Synthesis of Novel Organic Dyes Containing Coumarin Moiety for Solar Cell

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Novel organic dyes, JK-34, JK-35 and JK-36 containing bis-dimethylfluorenyl amino coumarin unit are designed and synthesized. Nanocrystalline TiO$_2$ dye-sensitized solar cells were fabricated using these dyes. Under standard global AM 1.5 solar condition, the JK-34 sensitized cell gave a short circuit photocurrent density of 10.05 mA cm$^{-2}$, open circuit voltage of 0.65 V, and a fill factor of 0.68, corresponding to an overall conversion efficiency $\eta$ of 4.54%. We found that the power conversion efficiency was shown to be quite sensitive to the structural modifications of bridging thiophene moiety.

**Key Words**: Fluorenyl, Coumarin, Organic dyes, Solar cell

**Introduction**

Increasing energy demands and concerns over global warming have led to a greater focus on renewable energy sources in recent years. The conversion of solar energy to electricity appears as one of the technologies that can replace fossil fuels. Dye-sensitized solar cells (DSSCs) based on mesoporous nanocrystalline TiO$_2$ films have attracted significant attention as low-cost devices and can reach light to high electric power conversion efficiencies of 8-11%. In these cells, the sensitizer is one of the key elements for high power conversion efficiency. Some polypyrrolid ruthenium (II) complexes have been used as efficient sensitizers because they have an intense metal-to-ligand charge transfer transition in the visible region. Although the ruthenium complexed dyes exhibited high efficiency and long-term stability, they contain a limited precious metal and they are hard to purify. Recently, impressive photovoltaic performance has been obtained with some organic coumarins, indoline, oligoene, neroxyanine, and hemicyanine dyes having efficiencies in the range of 5-9%. Very recently, we reported highly efficient and stable organic dyes containing bis-dimethylfluorenyl amino donor unit. The bis-dimethylfluorenyl moiety was introduced to prevent aggregation via molecular stacking by the bulky nonplanar structure and to ensure greater resistance to degradation when exposed to light and high-temperature. A major factor responsible for the high photoconversion efficiency of an organic dye-sensitized solar cell can be tuned by the structural modification. In our previous works, we adapted the $(9,9$-dimethylfluorene-2-yl)amino phenyl, benzo[b]furan, benzo[b]thiophene and N-aryl carbazole moiety as the donor moiety. Another promising design strategy is replacement of the above moieties with the coumarin electron donor. Changing the electron donor would affect the highest occupied molecular orbital and lowest unoccupied molecular orbital levels of the dye and consequently, the absorption properties.

In this article, we report three new organic dyes containing [bis(9,9-dimethylfluorene-2-yl)amino]coumarin as electron donor and cyano acrylic acid as electron acceptor bridged by thiophene unit or vinylene thiophene unit (Figure 1).

**Results and Discussion**

The novel organic dyes JK-34–36 were prepared by the stepwise synthetic protocol illustrated in Scheme 1. The reaction started with 7-amino-3-bromo-4-methylcoumarin.

![Figure 1. Structure of JK-34, JK-35, JK-36 and N3.](image-url)
The coumarin mono- and bithiophenes 1 and 2 were synthesized by coupling reaction of 7-amino-3-bromo-4-methyl-coumarin with stannylthiophene units in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0) according to the Stille reaction conditions. Fluorene substituted coumarin derivatives 3 and 4 were obtained by Ullmann coupling reaction. These thiophene derivatives were converted into their corresponding thiophene aldehydes 5 and 6 by dedioxanylation with trifluoroacetic acid (TFA). An acetonitrile solution of thiophene aldehyde derivatives (5 and 6) and cyanoacetic acid were refluxed in the presence of piperidine for 8 h. Solvent removal followed by purification using chromatography yielded JK-34 and JK-35. We have also designed to insert the ethylene unit between two thiophenes in order to lengthen the π-conjugation. Introduction of ethylene unit augmented the absorption extinction coefficient and red-shifted the absorption peaks. Coupling reaction of aldehyde 5 with diethyl(5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)methylphosphonate under Horner-Emmons-Wittig coupling condition using potassium tert-butoxide in THF led to 7. This was then converted to the aldehyde 8, which yielded the dye JK-36 on treatment of cyanoacetic acid.

For the fabrication of DSSC, three sensitizers have been used to manufacture solar cell devices to explore current-voltage characteristics using 12 + 4 μm TiO₂ transparent layers. The first TiO₂ layer of 12 μm thickness was prepared by screen printing TiO₂ paste (Solaronix, 13 nm paste), and the second TiO₂ scattering layer of 4 μm thickness was coated with a different paste (CCIC, HWP-400) for the photo-scattering. The double layer film was treated with 40 mM TiCl₄ solution. The resulting layer was dried at 500 °C for 30 min. After cooling to 100 °C, the films were immersed into the JK-34, JK-35, and JK-36 solution (0.3 mM dyes in ethanol containing 10 mM of chenodeoxycholic acid). The stained TiO₂ 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 3-3 hexyl-1,2-dimethylimidazolium iodide, 0.04 M 0.025 M LiI, 0.05 M guanidium thiocyanate and 0.28 M tert-butylpyridine in acetonitrile.

The UV-vis and emission spectra of JK-34 and JK-36 in ethanol are shown in Figure 2 and listed Table 1, together with the UV-vis spectra of the corresponding dyes absorbed on TiO2 film. The absorption spectra of the JK-34 and JK-35 display visible band at 429 nm and 431 nm, respectively, which is due to the π-π transition of the conjugated molecule. A slight red-shifted band at about 2 nm and a large extinction coefficient of JK-35 compared to those of JK-34 are due to the increase of the π-conjugation system by thiochrome unit. The introduction of ethylene unit in JK-36 also induced the red-shifted band at about 20 nm compared to JK-34 and JK-35. The absorption spectra of all the dyes JK-34-JK-36 on TiO2 film are broadened due to the interaction of the anchoring group with the organic dyes in TiO2 electrodes. Such broadening of the absorption spectrum is desirable for harvesting the solar spectrum and leads to a large photocurrent. The dyes on TiO2 film have red-shifted bands via J-aggregation. We also observed that the dyes JK-34-JK-36 exhibited strong luminescence maxima of 578-643 nm when they are excited within their π-π* bands in an air-equilibrated solution at 298 K.

Electrochemical properties of the dyes JK-34-JK-36 were evaluated by cyclic voltammetry in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate using TiO2 film with adsorbed dyes as working electrode. The results are listed in Table 1. The three organic dyes adsorbed on TiO2 film showed quasi-reversible behaviors. The oxidation potentials of three organic dyes were measured to be 1.37-1.39 V vs. NHE, an oxidation potential energetically favorable for iodide oxidation. The reduction potentials of three dyes calculated from the oxidation potentials and the \( E_0 \) determined from the intersection of absorption and emission spectra is listed in Table 1. The excited state oxidation potentials (\( E_{OX}^* \)) of the dyes (JK-34: -0.09 V vs. NHE; JK-35: -0.03 V vs. NHE; JK-36: -0.08 V vs. NHE) are much negative than the conduction band of TiO2 at approximately -0.5 V vs NHE.

**Figure 2.** Absorption and emission spectra of JK-34 (solid line) and JK-36 (dotted line) in ethanol and absorption spectra of JK-34 (dashed dotted line) and JK-35 (short dashed line) absorbed on TiO2 film. The emission spectra were obtained using the same solution by excitation at 429 nm for JK-34 and 450 nm for JK-36 at 298 K.

**Figure 3.** Isodensity surface plots of the HOMO and LUMO of (a) JK-34, (b) JK-35, and (c) JK-36.

<table>
<thead>
<tr>
<th>Dye</th>
<th>( J_{abs} ) (cm(^{-1}) ( \epsilon ) M(^{-1}) cm(^{-1}))</th>
<th>( E_{em} ) V</th>
<th>( E_{ox} ) V</th>
<th>( E_{LUMO} ) V</th>
<th>( J_{sc} ) (mA cm(^{-2}))</th>
<th>( V_{oc} ) (V)</th>
<th>FF</th>
<th>( \eta ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JK-34</td>
<td>429 (22900)</td>
<td>1.38</td>
<td>2.47</td>
<td>-1.09</td>
<td>10.05</td>
<td>0.65</td>
<td>0.68</td>
<td>4.54</td>
</tr>
<tr>
<td>JK-35</td>
<td>431 (39000)</td>
<td>1.37</td>
<td>2.40</td>
<td>-1.03</td>
<td>9.44</td>
<td>0.65</td>
<td>0.70</td>
<td>4.34</td>
</tr>
<tr>
<td>JK-36</td>
<td>450 (25000)</td>
<td>1.39</td>
<td>2.37</td>
<td>-0.98</td>
<td>9.87</td>
<td>0.64</td>
<td>0.69</td>
<td>4.41</td>
</tr>
<tr>
<td>N3</td>
<td>13.13</td>
<td>0.73</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6.32</td>
</tr>
</tbody>
</table>

*Absorption spectra were measured in ethanol solution. Oxidation potentials of dyes on TiO2 were measured in CH2CN with 0.1 M (t-butylammonium hexafluorophosphate with a scan rate of 50 mVs\(^{-1}\) V vs. NHE. \( E_{ox} \) was determined from intersecting absorption and emission spectra in ethanol. \( E_{LUMO} \) was calculated by \( E_{LUMO} = E_{ox} - E_0 \). Performances of DSSCs were measured with 0.18 cm\(^2\) working area. \( \epsilon \): Absorption coefficient; \( E_{ox} \): oxidation potential; \( E_{LUMO} \): voltage of intersection point between absorption and emission spectra; \( J_{sc} \): short-circuit photocurrent density; \( V_{oc} \): open-circuit photovoltage; FF: fill factor; \( \eta \): total power conversion efficiency.
To gain insight into the geometrical configuration and photophysical properties, molecular orbital calculations of the three sensitizers were performed with the TD-DFT on B3LYP/3-21G* (Figure 3). The calculation illustrates that the HOMO of JK-34 and JK-35 is delocalized over the π-conjugated system through the phenyl amino group and the LUMO is delocalized over the cyanoacrylic unit through thiophene. On the other hand, the HOMO of JK-36 is heavily delocalized over the conduct channel from phenyl amino unit to thiophene group. Examination of the HOMO and LUMO of these dyes indicates that HOMO-LUMO excitation move the electron distribution from the phenyl amino unit to the cyanoacrylic acid moiety and the photoinduced electron transfer from the dyes to TiO2 electrode can be efficiently occurred by the HOMO-LUMO transition.

The J-V curve for the DSSCs based on JK-34 and JK-35 is presented and compared with N3 dye in Figure 4. Under standard global AM 1.5 solar condition, the JK-34, JK-35 and JK-36 sensitized cell gave the short circuit photocurrent density (JSC) of 10.95, 9.44 and 9.87 mA cm−2, open circuit voltage (Voc) of 0.65, 0.65 and 0.64 V and a fill factor of 0.68, 0.70 and 0.69, corresponding to an overall conversion efficiency η of 4.54, 4.34 and 4.44%, respectively. Under the same condition, the N3 sensitized cell gave a JSC of 13.13 mA cm−2, Voc of 0.73 V and a fill factor of 0.66, corresponding to η of 6.32%. From these results, we have observed that the solar energy-to-electricity efficiency of JK-34 was slightly higher than that of JK-36 even though JK-36 has a high molar extinction coefficient and red-shifted compared to those of JK-34. In this stage, we can not explain this photophysical property clearly. However, it was well observed that because the more conjugated organic dyes with a vinyl unit are more flexible on TiO2 surface than that of rigid conjugated dyes, the flexible conjugated organic dyes can lie on the neighboring TiO2 surface and can affect the electronic state of the conduction potential of TiO2, and this effect can reduce the electron injection efficiency from dye to TiO2.

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-34 and JK-35 sensitizers in the peak maximum region are about 72% at 445 nm. However, the maximum IPCE value (60%) of JK-36 is lower than those of JK-34 and JK-35. A likely region for this may be attributed to the aggregation of the dye molecule on the TiO2 electrode. Although the DCA as co-adsorbent to prevent the aggregation of dye on TiO2 film was used, their red shifts of maximum absorbance between in solution and on TiO2 film were observed with 13 nm for JK-34, 9 nm for JK-35 and 8 nm for JK-36.

In summary, we have designed and synthesized three organic dyes containing coumarin moiety bridged by thiophene units. The power conversion efficiency of the DSSCs based on the JK-34-JK-36 sensitizers reaches 4.34–4.54%. The power conversion efficiency was shown to be sensitive to the structural modifications of bridging moieties. Contrary to our expectation, the JK-36 sensitizer with a high molar extinction coefficient and red-shifted absorption band showed slightly lower conversion efficiency than JK-34 due probably to the aggregation and interaction between the dye and TiO2 film. Expanding the π-conjugation is necessary for the high molar extinction coefficient, but the introduction of methine unit is worse in our case because the non-rigid conformation of bridging moiety occurs the energy loss via photoisomerization. Accordingly, the introduction of rigid π-conjugated expansion without a significant lowering of LUMO should be attained for the high efficiency of dye.

**Experimental Section**

**General methods.** All reactions were carried out under an argon atmosphere. Solvents were distilled from appropriate reagents. All reagents were purchased from Sigma-Aldrich. 7-Amino-3-bromo-4-methylcoumarin was synthesized using a modified procedure of previous reference. 1H and
The 1\(^\text{C}\) 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 JEOI JMS-SX102A instrument. The absorption and photoluminescence spectra were recorded on a Perkin-Elmer Lambda 25 UV-visible spectrometer and a Perkin LS fluorescence spectrometer, respectively.

**Cyclovoltamogram:** 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 potentials of dyes on TiO\(_2\) were measured in CH\(_3\)CN with 0.1M (n-C\(_6\)H\(_{12}\))N\(\text{PF}_6\) as a scan rate between 50 mV/s \(\text{(vs. FeC}^2\text{)}\).

7-Amino-3-((5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)-4-methylcoumarin (1): A stirred mixture of 7-amino-3-bromo-4-methylcoumarin (2 g, 7.87 mmol), tributyl(5-((5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)stanannane (4.6 g, 9.44 mmol) and Pd(PPh\(_3\))\(_4\) (0.454 g, 0.39 mmol) in toluene (50 mL) was refluxed for 12 h. After cooling the solution, H\(_2\)O (10 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 EA:CH\(_3\)Cl = 1:3, R\(_f\) = 0.3) as a green solid in 70% yield. MP: 210 °C. \(^1\)H NMR (DMSO-d\(_6\)): \(\delta\) 7.50 (d, \(J = 8.4 \text{ Hz}, 1 \text{H}\)), 7.08 (d, \(J = 3.3 \text{ Hz}, 1 \text{H}\)), 6.94 (d, \(J = 3.3 \text{ Hz}, 1 \text{H}\)), 6.60 (d, \(J = 8.4 \text{ Hz}, 1 \text{H}\)), 6.43 (s, 1H), 6.22 (br, 2H), 5.69 (s, 1H), 3.65 (br, 4H), 2.32 (s, 3H), 1.16 (s, 3H), 0.75 (s, 3H). \(^1\)C\(^{13}\) NMR (CDCl\(_3\)): \(\delta\) 161.0, 154.4, 153.2, 150.9, 142.2, 135.7, 128.4, 127.2, 124.4, 112.1, 111.6, 108.9, 98.1, 79.4, 76.4, 29.7, 22.6, 21.3, 16.5. MS: \(m/z\) 371 [M\(^+\)]. Anal. Calc. for C\(_{20}\)H\(_{20}\)NO\(_4\)S: C, 64.67; H, 5.70. Found: C, 64.32; H, 5.45.

7-Amino-3-((5,5-dimethyl-1,3-dioxan-2-yl)-2,2'-bithiophen-5-yl)-4-methylcoumarin (2): Compound 2 was synthesized by a procedure similar to 1 except that tributyl(5-((5,5-dimethyl-1,3-dioxan-2-yl)-2,2'-bithiophen-5-yl)stanannane (5.37 g, 9.44 mmol) was used in place of tributyl(5-((5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)stanannane. **Yield:** 76%. MP: 208 °C. \(^1\)H NMR (DMSO-d\(_6\)): \(\delta\) 7.53 (d, \(J = 8.4 \text{ Hz}, 1 \text{H}\)), 7.29 (d, \(J = 3.9 \text{ Hz}, 1 \text{H}\)), 7.18 (d, \(J = 3.3 \text{ Hz}, 1 \text{H}\)), 7.07 (d, \(J = 3.3 \text{ Hz}, 1 \text{H}\)), 6.62 (d, \(J = 8.4 \text{ Hz}, 1 \text{H}\)), 6.44 (s, 1H), 6.28 (br, 2H), 5.68 (s, 1H), 3.65 (br, 4H), 2.40 (s, 3H), 1.17 (s, 3H), 0.75 (s, 3H). \(^1\)C\(^{13}\) NMR (CDCl\(_3\)): \(\delta\) 161.0, 154.3, 153.3, 150.8, 140.2, 137.0, 136.3, 135.8, 135.1, 130.5, 127.3, 126.3, 123.3, 123.0, 111.7, 109.0, 98.0, 97.1, 76.3, 29.8, 22.6, 21.3, 16.7. MS: \(m/z\) 453 [M\(^+\)]. Anal. Calc. for C\(_{24}\)H\(_{21}\)NO\(_4\)S: C, 63.55; H, 5.11. Found: C, 63.68; H, 4.98.

7-(Bis(9,9-dimethylfluorenyl-2-yl)-3-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)-4-methylcoumarin (3): A stirred mixture of 1 (2 g, 5.38 mmol), 2-ido-9,9-dimethylfluorene (5.17 g, 16.15 mmol), powdered anhydrous potassium carbonate (2.23 g, 16.15 mmol), copper bronze (1.02 g, 16.15 mmol) and 18-crown-6 (0.43 g, 1.615 mmol) in 1,2-dichlorobenzene (70 mL) was refluxed for 48 h. After cooling, the insoluble inorganic material was filtered off under suction and the dark brown filtrate was collected. The insoluble material was washed with dichloromethane (3 x 50 mL). The combined filtrate and organic phase were washed with dilute aqueous ammonia and water and dried with magnesium sulfate. The solvent was removed under reduced pressure. The pure product 3 was obtained by silica gel chromatography (eluent EA:CH\(_3\)Cl = 1:4, R\(_f\) = 0.3) to afford 3 in 95% yield. MP: 189 °C. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 9.93 (s, 1H), 7.77 (d, \(J = 3.9 \text{ Hz}, 1 \text{H}\)), 7.69 (t, \(J = 8.1 \text{ Hz}, 2 \text{H}\)), 7.68 (d, \(J = 8.2 \text{ Hz}, 2 \text{H}\)), 7.50 (d, \(J = 8.7 \text{ Hz}, 1 \text{H}\)), 7.42 (d, \(J = 8.2 \text{ Hz}, 2 \text{H}\)), 7.39 (d, \(J = 8.7 \text{ Hz}, 2 \text{H}\)), 7.33 (t, \(J = 8.1 \text{ Hz}, 2 \text{H}\)), 7.26 (s, 2H), 7.21 (d, \(J = 3.9 \text{ Hz}, 1 \text{H}\)), 7.19 (d, \(J = 9.0 \text{ Hz}, 2 \text{H}\)), 7.06 (d, \(J = 9.0 \text{ Hz}, 1 \text{H}\)), 7.00 (s, 1H), 2.46 (s, 3H), 1.43 (s, 12H). \(^1\)C\(^{13}\) NMR (CDCl\(_3\)): \(\delta\)
7-(Bis(9,9-dimethylfluorenyl-2-yl)-3-(5-(formyl-2',3'-dithiophen-2-yl)vinyl)thiophen-2-yl)-4-methylcoumarin (6): Compound 6 was synthesized by a procedure similar to 5 except that compound 4 was used in place of compound 3. Yield: 95%. Mp: 189 °C. \( \text{H NMR (CDCl}_3\text{): } \delta 8.66 \text{(s, 1H), 7.70 (d, } J = 3.9 \text{ Hz, 1H), 7.68 (t, } J = 8.1 \text{ Hz, 2H), 7.67 (d, } J = 7.6 \text{ Hz, 2H), 7.50 (d, } J = 9.0 \text{ Hz, 2H), 7.43-7.37 \text{(m, 3H), 7.35 (d, } J = 3.9 \text{ Hz, 1H), 7.33 (t, } J = 8.1 \text{ Hz, 2H), 7.28 (d, } J = 3.9 \text{ Hz, 1H), 7.26 (s, 2H), 7.18 (d, } J = 7.6 \text{ Hz, 2H), 7.07 (d, } J = 9.0 \text{ Hz, 1H), 7.05 (d, } J = 3.9 \text{ Hz, 1H), 7.01 (s, 1H), 2.57 (s, 3H), 1.43 \text{(s, 12H).} \text{C}^{13}\text{H NMR (CDCl}_3\text{): } \delta 182.1, 160.7, 153.5, 153.7, 152.1, 151.7, 151.4, 149.4, 145.5, 142.8, 141.5, 138.6, 137.4, 136.3, 136.6, 127.8, 127.2, 126.7, 126.0, 125.8, 125.6, 124.8, 122.7, 121.1, 120.6, 120.2, 119.9, 119.7, 114.7, 116.4, 139.3, 131.9, 107.3, 47.0, 27.1, 17.1. MS: m/z 669 [M]^+\text{.} \text{Anal. Calc. for C}_42\text{H}_34\text{N}_4\text{O}_4\text{S}_2\text{C}: 78.73, 7.10. Found: C, 78.42; H, 4.91.\)

(E)-3-(5-(7-(Bis(9,9-dimethylfluorenyl-2-yl)amino)-4-methylcoumarin-3-yl)thiophen-2-yl)-2-cyanoacrylic acid (JK-34): A mixture of 5 (0.25 g, 0.37 mmol) and cyanoacetic acid (0.06 g, 0.74 mmol) were vacuum-dried and added MeCN (60 mL) and piperidine (0.036 mL, 0.37 mmol). The solution was refluxed for 8 h. After cooling the solution, the organic layer was removed in vacuo. The pure product JK-34 was obtained by silica gel chromatography (eluent MeOH:EtOAc = 1:1, Rf = 0.6) to afford JK-34 in 51% yield. Mp: 231 °C. \( \text{H NMR (DMSO-d}_6\text{): } \delta 8.05 \text{(s, 1H), 7.87 (d, } J = 8.4 \text{ Hz, 2H), 7.79 (t, } J = 7.2 \text{ Hz, 2H), 7.67 (d, } J = 3.9 \text{ Hz, 1H), 7.53 (d, } J = 7.2 \text{ Hz, 2H), 7.46-7.28 \text{(m, 5H), 7.22 (d, } J = 8.4 \text{ Hz, 2H), 7.23 (s, 2H), 6.95 (d, } J = 3.9 \text{ Hz, 2H), 6.76 \text{(s, 1H), 2.44 (s, 3H), 1.40 (s, 12H).} \text{C}^{13}\text{H NMR (DMSO-d}_6\text{): } \delta 162.8, 159.3, 155.2, 151.3, 151.2, 155.4, 144.9, 141.7, 140.5, 140.1, 137.3, 134.7, 135.8, 134.8, 129.5, 128.7, 128.1, 127.1, 124.9, 123.9, 123.1, 122.7, 121.4, 120.4, 119.9, 115.0, 113.1, 107.5, 46.7, 26.6, 17.1. MS: m/z 736 [M]^+\text{.} \text{Anal. Calc. for C}_49\text{H}_32\text{N}_2\text{O}_4\text{S}_2\text{C}: 78.74; C, 77.48; H, 4.81.\)

(E)-3-(5-(7-(Bis(9,9-dimethylfluorenyl-2-yl)amino)-4-methylcoumarin-3-yl)thiophen-2-yl)-2'-bithiophen(5-yl)-2'-cyanoacrylic acid (JK-35): Compound JK-35 was synthesized by a procedure similar to JK-34. Yield: 58%. Mp: 239 °C. \( \text{H NMR (DMSO-d}_6\text{): } \delta 8.08 \text{(s, 1H), 7.86 (d, } J = 7.8 \text{ Hz, 2H), 7.78 (t, } J = 8.1 \text{ Hz, 2H), 7.67 (d, } J = 4.2 \text{ Hz, 2H), 7.53 (d, } J = 7.8 \text{ Hz, 2H), 7.49-7.43 \text{(m, 8H), 7.31 (t, } J = 8.1 \text{ Hz, 2H), 7.21 (s, 2H), 6.96 (d, } J = 4.2 \text{ Hz, 1H), 6.79 (s, 1H), 2.44 (s, 3H), 1.40 (s, 12H).} \text{C}^{13}\text{H NMR (DMSO-d}_6\text{): } \delta 162.5, 159.2, 155.2, 154.5, 151.3, 154.9, 141.2, 140.5, 140.1, 138.3, 137.2, 136.8, 130.6, 129.5, 128.7, 128.1, 127.1, 125.3, 124.9, 123.9, 123.1, 122.7, 121.2, 120.4, 119.9, 115.0, 114.1, 109.7, 46.5, 26.6, 17.3. MS: m/z 819 [M]^+\text{.} \text{Anal. Calc. for C}_49\text{H}_32\text{N}_2\text{O}_4\text{S}_2\text{C}: 79.75; H, 4.68. Found: C, 75.47; H, 4.59.\)

(Z)-3-(5-(7-(Bis(9,9-dimethylfluorenyl-2-yl)amino)-4-methylcoumarin-3-yl)thiophen-2-yl)-2'-cyanoacrylic acid (JK-36): Compound JK-36 was synthesized by a procedure similar to JK-34. Yield: 53%. Mp: 221 °C. \( \text{H NMR (DMSO-d}_6\text{): } \delta 8.11 \text{(s, 1H), 7.83 (t, } J = 8.1 \text{ Hz, 2H), 7.74 (d, } J = 7.8 \text{ Hz, 2H), 7.63 (d, } J = 3.6 \text{ Hz, 1H), 7.52 (d, } J = 7.2 \text{ Hz, 2H), 7.46-7.27 \text{(m, 10H), 7.24 (s, 1H), 7.20 (d, } J = 7.8 \text{ Hz, 2H), 7.13 (d, } J = 3.6 \text{ Hz, 1H), 6.94 (d, } J = 8.1 \text{ Hz, 1H), 6.74 (s, 1H), 2.45 (s, 3H), 1.39 (s, 12H).} \text{C}^{13}\text{H NMR (DMSO-d}_6\text{): } \delta 163.5, 159.7, 156.2, 153.4, 152.3, 150.3, 146.9, 141.7, 140.8, 140.1, 138.3, 137.2, 135.8, 132.6, 129.5, 128.7, 128.1, 126.1, 126.5, 124.8, 124.1, 123.4, 123.1, 122.9, 122.5, 121.1, 121.4, 120.8, 120.4, 119.9, 118.4, 117.0, 113.1, 110.7, 46.5, 26.6, 17.1.\)
**Coumarin Dye for DSSCs**

MS: m/z 845 [M+]. Anal. Calc. for C_{36}H_{39}N_{2}O_{4}S_{2}: C, 76.75; H, 4.77. Found: C, 76.34; H, 4.57.

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**References**