a mixture of methylene chloride and *n*-hexane (1:3) as an eluent (yield: 80%). Mp: 163 °C. ^{1}H NMR ($CDCl_3$): δ 7.72 (d, 2H, J = 8.4 Hz), 7.34 (d, 1H, J = 8.1 Hz), 7.25 (s, 2H), 7.19 (d, 2H, J = 8.4 Hz), 7.05 (m, 2H), 6.91 (s, 2H), 6.33 (d, 1H, J = 8.1 Hz), 5.62 (S, 1H), 3.78 (d, 2H, J = 7.5 Hz), 3.66 (d, 2H, J = 7.5 Hz), 2.44 (t, 4H, J = 7.8 Hz), 1.53 (m, 4H), 1.27 (m, 12H), 1.12 (S, 3H), 0.91 (S, 3H), 0.81 (t, 6H, J = 5.1 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 147.0, 145.1, 141.2, 141.0, 137.6, 136.9, 134.5, 127.9, 127.1, 126.7, 126.4, 126.1, 125.7, 123.8, 123.7, 123.1, 122.5, 118.1, 98.1, 76.7, 34.9, 31.6, 31.2, 29.0, 22.5, 21.4, 21.1, 14.0.

MS: *m*/*z* 751 [M$^+$]. Anal. Calcd. for $C_{44}H_{49}NO_2S_4$: C, 70.26; H, 6.57. Found: C, 70.01; H, 6.45.

*2.5.10. Bis(3-hexyl-6,1-phenylene)-5-(5-(DTTPA-2-yl)thiophen-2-yl)thiophen-2-carbaldehyde (**10**)*

THF (30 mL) and water (10 mL) were added to a flask containing acetal **9** (0.4 g, 0.53 mmol). TFA (5 mL) was added to the solution. The resulting reaction mixture was stirred for 6 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 with Na_2SO_4, and evaporated *in vacuo*. The pure product **10** was obtained by silica gel chromatography using a mixture of methylene chloride and *n*-hexane (1:1) as an eluent (yield: 91%). Mp: 188 °C. ^{1}H NMR ($CDCl_3$): δ 9.84 (s, 1H), 7.68 (d, 2H, *J* = 8.1 Hz), 7.65 (d, 2H, *J* = 8.1 Hz), 7.33 (m, 5H), 6.99 (s, 1H), 6.76 (d, 1H, *J* = 8.1 Hz), 6.44 (d, 1H, *J* = 8.1 Hz), 2.45 (t, 4H, *J* = 7.8 Hz), 1.52 (m, 4H), 1.26 (m, 12H), 0.86 (t, 6H, *J* = 5.1 Hz). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 182.5, 147.2, 145.5, 141.8, 138.2, 137.4, 137.3, 135.3, 128.5, 127.9, 127.7, 127.3, 127.2, 126.9, 126.2, 124.4, 124.2, 123.6, 118.5, 35.0, 31.8, 31.4, 29.1, 22.7, 14.2. MS: *m*/*z* 665 [M$^+$]. Anal. Calcd. for $C_{39}H_{39}NOS_4$: C, 70.33; H, 5.90; N, 2.10. Found: C, 70.12; H, 5.78; N, 178.

*2.5.11. 2-Cyano-3-((bis(3-hexyl-6,1-phenylene)-5-(5-(DTTPA-2-yl)thiophen-2-yl)thiop-hen-2-yl)acrylic acid) (**JK-206**)*

A mixture of **9** (0.40 g, 0.60 mmol) and cyanoacetic acid (0.07 g, 0.78 mmol) was vacuum-dried and added acetonitrile (20 mL), chloroform (15 mL) and piperidine (0.02 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 using a mixture of methylene chloride and methanol (9:1) as an eluent (yield: 87%). Mp: 254 °C. ^{1}H NMR ($CDCl_3$): δ 8.11 (s, 1H), 7.87 (s, 2H), 7.70 (d, 2H, *J* = 6.9 Hz), 7.59 (d, 1H, *J* = 6.9 Hz), 7.53 (d, 2H, *J* = 8.4 Hz), 7.32 (d, 1H, *J* = 8.4 Hz), 6.98 (s, 2H), 6.85 (d, 1H, *J* = 8.1 Hz), 6.40 (d, 1H, *J* = 8.1 Hz), 2.43 (t, 4H, *J* = 7.8 Hz), 1.47 (m, 4H), 1.23 (m, 12H), 0.83 (t, 6H, *J* = 5.1 Hz). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 163.3, 145.6, 145.1, 140.2, 138.1, 136.4, 136.1, 134.2, 132.9, 127.9, 127.6, 127.4, 127.1, 126.8, 126.4, 125.9, 123.8, 123.5, 122.9, 118.3, 34.8, 31.6, 31.3, 29.0, 22.4, 14.1. MS: *m*/*z* 732 [M$^+$]. Anal. Calcd. for $C_{42}H_{40}N_2O_2S_4$: C, 68.82; H, 5.50; N, 3.82. Found: C, 68.71; H, 5.37; N, 3.72.

*2.5.12. 5-(5-(4,9-Dibromo-DTTPA-2-yl)thiophen-2-yl)thiophen-2-carbaldehyde (**11**)*

To a solution of **3** (0.17 g, 0.35 mmol) in dichloromethane (20 mL) and freshly distilled acetonitrile (20 mL) was added pyridinium bromide perbromide (0.248 g, 0.78 mmol) in portions over a period of 20 min. The pure product was obtained by silica gel chromatography using a mixture of methylene chloride and hexane (1:2) as an eluent (yield: 30%). Mp: 181 °C. ^{1}H NMR ($CDCl_3$): δ 9.89 (s, 1H), 7.68 (s, 2H), 7.55 (s, 2H), 7.48 (d, 2H, *J* = 7.8 Hz), 7.37 (d, 1H, *J* = 7.8 Hz), 7.28 (m, 2H), 7.14 (d, 1H, *J* = 8.1 Hz), 7.02 (m, 2H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 182.1, 147.9, 146.2, 145.4, 143.2, 142.7, 139.9, 138.0, 135.8, 134.1, 130.9, 130.7, 130.1, 128.7, 127.9, 126.4, 125.9, 124.8, 121.3. MS: *m*/*z* 654 [M$^+$]. Anal. Calcd. for $C_{27}H_{13}Br_2NOS_4$: C, 49.47; H, 2.00. Found: C, 49.31; H, 1.88.

*2.5.13. 2-(5-(5-(4,9-Dibromo-DTTPA-2)thiophen-2yl)thiophen-2-yl)-5,5-dimethyl-1,3-dioxane (**12**)*

To a stirred solution of **11** (0.4 g, 0.60 mmol) and *p*-toluenesulfonic acid monohydrate (0.012 g, 0.06 mmol) in benzene (50 mL) was added neophentylglycol (0.08 g, 0.72 mmol) in benzene. The mixture was refluxed at 90 °C for 8 h. After cooling the solution, aqueous sodium bicarbonate (40 mL) was added to the solution and extracted by H_2O and dichloromethane (40 mL × 3). The organic layer was separated and dried in $MgSO_4$. The solvent was removed *in vacuo*. The pure product **12** was obtained by silica gel chromatography using a mixture of methylene chloride and *n*-hexane (1:1) as an eluent (yield: 70%). Mp: 157 °C. ^{1}H NMR ($CDCl_3$): δ 7.54 (s, 2H), 7.46 (d, 2H, *J* = 8.1 Hz), 7.36 (d, 1H, *J* = 7.2 Hz), 7.27 (m, 2H), 7.20–7.01 (m, 3H), 7.00 (s, 2H), 5.62 (s, 1H), 3.78 (d, 2H, *J* = 11.1 Hz), 3.66 (d, 2H, *J* = 11.1 Hz), 1.29 (S, 3H), 0.81 (S, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 142.8, 142.5, 142.1, 141.3, 138.4, 137.5, 132.9, 131.6, 129.1, 128.5, 128.1, 127.8, 127.6, 126.7, 126.1, 125.7, 124.4, 121.5, 98.6, 77.9, 23.3, 22.1. MS: *m*/*z* 740 [M$^+$]. Anal. Calcd. for $C_{32}H_{23}Br_2NO_2S_4$: C, 51.83; H, 3.13. Found: C, 51.31; H, 2.99.

*2.5.14. Bis(4,9-hexylsulfanyl)-5-(5-(DTTPA-2-yl)thiophen-2-yl)thiophen-2-carbaldehyde (**13**)*

To the solution of 1-hexanethiol (0.12 g, 0.77 mmol) in HMPA (30 mL, dried over 4 Å molecular sieve) was added sodium hydride (60% dispersion in mineral oil, 0.03 g, 0.77 mmol) in one portion. The mixture was stirred under argon until the hydrogen evolution ceased, then heated with an oil-bath at 100 °C for 5 min. Compound **12** (0.1 g, 0.18 mmol) was added and the mixture was stirred at 100 °C under argon atmosphere for 5 h to afford a yellow solution. Ice-water (50 mL) was added followed by the addition of hydrochloric acid to adjust the pH to about 1. The mixture was extracted with dichloromethane (2 × 50 mL) and the DCM phase was dried over $MgSO_4$. The solvent was removed *in vacuo*. The pure product **13** was obtained by silica gel chromatography using a mixture of methylene chloride and *n*-hexane (1:3) as an eluent (yield: 55%). Mp: 189 °C. ^{1}H NMR ($CDCl_3$): δ 9.87 (s, 1H), 7.69 (d, 2H, *J* = 6.9 Hz), 7.60 (d, 1H, *J* = 6.6 Hz), 7.51 (s, 2H), 7.42 (d, 2H, *J* = 6.9 Hz), 7.22 (m, 3H), 7.01 (s, 2H), 2.87 (t, 4H, *J* = 7.5 Hz), 1.64 (m, 4H), 1.41 (m, 4H), 1.33 (m, 8H), 0.88 (t, 6H, *J* = 6.9 Hz). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 182.5, 147.0, 146.4, 144.2, 142.9, 141.8, 137.2, 135.4, 130.7, 130.5, 130.1, 128.9, 128.3, 126.2, 125.5, 124.8, 122.1, 120.4, 117.5, 36.7, 32.4, 32.0, 30.2, 23.4, 14.6. MS: *m*/*z* 729 [M$^+$]. Anal. Calcd. For $C_{39}H_{39}NOS_6$: C, 64.16; H, 5.38. Found: C, 63.89; H, 5.15.

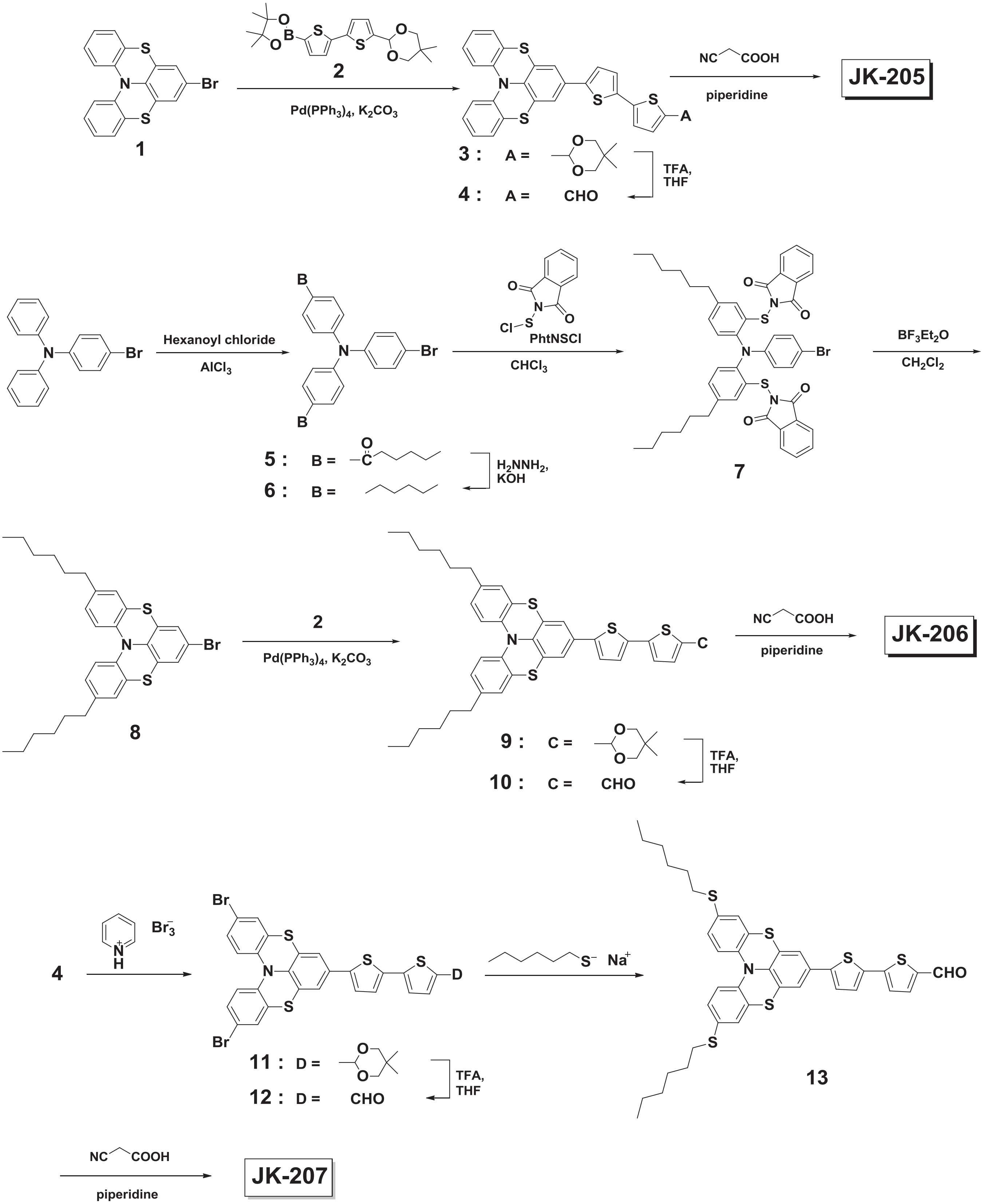
*2.5.15. 2-Cyano-3-(bis(4,9-hexylsulfanyl)-5-(5-(DTTPA-2-yl)thiophen-2-yl)thiophen-2-yl)acrylic acid (**JK-207**)*

A mixture of **13** (0.07 g, 0.10 mmol) and cyanoacetic acid (0.012 g, 0.14 mmol) was vacuum-dried and added acetonitrile (20 mL), chloroform (20 mL) and piperidine (0.02 mL). The solution was refluxed for 6 h. After cooling the solution, the organic layer was removed *in vacuo*. The pure product of **JK-207** was obtained by silica gel chromatography using a mixture of methylene chloride and methanol (9:1) as an eluent (yield: 70%). Mp: 241 °C. ^{1}H NMR ($CDCl_3$): δ 8.08 (s, 1H), 7.65 (d, 2H, *J* = 6.9 Hz), 7.62 (s, 2H), 7.50 (m, 3H), 7.15 (m, 5H), 2.84 (t, 4H, *J* = 7.5 Hz), 1.61 (m, 4H), 1.38 (m, 4H), 1.19 (m, 8H), 0.86 (t, 6H, *J* = 6.9 Hz). $^{13}C\{^{1}H\}$ NMR (DMSO): δ 163.1, 146.0, 145.1, 143.8, 142.1, 141.2, 136.7, 134.1, 132.5, 130.1, 129.6, 129.3, 128.4, 128.1, 125.9, 125.1, 124.2, 121.7, 119.8, 117.1, 36.3, 32.1, 31.6, 29.8, 22.9, 14.3. MS: *m*/*z* 796 [M$^+$]. Anal. Calcd. For $C_{42}H_{40}N_2O_2S_6$: C, 63.28; H, 5.06; N, 3.51. Found: C, 63.02; H, 4.89; N, 3.38.

3. Results and discussion

3.1. Synthesis

Scheme 1 outlines the stepwise synthetic protocol of **JK-205–207**. Compound **1** was synthesized by bromination of a thia-bridged triarylamine heterohelicene with NBS in $CHCl_3$ [28]. The Suzuki coupling reaction [29–31] of **1** with 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, **2**, followed by subsequent cleavage of 1,3-dioxalane protecting group in TFA



Scheme 1. Synthetic route of dyes **JK-205–207**.

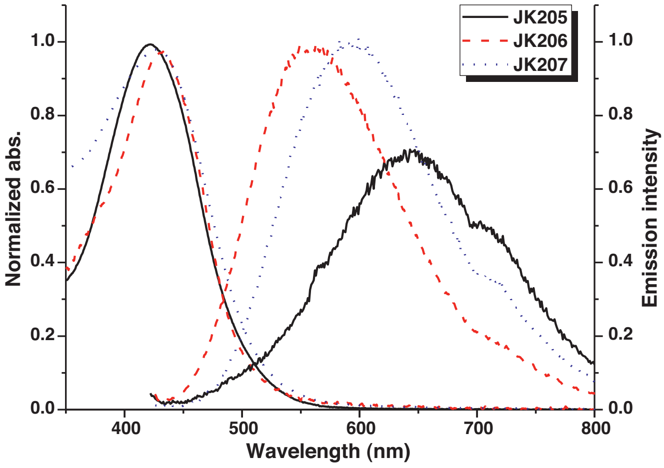


Fig. 1. Absorption and emission spectra of **JK-205** (solid line), **JK-206** (dash line), and **JK-207** (dot line) in THF.

produced the aldehyde **4**. The aldehyde **4** reacted with cyanoacetic acid in the presence of a catalytic amount of piperidine to yield the **JK-205**. For the synthesis of the dyes **JK-206** and **JK-207** the compounds **7** and **11** are key intermediates. The first key intermediate **7** was synthesized by disulfenylation of phenyl unit *ortho* to the amine nitrogen atom using the phthalimidesulfenyl chloride (PhtNSCl) [32]. The second key material is the compound **11**, which is synthesized by bromination of **3** using pyridinium bromide perbromide. The three organic dyes are obtained in moderate yields and soluble in common organic solvents.

3.2. Spectroscopic studies and theoretical calculations of geometrical properties

Fig. 1 shows the electronic absorption spectrum of **JK-205**–**207** in THF. The absorption spectrum of **JK-206** exhibits one strong absorption peak at 432 nm, which is due to the π–π* transition of the conjugate molecule. Under similar conditions the **JK-205** sensitizer shows an absorption peak at 422 nm that is slightly blue-shifted relative to that of **JK-206**. A slight blue shift of **JK-205** relative to **JK-206** can be readily interpreted by the molecular modeling study of the two dyes. The ground state structure of **JK-205** possesses at 25.6° twist between phenylamine and thienyl unit. The dihedral angle of the two thienyl units in **JK-205** is 6.3° (Fig. 2). For **JK-206**, the dihedral angles of the corresponding units are 22.6° and 6.1°, respectively, giving a more planar configuration. Accordingly, a red shift of **JK-206** compared to **JK-205** derives from more delocalization over an entire conjugated system in **JK-206**.

The introduction of hexylsulfanyl unit in **JK-205** decreases the dihedral angles between phenyl amine and thienyl unit and the two thienyl units from 25.6° and 6.3° in **JK-205** to 23.3° and 5.9° in **JK-207**, giving a more planar configuration (Fig. 2). A slight blue shift relative to **JK-206** can be interpreted as the *H*-aggregation due to the intermolecular S···S interaction. Such an intermolecular S···S contact has been observed in thiadiazole units incorporated into polythiophene chains [33]. When the **JK-205**, **JK-206**, and **JK-207** sensitizers are excited within their π–π* bands in an air-equilibrated solution at 298 K, the photoluminescence spectrum of **JK-205** gives a broad absorption with a maximum centered at 643 nm. However, the PL spectra of **JK-206** and **JK-207** exhibit strong luminescence maxima of 559 and 592 nm, respectively. The blue shift of 84 nm in **JK-206** and 51 nm in **JK-207** from the **JK-205** PL maximum at 643 nm is related to the narrow energy gap between the ground and excited state due to the rigidity of both organic dyes, which are difficult to rotate. Therefore, the large Stokes shift of **JK-205** relative to that of **JK-206** and **JK-207** may be attributable to the easy rotation of **JK-205** relative to **JK-206** and **JK-207** having long alkyl chains.

3.3. Redox behavior of dyes

Cyclic voltammetry measurements were used to study the redox behavior of the three dyes in THF (Table 1). The three dyes adsorbed on TiO_2 films show quasi-reversible couples. The oxidation potentials of three dyes (1.15–1.41 V *vs* NHE) are more positive than the Nernst potential of $I^-/I_3{}^-$ redox couple. The excited state oxidation potentials (E^*_{ox}) of the dyes (−1.16 to −1.32 V *vs* NHE) are sufficiently negative than the conduction band of TiO_2 (−0.5 V *vs* NHE), ensuring the thermodynamic driving force for electron injection [34–36].

3.4. Theoretical calculations of electronic properties

We performed DFT/TDDFT calculations to gain insight into the nature of the electronic absorption origin. The calculation shows that the HOMO−1 and HOMO of **JK-205** are delocalized over the π-conjugated system throughout the dye (Fig. 3). The LUMO is a π* orbital delocalized over π-conjugated system, with a sizable electron density distribution over the cyanoacrylic unit. Theoretical excited-state TDDFT calculations illustrate that the lowest transition of **JK-205** at 439 nm (f = 0.90) is mainly characterized by a mixture of HOMO−1 → LUMO (64%) and HOMO → LUMO excitation, affording a charge flow from the amino core to the anchoring unit.

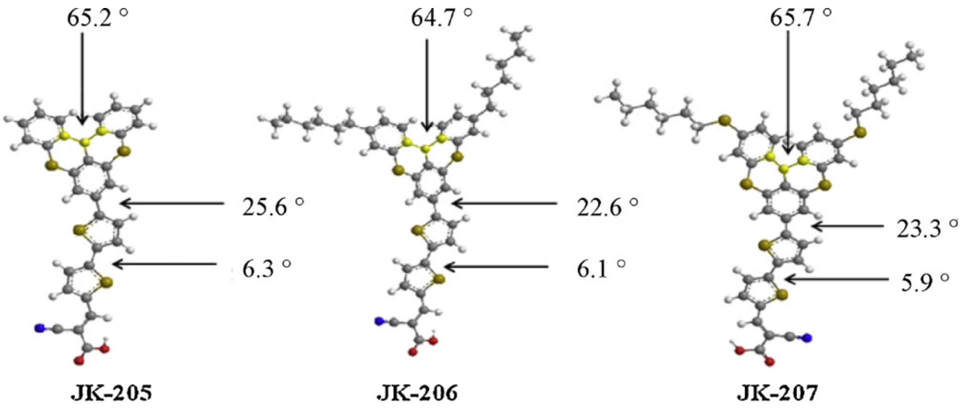


Fig. 2. The optimized structure calculated with TDDFT on B3LYP/3-21G* of **JK-205**, **JK-206**, and **JK-207**.

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 [e] (%)
JK-205	422(17,370)	1.15	2.47	−1.32	12.19	0.67	0.73	5.96
JK-206	432(13,090)	1.24	2.4	−1.16	13.44	0.71	0.74	7.08
JK-207	427(12,900)	1.41	2.43	−1.02	10.88	0.63	0.75	5.24

[a] Absorption spectra were measured in THF solution.

[b] Oxidation potentials of dyes on TiO_2 were measured in CH_3CN with 0.1 M (n-C_4H_9)$_4$$NPF_6$ with a scan rate of 50 mV s^{-1} (*vs* NHE).

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

[d] E_{LUMO} was calculated by $E_{ox} - E_{0-0}$.

[e] Performances of DSSCs were measured with 0.18 cm^2 working area. ε: absorption coefficient; E_{ox}: oxidation potential; E_{0-0}: voltage of intersection point between absorption and emission spectra; J_{sc}: short circuit photocurrent density; V_{oc}: open circuit photovoltage; *ff*: fill factor; η: total power conversion efficiency.

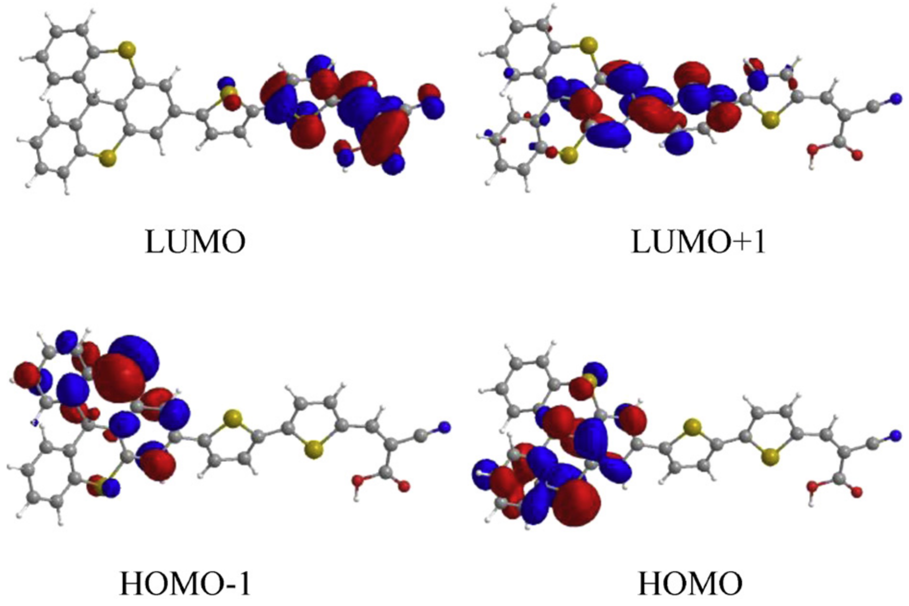


Fig. 3. The molecular structures and the frontier molecular orbitals of the HOMO−1, HOMO and LUMO, LUMO+1 calculated with B3LYP/3-21G* of **JK-205**.

3.5. Photovoltaic performance

The photovoltaic performances of the three dye-sensitized cells are shown in Table 1.

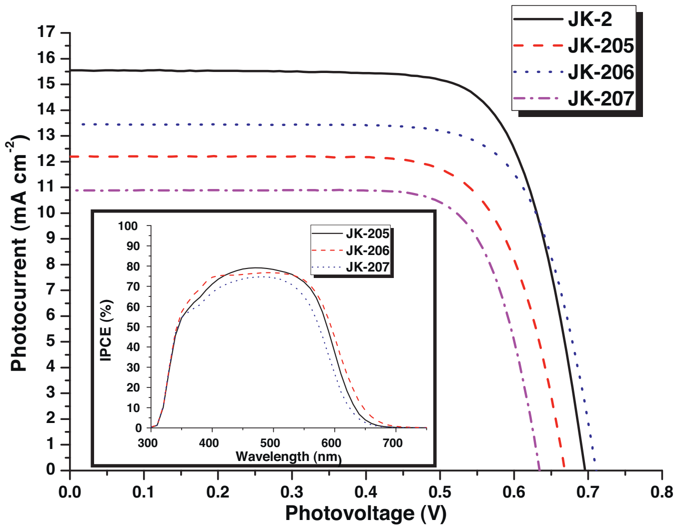


Fig. 4. Photocurrent–voltage characteristics of representative TiO_2 electrodes sensitized with dye: **JK-205** (solid line), **JK-206** (dash line), and **JK-207** (dot line). The inset shows the IPCE spectra of the DSSCs as a function of the wavelength of the light.

For reference, the photovoltaic performance of **JK-2** is included. The incident monochromatic photon-to-current conversion efficiency (IPCE) of **JK-206** exceeds 70% over the spectral region from 380 to 590 nm, reaching its maximum of 77% at 525 nm (inset of Fig. 4). The bands tail off toward 710 nm, under standard global air mass (AM) 1.5 solar conditions, the **JK-206** sensitized cell gave a short-circuit photo current density (J_{sc}) of 13.44 mA cm^{-2}, an open-circuit voltage (V_{oc}) of 0.71 V, and a fill factor (*ff*) of 0.74, affording an overall conversion efficiency (η) of 7.08%. Under the same conditions, the **JK-205** sensitized cell gave a J_{sc} value of 12.19 mA cm^{-2}, a V_{oc} of 0.67 V and a *ff* of 0.73, corresponding to an η value of 5.96%. From these results (Table 1), we have observed that the η value of **JK-206** based cell is higher than that of **JK-205** based cell due to a large photocurrent and voltage. Of particular importance is the 40 mV increase of open-circuit voltage in **JK-206** relative to the **JK-205** based cell. It has well been documented that alkyl substitution of the sensitizer improved the V_{oc} due to the blocking effect of the charge recombination between I_3^- and electrons injected in the nanocrystalline electrode [37–41]. Similarly, the power conversion efficiency of **JK-207** is relatively low compared to that of **JK-205**. To clarify the above result, we have measured the amount of dyes adsorbed on the TiO_2 film. The adsorbed amounts of 2.86×10^{-6} mmol cm^{-2} for **JK-205**, 2.68×10^{-6} mmol cm^{-2} for **JK-206**, and 2.32×10^{-6} mmol cm^{-2} for **JK-207** are observed. Therefore, the large adsorbed amount of **JK-205** relative to **JK-207** contributes a high V_{oc} due to the decrease of dark current.

Another explanation is that the bent hexylsulfanyl units with a large sweeping angle in **JK-207** lead to a loose packing, leaving more

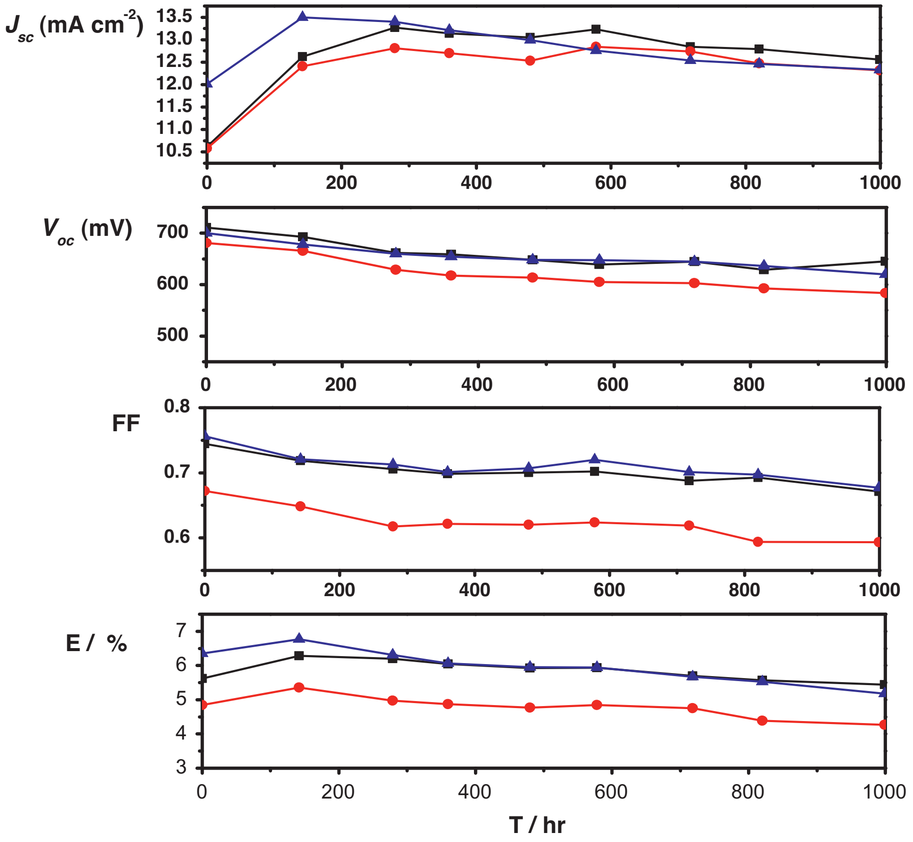


Fig. 5. Evolution of solar-cell parameters with **JK-205** (●), **JK-206** (■) and **JK-2** (▲) during visible-light soaking (AM 1.5 G, 100 mW cm^{-2}) at 60 °C. A 420 nm cut-off filter was placed on the cell surface during illumination. Ionic liquid electrolyte 2: 0.2 M iodine, 0.5 M NMBI, 0.1 M GuNCS in PMII/EMINCS (13:7).

vacant sites between dye molecules. This may lead to facilitate the charge recombination between the electrons and I_3^-.

3.6. *Stability of dyes*

Fig. 5 shows the photovoltaic performance during long-term accelerated aging test of **JK-205** and **JK-206** using an ionic-liquid electrolyte composed of 0.2 M I_2, 0.5 M *N*-methyl benzimidazole (NMBI), and 0.1 M guanidiniun thiocyanate (GuNCS) in 1-meth yl-3-propylimidazolium iodide (PMII)/1-methyl-3-ethylimidazolium thiocyanate (EMI NCS) (13:7). The device of **JK-206** showed an excellent long-term stability. The initial efficiency of 5.6% slightly decreased to 5.4% during the 1000 h light-soaking test at 60 °C. After 1000 h of light soaking test, the V_{oc} of **JK-206** decreased by 66 mV, but the loss was compensated by a slight increase in the short-circuit current density.

On the other hand, the initial efficiency of 4.8% in **JK-205** sharply decreased to 4.2% after 1000 h of light soaking at 60 °C because the V_{oc} of **JK-205** sharply decreased by 97 mV. The enhanced long stability of **JK-206** relative to **JK-205** can be related to the introduction of hexyl units by suppressing the approach of I_3^- to the TiO_2 film, resulting in preventing the dark current.

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

Fig. 6 shows the lifetimes of the DSSCs employing three dyes (**JK-205**, **JK-206**, and **JK-207**) displayed as a function of the V_{oc}. The order of magnitude of the τ_e values was well consistent with that of the V_{oc} shown in Table 1. The **JK-206** dye having hexyl groups exhibited approximately 3.7 times longer electron lifetime compared with that of **JK-205**. However, the τ_e values of **JK-207** with the sulfur linkage in the alkyl group were much smaller than that of **JK-206** because the S···S interaction of hexylsulfanyl units may lead to the dye aggregation.

3.8. *Electrochemical impedance study*

Fig. 7 shows the ac impedance spectra of the DSSCs measured under illumination. A smaller radius of the semicircle in this intermediate frequency regime implies a lower rate of

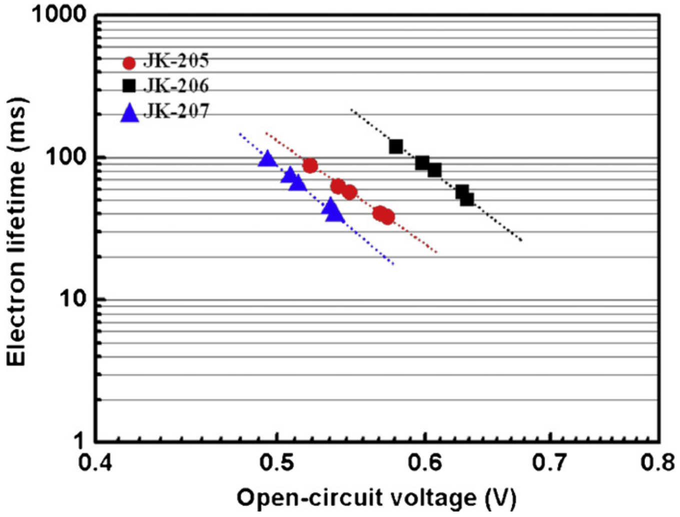


Fig. 6. Electrochemical impedance spectra measured under the illumination (100 mW cm^{-2}) for the cells employing different dyes (i.e. **JK-205**, **JK-206**, and **JK-207**).

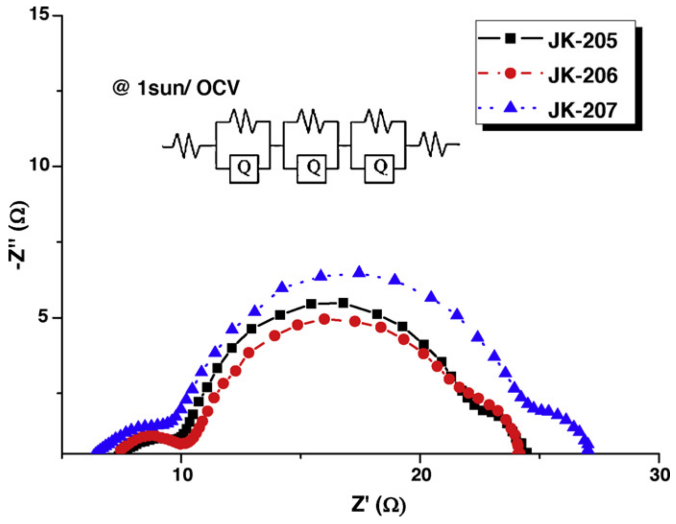


Fig. 7. Electrochemical impedance spectra measured under the illumination (100 mW cm^{-2}) for the cells employing different dyes (i.e. **JK-205**, **JK-206**, and **JK-207**).

electron recombination at the TiO_2/dye/electrolyte interface. Upon illumination under open-circuit conditions (100 mW cm^{-2}), the response of intermediate semicircle is attributable to the deposited dye on the TiO_2/electrolyte. A capacitance (689.3 μF/cm^2) of **JK-206** derived from $(Y_0 \times R)^{(1/n)/R}$, where Y_0 [s^n cm^{-2}] is the symbol for the constant phase element, n is freq power, and R is resistance, is higher than that of **JK-205** (523 μF/cm^2), and **JK-207** (428.3 μF/cm^2) and the resistance of **JK-206** (13.42 Ω) is low compared with that of **JK-205** (14.36 Ω) and **JK-207** (15.44 Ω). As a result, the photocurrent of **JK-206** (13.44 mA cm^{-2}), **JK-205** (12.19 mA cm^{-2}), and **JK-207** (10.88 mA cm^{-2}) is in good agreement with the trends observed in the above data.

4. Conclusion

We have meticulously designed and synthesized a new class of thia-bridged heterohelicene dyes. A solar-cell device based on the sensitizer **JK-206** in conjunction with a volatile electrolyte gave an overall conversion efficiency of 7.08%. The power conversion efficiency of the DSSCs based on the three sensitizers was shown to be sensitive to the substituents. The **JK-206** device showed an excellent stability under light soaking at 60 °C for 1000 h. We believe that development of highly efficient DS SCs devices with robustness is possible through the structural modifications, and work on these is now in progress.

Acknowledgment

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