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Synthesis of new julolidine dyes having bithiophene derivatives for solar cell

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Abstract—Three novel organic dyes containing julolidine and bithiophene derivatives were synthesized. Nanocrystalline TiO_2 dye-sensitized solar cells were fabricated using these dyes. A solar-to-electric conversion efficiency of 2.95% is achieved with **JK-14**. We found that the power conversion efficiency was shown to be quite sensitive to the structural variations of bridging bithiophene moiety.

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1. Introduction

Dye-sensitized solar cells are attracting widespread interest for a new renewable energy source because of the low cost and high efficiency.[1] Several Ru(II) polypyridyl complexes have achieved power conversion efficiencies over 11.1% in standard global air mass 1.5 and good stability.[2] Some metal free organic dyes are shown to be promising sensitizers for nanocrystalline solar cells in view of their properties such as high absorption efficiency, chemical stability of the redox reactions, and intramolecular charge-transfer(CT)-type absorption.[3] Recently impressive photovoltaic performance has been obtained with some organic coumarin,[4] indoline,[5] merocyanine,[6] and hemicyanine dyes[7] having efficiencies in the range of 5–9%. All the organic dyes should contain a structure with donor-to-acceptor moieties bridged by a π-conjugation unit. In most dyes, the amine derivatives act as the electron donor while a 2-cyanoacrylic acid or rhodanine moiety acts as the electron acceptor. These two parts are connected by π-conjugated systems such as the methine unit or thiophene chain. Changes in the electron-donating nature and structural variations of amine unit can result in a variation of electronic properties. For example, the absorption spectrum of **NKX-2510**, whose coumarin framework bears a diethylamino group, is blue-shifted relative to the spectrum of **NKX-2311** with a ring structure amino group.[8] Absorption spectrum and redox potentials were also found to be controllable by expansion of π-conjugated length. Extension of methine unit or the introduction of thiophene chain and aromatic unit extends the π-conjugation system, leading to red shift of dye absorption.[9] The length of the conjugated system may affect the redox potentials of the ground and excited states of the dyes. As part of our efforts to investigate the structural modifications that can enhance the efficiency and stability, small molecules containing julolidine structural motifs[10] instead of coumarin unit have been synthesized for DSSCs. The bridging thiophene units are used to increase the molar extinction coefficient of the dye as well as to increase the stability. The power conversion efficiency is quite sensitive to the structural modifications of the bridging bithiophene moiety due to the twisted nonplanar geometry. In this article, we report three new organic dyes containing julolidine as electron donor and cyanoacrylic acid as electron acceptor bridged by a bithiophenyl, 3,3′-dimethyl-2,2′-bithiophen-5-yl or 2,2′-bis(3,4-ethylenedioxythiophen)-5-yl unit (Fig. 1). We also investigated the effect of bridged structural modifications on the power conversion efficiency.

2. Results and discussion

The novel organic dyes **JK-13**, **JK-14**, and **JK-21** were prepared by the stepwise synthetic protocol illustrated in Scheme 1. New dyes are conveniently synthesized in four steps from the *cis*,*cis*-1,7-diethoxy-3-isopropyljulolidine.[10] The bromojulolidine **1** was synthesized by bromination with NBS in $CHCl_3$. The Suzuki coupling of **1** with 1.2 equiv of 2-(2,2′-bithiophen-5-yl)-1,3,2-dioxaborolane **2a**–**2c**[11] yielded **3a**–**3c**. Compounds **4a**–**4c** was prepared from **3a**–**3c** by a lithiation with 1.2 equiv *n*-butyllithium and subsequent quenching with DMF. The aldehyde **4a**–**4c**, on

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Keywords: Julolidine; Dye; Bithiophene; Solar cell.
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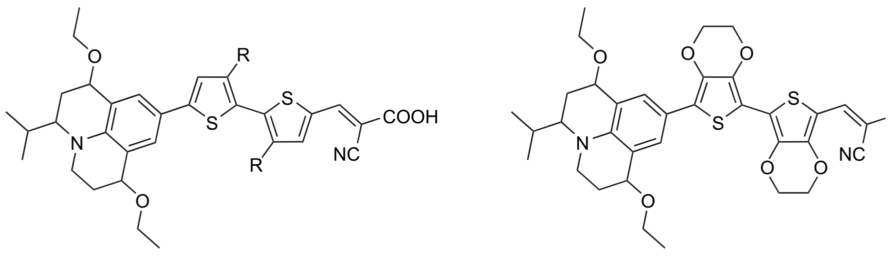
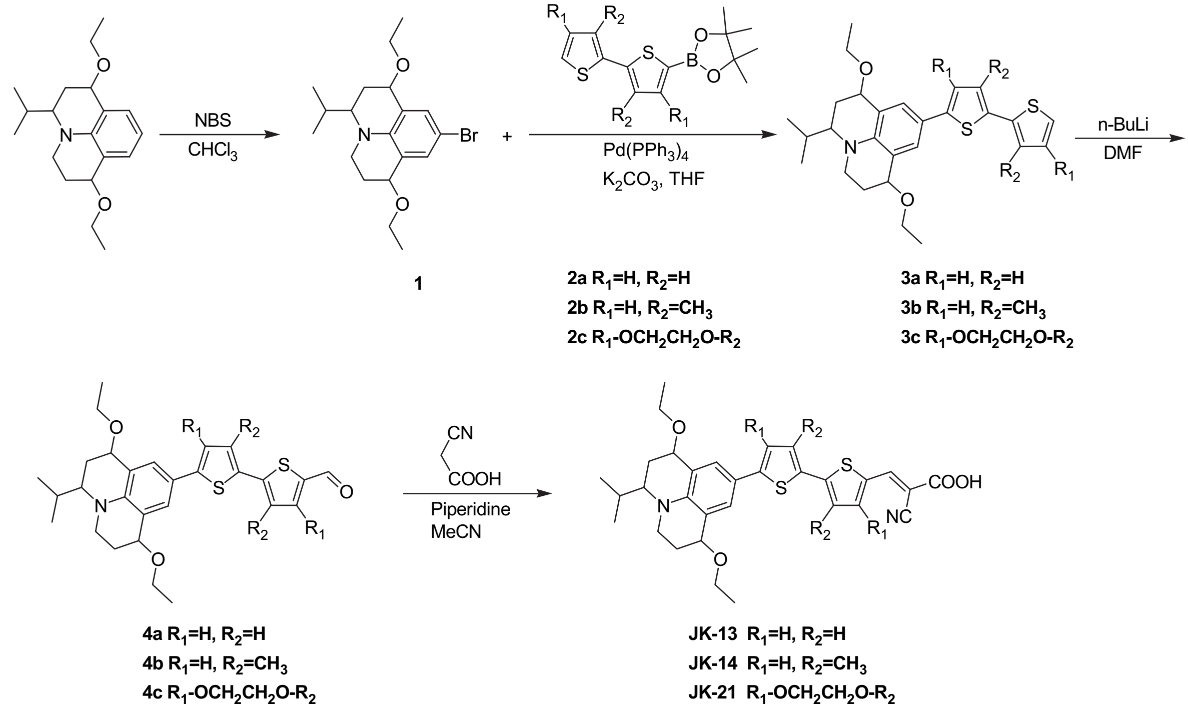


JK-13 : R = H
JK-14 : R = CH_3

JK-21

Figure 1. Structure of the dyes of **JK-13**, **JK-14**, and **JK-21**.



Scheme 1. Schematic diagram for the synthesis of organic dyes **JK-13**, **JK-14**, and **JK-21**.

reaction with cyanoacetic acid in the presence of piperidine in CH_3CN, produced the **JK-13**, **JK-14**, and **JK-21** dyes.

Figure 2 shows the absorption and emission spectra of **JK-13** in ethanol. The absorption spectrum of the **JK-13** sensitizer shows two absorption maxima at 462 (ε=17,400 dm^3 mol^{-1} cm^{-1}) and 352 nm (ε= 10,100 dm^3 mol^{-1} cm^{-1}), which are due to the π–π* transitions of the conjugated molecule. Under similar conditions the **JK-14** sensitizer exhibits absorption peaks at 422 (ε=12,000 dm^3 mol^{-1} cm^{-1}) and 347 nm (ε= 20,000 dm^3 mol^{-1} cm^{-1}) that are blue-shifted relative to the peaks of **JK-13**. On the other hand, introducing a bis-EDOT group to **JK-13**, giving **JK-21**, caused a further red shift to 506 nm. This can be understood from molecular modeling studies of the dyes. The ground state structure of **JK-13** possesses a 20.7° twist between the julolidine and the thienyl unit (Fig. 3). The dihedral angle of two thienyl units is 4.2°. For the 3,3′-dimethyl-2,2′-bithiophen-5-yl case, the dihedral angles between the julolidine and the thienyl unit and two thienyl units are 21.9 and 29.0°, respectively, giving more

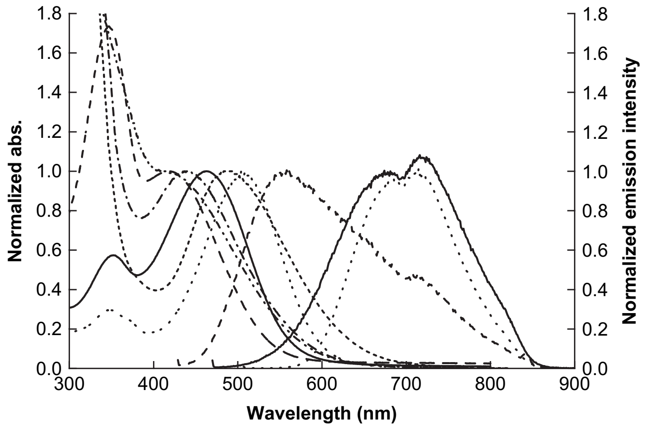


Figure 2. Absorption and emission spectra of **JK-13** (solid line), **JK-14** (dashed line), and **JK-21** (dotted line) in ethanol and absorption spectra of **JK-13** (dashed dot line), **JK-14** (dashed dot-dot line), and **JK-21** (short dashed line) absorbed on TiO_2 film. The emission spectra were obtained using the same solution by exciting at 450 nm for **JK-13**, 410 nm for **JK-14**, and 500 nm for **JK-21** at 298 K.

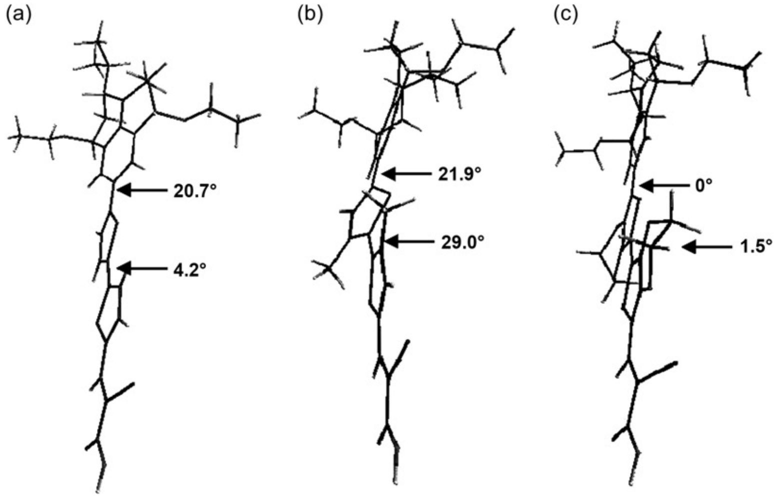


Figure 3. The optimized structure calculated with TD-DFT on B3LYP/3-21G* of (a) **JK-13**, (b) **JK-14**, and (c) **JK-21**.

twisted than those of **JK-13**. On the other hand, the dihedral angles of julolidine and 3,4-ethylenedioxythiophene and bis(3,4-ethylenedioxythiophene) in **JK-21** are 0 and 1.5°, respectively, giving almost a planar configuration. A significant red shift of **JK-21** relative to **JK-13** and **JK-14** derives from the fully delocalization over an entire conjugated system in **JK-21**. When the **JK-13** sensitizer was absorbed on TiO_2 electrode, a slight blue shift from 462 to 448 nm was found due to the H-aggregation. The absorption spectrum of **JK-14** on TiO_2 electrode is broadened. Such broadening of the absorption spectrum is due to an interaction between the dyes and TiO_2.[12] When the **JK-13** and **JK-14** sensitizers are excited within their π–π* bands in an air-equilibrated solution and at 298 K, they exhibit strong luminescence maxima at 673 and 556 nm, respectively. 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 electrodes is efficient.

To judge the possibility of electron transfer from the excited dye molecules to the conduction band of TiO_2 electrode, redox potentials of the three dyes were scrutinized by cyclic voltammetry. The redox potentials of the three dyes were measured in MeCN with 0.1 M tetrabutylammonium hexafluorophosphate. TiO_2 films stained with sensitizer were used as working electrodes. The three organic dyes absorbed on TiO_2 films show quasi-reversible couples. The oxidation potential of **JK-13** dye was measured to be 1.34 V versus NHE with a separation of 0.15 V between anodic-to-cathodic peak, energetically favorable for iodide oxidation (Table 1). Under similar conditions the **JK-14** and **JK-21** dyes show the redox couple located at 1.37 and 1.10 V versus NHE, respectively. The reduction potentials of the three dyes calculated from the oxidation potentials and the $E_{0\text{–}0}$ determined from the intersection of absorption and emission spectra were listed in Table 1. The excited state oxidation potentials (E^*_{ox}) of the dyes (**JK-13**: −0.87 V vs. NHE; **JK-14**: −1.18 V vs. NHE; **JK-21**: −0.90 V vs. NHE) are relatively negative than the conduction band of TiO_2 at approximately −0.5 V versus NHE. The positive shift of the reduction potential in **JK-13** and **JK-21** compared to that of **JK-14** is due to more delocalization of the π-conjugation system, in keeping with the theoretical analysis presented above.

To gain insight into the geometrical electronic structure of the three dyes we performed DFT calculations on the **JK-13**, **JK-14**, and **JK-21** sensitizers using the Gaussian 03 program package. In particular we used B3LYP as exchange-correlation functional and 3-21G* as basis set. The HOMO of **JK-13** is delocalized over the π-conjugated system via the aniline and the first thiophene units (Fig. 4). On the other hand, the HOMO of **JK-21** is more delocalized through the aniline and bis-EDOT, as demonstrated that the **JK-21** dye has a planar configuration (Fig. 4). Examination of the HOMO and LUMO of the three dyes indicates

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

Dye	λ_{abs}[a], nm (ε, dm^{-3} mol^{-1} cm^{-1})	E_{ox}[b], V	$E_{0\text{–}0}$[c], V	E_{LUMO}[d], V	J_{sc}, mA cm^{-2}	V_{oc}, V	ff	η[e], %
JK-13	462 (17,400)	1.34	2.21	−0.87	6.26	0.61	0.64	2.47
JK-14	422 (12,000)	1.37	2.55	−1.18	6.58	0.61	0.73	2.95
JK-21	506 (31,500)	1.10	2.00	−0.90	2.26	0.55	0.59	0.74
N719					16.29	0.75	0.64	7.84

ε: absorption coefficient; E_{ox}: oxidation potential; $E_{0\text{–}0}$: 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.

[a] Absorption spectra were measured in ethanol solution.

[b] Oxidation potential of dyes on TiO_2 were measured in CH_3CN with 0.1 M $(n\text{-}C_4H_9)_4NPF_6$ with a scan rate of 50 mV s^{-1} (vs. NHE).

[c] $E_{0\text{–}0}$ was determined from intersection of absorption and emission spectra in ethanol.

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

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

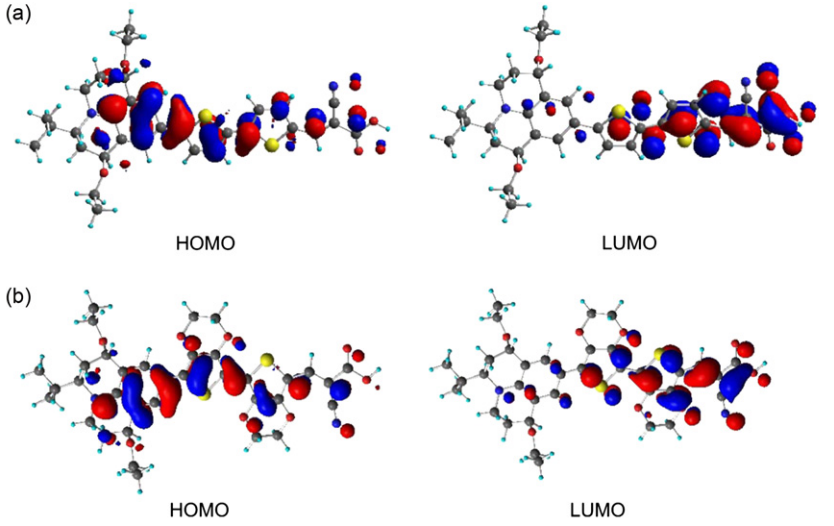


Figure 4. Isodensity surface plots of the HOMO and LUMO of (a) **JK-13** and (b) **JK-21**.

that HOMO–LUMO excitation moved the electron distribution from the aniline unit to the cyanoacrylic acid group. Therefore, the change in electron distribution induced by photoexcitation results in an efficient charge separation.

Three sensitizers have been used to manufacture solar cell devices to explore current–voltage characteristics using 12+8 μm TiO_2 transparent layers. The first TiO_2 layer of 12 μm thickness was prepared by screen printing TiO_2 paste (Solaronix, 13 nm paste), and the second TiO_2 scattering layer of 8 μm thickness was coated with a different paste (CCIC, HWP-400) for the photoscattering. The double layer film was treated with 40 mM $TiCl_4$ solution as reported by the Grätzel group.[13] The resulting layer was dried at 500 °C for 30 min. After cooling to 60 °C, the films were immersed into the **JK-13**, **JK-14**, and **JK-21** solutions (0.3 mM dyes in ethanol containing 10 mM of chenodeoxycholic acid). The stained TiO_2 electrode and Pt-counter electrode were assembled into a sealed sandwich cell by heating with a hot-melt film (Surlyn 1702, 25 μm thickness) as a spacer between the electrodes. The electrolyte was composed of 0.6 M 3-hexyl-1,2-dimethyl imidazolium iodide, 0.04 M I_2, 0.025 M LiI, 0.05 M guanidium thiocyanate, and 0.28 M *tert*-butyl-pyridine in acetonitrile.

Figure 5 shows the incident monochromatic photon-to-current conversion efficiency (IPCE) for the DSSCs based on the three dyes. The IPCE data of **JK-13** and **JK-14** sensitizers in the peak maximum region are about 50%. The **JK-21** sensitizer IPCE spectrum is red shifted by about 30 nm compared to **JK-13** as a result of extended π-conjugation, which is consistent with the absorption spectra of the **JK-21** sensitizer. The maximum IPCE value (27%) of **JK-21** sensitizer is lower than those obtained in **JK-13** and **JK-14** sensitizers. A likely reason for this may be aggregation of the dye molecules on the TiO_2 electrode. The photovoltaic performance of the device is listed in Table 1. Under standard global AM 1.5 solar condition, an overall conversion efficiency (η) of 2.47% for **JK-13** and 2.95% for **JK-14** sensitized cells (for **JK-13**: short-circuit photocurrent density, J_{sc}=6.26 mA cm^{-2}; open-circuit photovoltage, V_{oc}=0.61 V; fill factor, ff=0.64. For **JK-14**: J_{sc}=6.58 mA cm^{-2}; V_{oc}=0.61 V; ff=0.73) was obtained (Fig. 6). On the other hand, the **JK-21** sensitized cell gave an overall efficiency (η) of 0.74%. We have measured the amount of dyes absorbed on TiO_2 film to explain the higher efficiency of the **JK-13** and **JK-14** sensitized cells compared

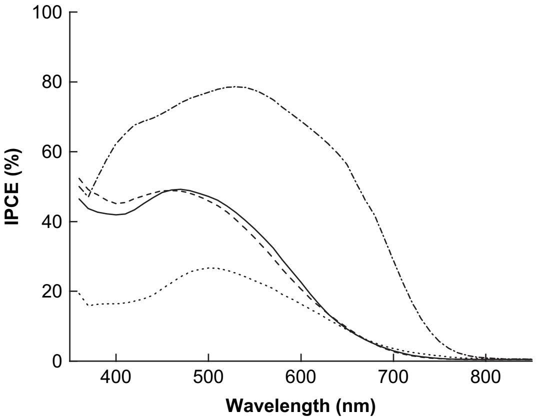


Figure 5. Spectra of monochromatic incident photon-to-current conversion efficiencies (IPCEs) for DSSCs based on spectra of **JK-13** (solid line), **JK-14** (dashed line), **JK-21** (dotted line), and **N719** (dashed dot line).

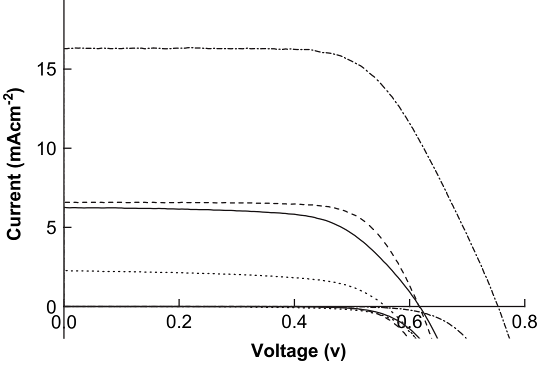


Figure 6. A photocurrent voltage curve obtained with a DSSC based **JK-13** (solid line), **JK-14** (dashed line), **JK-21** (dotted line), and **N719** (dashed dot line) under AM 1.5 radiation (100 mW cm^{-2}).

to the **JK-21** sensitizer. The absorbed amounts of 2.27×10^{-6} mmol cm^{-2} for **JK-13**, 2.87×10^{-6} mmol cm^{-2} for **JK-14**, and 2.70×10^{-6} mmol cm^{-2} for **JK-21** are observed. Therefore, it is assumed that the efficiencies of the three dyes are originated from the aggregation of dyes on TiO_2 film rather than their absorbed amounts. We have also investigated the correlation between the twisted nonplanar geometry of dyes and aggregation on TiO_2 film. We observed that the more twisted geometry dyes have the more blue shifts of their maximum absorbance exhibited by H-aggregation from Figure 2. Although the 10 mM Cheno DCA as co-adsorbent to prevent the aggregation of dye on TiO_2 film was used, their blue shifts of maximum absorbance between in solution and on TiO_2 film were observed with 9 nm for **JK-13**, 0 nm for **JK-14**, and 15 nm for **JK-21**. From these results, we can interpret that the efficiencies based on the aggregation of dyes are affected by their twisted nonplanar geometry.

In summary, we have designed and synthesized three novel organic dyes containing julolidine bridged by three different thiophene units. The power conversion efficiency of the DSSCs based on the **JK-13** and **JK-14** sensitizers reaches 2.47 and 2.95%, respectively. The power conversion efficiency was shown to be sensitive to the structural modifications of bridging bithiophene moieties. The more twisted between the julolidine and the thienyl units are, the higher the power conversion efficiencies get.

3. Experimental

3.1. General methods

All reactions were carried out under an argon atmosphere. Solvents were distilled from appropriate reagents. All reagents were purchased from Sigma–Aldrich. *cis*,*cis*-1,7-Diethoxy-3-isopropyljulolidine, **2a**, **2b**, and **2c** 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.

3.1.1. Cyclic voltammogram. 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 between 50 mV s^{-1} (vs. Fc/Fc$^+$).

3.1.2. 9-Bromo-*cis*,*cis*-1,7-diethoxy-3-isopropyljulolidine (1). A mixture of *cis*,*cis*-1,7-diethoxy-3-isopropyljulolidine (5 g, 16.47 mmol) and *N*-bromosuccinimide (2.91 g, 16.47 mmol) in chloroform (100 ml) was stirred for 2 h. H_2O (30 ml) and brine were added to the solution. The organic layer was separated and dried in $MgSO_4$. The solvent was removed in vacuo. The pure product **1** was obtained by chromatographic work-up (eluent MC:Hx=1:1, R_f=0.5) as a colorless oil in 70% yield. ^{1}H NMR ($CDCl_3$): δ 7.27 (s, 1H), 7.17 (s, 1H), 4.34 (t, J=6.0 Hz, 1H), 4.19 (t, J=3.9 Hz, 1H), 3.72 (m, 2H), 3.57 (m, 2H), 3.22 (m, 2H), 3.00 (m, 1H), 2.36 (oct, J=6.6 Hz, 1H), 1.97 (m, 4H), 1.26 (q, J=6.6 Hz, 6H), 0.97 (d, J=6.6 Hz, 3H), 0.85 (d, J=6.9 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 141.0, 131.3, 130.3, 125.0, 124.1, 107.2, 73.8, 64.2, 63.7, 61.9, 42.9, 28.8, 27.4, 27.1, 20.5, 17.0, 15.7, 15.6. MS: *m*/*z* 381 [M$^+$]. Anal. Calcd for $C_{19}H_{28}BrNO_2$: C, 59.69; H, 7.38. Found: C, 59.42; H, 7.24.

3.1.3. 9-(2,2′-Bithiophen-5-yl)-*cis*,*cis*-1,7-diethoxy-3-isopropyljulolidine (3a). A mixture of **1** (1 g, 2.61 mmol), 2-(2,2′-bithiophen-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.915 g, 3.132 mmol), $Pd(PPh_3)_4$ (0.150 g, 0.13 mmol), and 2 M K_2CO_3 aqueous solution (2 ml) in THF (30 ml) was refluxed for 12 h. After cooling the solution, H_2O (20 ml) and brine were added to the solution. The organic layer was separated and dried in $MgSO_4$. The solvent was removed in vacuo. The pure product **3a** was obtained by chromatographic work-up (eluent MC:Hx=1:1, R_f=0.3) as a yellow solid in 70% yield. Mp: 189 °C. ^{1}H NMR ($CDCl_3$): δ 7.42 (s, 1H), 7.32 (s, 1H), 7.15 (t, J=6.3 Hz, 1H), 7.08 (d, J=3.9 Hz, 1H), 7.03 (d, J=3.9 Hz, 1H), 7.00 (d, J=3.3 Hz, 1H), 6.99 (d, J=3.3 Hz, 1H), 4.42 (t, J=5.1 Hz, 1H), 4.30 (t, J=3.9 Hz, 1H), 3.75 (m, 2H), 3.67 (m, 2H), 3.27 (m, 2H), 3.05 (m, 1H), 2.42 (oct, J=6.9 Hz, 1H), 2.06 (m, 4H), 1.29 (q, J=7.1 Hz, 6H), 0.99 (d, J=6.6 Hz, 3H), 0.88 (d, J=6.9 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 139.8, 138.7, 136.4, 135.5, 133.9, 133.3, 132.2, 131.5, 130.3, 128.2, 127.4, 124.8, 122.1, 109.8, 72.7, 70.8, 65.8, 63.8, 62.7, 42.8, 28.8, 27.4, 27.2, 20.4, 19.3, 15.4, 15.2. MS: *m*/*z* 467 [M$^+$]. Anal. Calcd for $C_{27}H_{33}NO_2S_2$: C, 69.34; H, 7.11. Found: C, 69.12; H, 6.95.

3.1.4. 9-(3,3′-Dimethyl-2,2′-bithiophen-5-yl)-*cis*,*cis*-1,7-diethoxy-3-isopropyljulolidine (3b). The compound **3b** was prepared using the same procedure of **3a** except that 2-(3,3′-dimethyl-2,2′-bithiophen-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was used instead of 2-(2,2′-bithiophen-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Yield: 65%. Mp: 187 °C. ^{1}H NMR ($CDCl_3$): δ 7.40 (s, 1H), 7.29 (s, 1H), 7.24 (d, J=5.1 Hz, 1H), 6.95 (s, 1H), 6.91 (d, J=5.1 Hz, 1H), 4.42 (t, J=5.1 Hz, 1H), 4.29 (t, J=3.9 Hz, 1H), 3.77 (m, 2H), 3.63 (m, 2H), 3.26 (m, 2H), 3.05 (m, 1H), 2.40 (oct, J=6.9 Hz, 1H), 2.22 (s, 3H), 2.17 (s, 3H), 2.01 (m, 4H), 1.27 (q, J=6.9 Hz, 6H), 0.99 (d, J=6.6 Hz, 3H), 0.89 (d, J=6.1 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 139.0, 138.5, 137.3, 135.8, 134.1, 133.3, 130.5, 130.3, 129.4, 125.9, 125.3, 122.1, 121.0, 109.8, 72.1, 70.7, 65.8, 64.5, 63.8, 48.0, 31.9, 31.5, 29.2, 27.2, 27.1, 20.4, 19.4, 15.5, 15.1. MS: *m*/*z* 467 [M$^+$]. Anal. Calcd for $C_{29}H_{37}NO_2S_2$: C, 70.26; H, 7.52. Found: C, 69.89; H, 7.13.

3.1.5. 9-(2,2′-Bis(3,4-ethylenedioxythiophen)-5-yl)-*cis*,*cis*-1,7-diethoxy-3-isopropyljulolidine (3c). The compound **3c** was prepared using the same procedure of **3a** except that 4,4,5,5-tetramethyl-2-(2,2′,3,3′-tetrahydro-5,7′-bithieno[3,4-*b*][1,4]dioxin-7-yl)-1,3,2-dioxaborolane (1.278 g, 3.132 mmol) was used instead of 2-(2,2′-bithiophen-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Yield: 77%. Mp: 198 °C. ^{1}H NMR ($CDCl_3$): δ 7.55 (s, 1H), 7.42

(s, 1H), 6.23 (s, 1H), 4.43 (t, *J*=5.1 Hz, 1H), 4.34–4.25 (m, 8H), 4.24 (t, *J*=3.7 Hz, 1H), 3.74 (m, 2H), 3.66 (m, 2H), 3.26 (m, 2H), 3.03 (m, 1H), 2.41 (oct, *J*=6.9 Hz, 1H), 2.06 (m, 4H), 1.26 (q, *J*=7.2 Hz, 6H), 0.98 (d, *J*=6.9 Hz, 3H), 0.88 (d, *J*=6.3 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 141.4, 137.8, 136.5, 136.0, 127.9, 126.8, 122.5, 121.5, 119.8, 116.9, 110.6, 105.4, 97.0, 92.9, 73.9, 73.1, 65.9, 65.1, 65.0, 64.7, 63.7, 63.3, 62.3, 42.9, 29.2, 27.5, 25.7, 20.6, 17.6, 15.8, 15.7. MS: *m*/*z* 583 [M^+]. Anal. Calcd for $C_{31}H_{37}NO_6S_2$: C, 63.78; H, 6.39. Found: C, 63.55; H, 6.18.

3.1.6. 9-(5′-Formyl-2,2′-bithiophen-5-yl)-*cis*,*cis*-1,7-diethoxy-3-isopropyljulolidine (4a). *n*-BuLi (0.35 ml, 1.6 M solution in hexane) was added into **3a** (0.22 g, 0.47 mmol) solution in dry Et_2O, under argon. After 3 h DMF (0.05 g, 0.7 mmol) was added at 0 °C under argon. The reaction was continued for 2 h and washed with 5% KOH. The solution was dried with $MgSO_4$ and the solvent evaporated. The pure product **4a** was obtained by silica gel chromatography (eluent MC:Hx=1:1, R_f=0.2) to afford **4a** in 75% yield. Mp: 186 °C. ^1H NMR ($CDCl_3$): δ 9.82 (s, 1H), 7.64 (d, *J*=3.9 Hz, 1H), 7.43 (s, 1H), 7.33 (s, 1H), 7.28 (d, *J*=3.9 Hz, 1H), 7.28 (d, *J*=3.9 Hz, 1H), 7.20 (d, *J*=3.9 Hz, 1H), 7.08 (d, *J*=3.9 Hz, 1H), 4.41 (t, *J*=5.4 Hz, 1H), 4.30 (t, *J*=3.7 Hz, 1H), 3.77 (m, 2H), 3.65 (m, 2H), 3.28 (m, 2H), 3.08 (m, 1H), 2.41 (oct, *J*=6.3 Hz, 1H), 2.02 (m, 4H), 1.29 (q, *J*=6.9 Hz, 6H), 0.99 (d, *J*=6.6 Hz, 3H), 0.88 (d, *J*=6.3 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 182.6, 145.8, 143.2, 136.2, 134.5, 133.9, 133.3, 132.2, 131.5, 130.8, 128.2, 127.4, 124.8, 122.1, 111.8, 72.5, 70.1, 65.8, 63.8, 62.7, 42.8, 28.8, 27.4, 27.2, 20.4, 19.3, 15.4, 15.2. MS: *m*/*z* 495 [M^+]. Anal. Calcd for $C_{28}H_{33}NO_3S_2$: C, 67.84; H, 6.71. Found: C, 67.36; H, 6.24.

3.1.7. 9-(5′-Formyl-3,3′-dimethyl-2,2′-bithiophen-5-yl)-*cis*,*cis*-1,7-diethoxy-3-isopropyljulolidine (4b). The compound **4b** was prepared using the same procedure of **4a** except that **3b** was used instead of **3a**. Yield: 72%. Mp: 179 °C. ^1H NMR ($CDCl_3$): δ 9.82 (s, 1H), 7.58 (s, 1H), 7.40 (s, 1H), 7.29 (d, *J*=5.1 Hz, 1H), 6.98 (s, 1H), 4.41 (t, *J*=5.1 Hz, 1H), 4.29 (t, *J*=3.9 Hz, 1H), 3.74 (m, 2H), 3.63 (m, 2H), 3.27 (m, 2H), 3.07 (m, 1H), 2.41 (oct, *J*=6.9 Hz, 1H), 2.31 (s, 3H), 2.25 (s, 3H), 2.00 (m, 4H), 1.28 (q, *J*=7.2 Hz, 6H), 0.99 (d, *J*=6.9 Hz, 3H), 0.88 (d, *J*=6.3 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 182.8, 143.0, 141.2, 140.4, 139.2, 138.4, 137.0, 130.5, 127.1, 126.0, 125.0, 122.9, 122.0, 120.6, 112.1, 73.7, 73.1, 64.0, 63.5, 62.3, 42.9, 31.9, 31.5, 29.1, 27.2, 27.1, 22.6, 17.4, 15.8, 15.7. MS: *m*/*z* 523 [M^+]. Anal. Calcd. for $C_{30}H_{37}NO_3S_2$: C, 68.80; H, 7.12. Found: C, 68.55; H, 6.89.

3.1.8. 9-(5′-Formyl-2,2′-bis(3,4-ethylenedioxythiophen)-5-yl)-*cis*,*cis*-1,7-diethoxy-3-isopropyljulolidine (4c). The compound **4c** was prepared using the same procedure of **4a** except that **3c** was used instead of **3a**. Yield: 75%. Mp: 186 °C. ^1H NMR ($CDCl_3$): δ 9.86 (s, 1H), 7.58 (s, 1H), 7.45 (s, 1H), 4.42 (m, 9H), 4.31 (t, *J*=3.7 Hz, 1H), 3.73 (m, 2H), 3.64 (m, 2H), 3.27 (m, 2H), 3.04 (m, 1H), 2.41 (oct, *J*=6.3 Hz, 1H), 2.08 (m, 4H), 1.27 (q, *J*=7.5 Hz, 6H), 0.99 (d, *J*=6.6 Hz, 3H), 0.88 (d, *J*=6.0 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 179.6, 159.0, 156.0, 138.9, 137.7, 136.5, 133.4, 132.1, 130.5, 129.8, 128.7, 125.9, 124.9, 121.0, 106.9, 73.7, 73.3, 65.8, 65.4, 65.1, 64.7, 63.7, 63.3, 62.3, 42.3, 29.1, 27.2, 25.5, 20.7, 17.6, 15.8, 15.7. MS: *m*/*z* 611 [M^+]. Anal. Calcd for $C_{32}H_{37}NO_7S_2$: C, 62.82; H, 6.10. Found: C, 62.55; H, 5.95.

3.1.9. 2-Cyano-3-(5′-(*cis*,*cis*-1,7-diethoxy-3-isopropyljulolidinyl)-2,2′-bithiophen-5-yl)acrylic acid (JK-13). A mixture of **4a** (0.38 g, 0.76 mmol) and cyanoacetic acid (0.13 g, 1.53 mmol) was vacuum-dried and added MeCN (60 ml) and piperidine (0.07 ml, 0.76 mmol). The solution was refluxed for 6 h. After cooling the solution, the organic layer was removed in vacuo. The pure product **JK-13** was obtained by silica gel chromatography (eluent MC:MeOH=2:1, R_f=0.6) to afford **JK-13** in 51% yield. Mp: 225 °C. ^1H NMR (DMSO-d_6): δ 8.12 (s, 1H), 7.65 (d, *J*=3.3 Hz, 1H), 7.39 (d, *J*=3.6 Hz, 1H), 7.37 (d, *J*=3.6 Hz, 1H), 7.35 (s, 1H), 7.32 (s, 1H), 7.22 (d, *J*=3.3 Hz, 1H), 4.37 (t, *J*=5.8 Hz, 1H), 4.28 (t, *J*=3.9 Hz, 1H), 3.70 (m, 2H), 3.61 (m, 2H), 3.20 (m, 2H), 3.06 (m, 1H), 2.25 (oct, *J*=6.3 Hz, 1H), 1.90 (m, 4H), 1.19 (q, *J*=6.9 Hz, 6H), 0.94 (d, *J*=6.9 Hz, 3H), 0.82 (d, *J*=6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 164.3, 150.6, 145.8, 142.3, 142.0, 141.7, 140.6, 136.6, 135.3, 134.8, 131.7, 126.9, 123.6, 122.5, 122.0, 119.1, 118.7, 73.7, 72.8, 64.2, 63.0, 62.5, 41.4, 29.7, 28.6, 28.2, 22.5, 17.0, 15.4, 15.3. MS: *m*/*z* 562 [M^+]. Anal. Calcd for $C_{31}H_{34}N_2O_4S_2$: C, 66.16; H, 6.09. Found: C, 65.78; H, 5.87.

3.1.10. 2-Cyano-3-(5′-(*cis*,*cis*-1,7-diethoxy-3-isopropyljulolidinyl)-3,3′-dimethyl-2,2′-bithiophen-5-yl)acrylic acid (JK-14). The dye **JK-14** was prepared using the same procedure of **JK-13** except that **4b** was used instead of **4a**. Yield: 56%. Mp: 212 °C. ^1H NMR (DMSO-d_6): δ 8.03 (s, 1H), 7.55 (s, 1H), 7.32 (s, 1H), 7.28 (s, 1H), 7.15 (s, 1H), 4.37 (t, *J*=5.3 Hz, 1H), 4.28 (t, *J*=3.9 Hz, 1H), 3.69 (m, 2H), 3.57 (m, 2H), 3.27 (m, 2H), 3.08 (m, 1H), 2.35 (oct, *J*=6.8 Hz, 1H), 2.20 (s, 3H), 2.17 (s, 3H), 1.90 (m, 4H), 1.18 (q, *J*=7.2 Hz, 6H), 0.94 (d, *J*=6.9 Hz, 3H), 0.83 (d, *J*=6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 163.3, 149.0, 145.4, 144.8, 141.5, 137.8, 136.1, 135.6, 135.3, 134.8, 132.2, 128.9, 127.3, 125.5, 124.6, 124.1, 119.0, 73.8, 72.8, 64.3, 63.1, 61.5, 41.4, 40.4, 38.6, 29.7, 28.6, 28.4, 23.0, 17.2, 15.4, 15.1. MS: *m*/*z* 523 [M^+]. Anal. Calcd. for $C_{33}H_{38}N_2O_4S_2$: C, 67.09; H, 6.48. Found: C, 66.79; H, 6.33.

3.1.11. 2-Cyano-3-(5′-(*cis*,*cis*-1,7-diethoxy-3-isopropyljulolidinyl)-2,2′-bis(3,4-ethylene-dioxythiophen)-5-yl)acrylic acid (JK-21). The dye **JK-21** was prepared using the same procedure of **JK-13** except that **4c** was used instead of **4a**. Yield: 60%. Mp: 232 °C. ^1H NMR (DMSO-d_6): δ 8.03 (s, 1H), 7.44 (s, 1H), 7.35 (s, 1H), 4.42 (m, 8H), 4.35 (t, *J*=5.9 Hz, 1H), 4.27 (t, *J*=3.8 Hz, 1H), 3.70 (m, 2H), 3.57 (m, 2H), 3.16 (m, 2H), 3.10 (m, 1H), 2.35 (oct, *J*=6.8 Hz, 1H), 1.93 (m, 4H), 1.17 (q, *J*=7.3 Hz, 6H), 0.95 (d, *J*=6.3 Hz, 3H), 0.83 (d, *J*=6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 161.8, 155.9, 144.6, 140.9, 140.4, 135.9, 126.1, 125.4, 122.4, 120.1, 118.4, 118.1, 115.3, 109.1, 108.1, 104.7, 103.8, 72.5, 72.1, 67.2, 65.2, 64.4, 63.0, 61.2, 59.6, 47.3, 28.6, 23.0, 22.5, 20.1, 17.2, 15.5, 15.4. MS: *m*/*z* 678 [M^+]. Anal. Calcd for $C_{35}H_{38}N_2O_8S_2$: C, 61.93; H, 5.64. Found: C, 61.56; H, 5.34.

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