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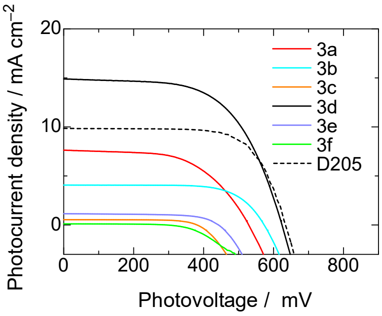
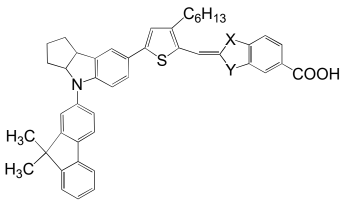


The best performance was obtained for **3d** due to suitable energy levels and sufficiently long singlet excited lifetime compared with the other derivatives.



Dye	X	Y
3a	S	C=O
3b	SO_2	C=O
3c	SO_2	$C=C(CN)_2$
3d	C=O	C=O
3e	$C=C(CN)_2$	C=OC
3f	$C=C(CN)_2$	$C=C(CN)_2$

Application of indoline dyes attached with strongly electron-withdrawing carboxylated indan-1,3-dione analogues linked with a hexylthiophene ring to dye-sensitized solar cells

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Abstract

An indoline dye attached with a carboxylated indan-1,3-dione moiety linked with a hexylthiophene ring exhibited the highest conversion efficiency among six analogues and **D205**. This result comes from the bathochromic UV-vis absorption band, suitable energy levels, good stability for redox process, and sufficiently long excited-state lifetime.

1. Introduction

Indoline dyes are one of the most efficient organic sensitizers in dye-sensitized solar cells (DSSCs).[1] Therefore, much effort has been devoted to obtain bathochromic indoline dyes by changing the pull moiety. Indoline dyes attached with cyanoacrylic acid,[2] single,[3] double,[4] and triple rhodanine acetic acid[5] pull moiety have been prepared and evaluated as the sensitizers. The first absorption maximum (λ_{max}) of triple rhodanine indoline dye was observed at 572 nm in chloroform.[5] Those of double rhodanine indoline dyes linked with mono-, di-, and trithienyl spacers were observed at 568, 564, and 550 nm, respectively.[6]

Thus, these indoline dyes are not bathochromic as expected. In 2012, carboxylated indan-1,3-dione was used as an electron acceptor anchor moiety in DSSCs.[7] Recently, an indoline dye attached with a 5-carboxyindan-1,3-dione pull anchor moiety linked with a thienyl ring has been reported to exhibit the $\lambda_{\max}$ at around 600 nm in chloroform and to show higher conversion efficiency than **D205**.[8] We consider that the indoline dyes having more electron-withdrawing pull moiety can show more bathochromic absorption bands to exhibit higher conversion efficiency. We report here the synthesis and photoelectrochemical properties of novel indoline dyes with a carboxylated benzo[*b*]thiophene-3(2*H*)one, benzo[*b*]thiophene-3(2*H*)one 1,1-dioxide, benzo[*b*]thiophene-3(2*H*)dicyanovinilidene 1,1-dioxide, indan-1,3-dione, indan-1-dicyanovinilidene-3-one, and indan-1,3-bis(dicyanovinilidene) anchor pull moiety linked with a hexylthiophene ring in DSSCs.

2. Results and Discussion

2.1.Synthesis

Novel indoline dyes **3a**, **3b**, **3c**, **3d**, **3e** and **3f** were synthesized as shown in Scheme 1. Compound **2a** was obtained by the intramolecular Friedel–Crafts alkanoyl reaction of **A**.[9] Compound **2b** was provided by the oxidation of **2a**. Compound **B**, prepared by the reaction of 4-mercaptobenzoic acid with ethanol in the presence of concentrated sulfuric acid, was allowed to react with chloroacetic acid to afford a carboxymethylthio derivative **C**, followed by the intramolecular Friedel–Crafts alkanoyl reaction to yield a sulfide **D**. Compound **D** was oxidized to provide a sulfone **E**, which was allowed to react with malononitrile followed by the hydrolysis of the ester moiety to give a dicyanovinilidene derivative **2c**. Compound **G** was allowed to react with ethyl acetoacetate to give a compound **H**, which was reacted with 3.0 molar amounts of malononitrile to provide both the mono(dicyanovinilidene) **I** and **I'** (51 %) and bis(dicyanovinilidene) derivatives **J** (28 %). The mono and bis derivatives were separated by column chromatography. For the mono derivative, both the 6- and 5-ethoxycarbonyl *regio* isomers **I** and **I'** were formed. These isomers were not separated by chromatography due to the same R_f value (SiO_2 TLC, $R_f = 0.35$, $CHCl_3$: MeOH = 3 : 1). However, when the mixture was recrystallized from ethanol, only the 6-ethoxycarbonyl isomer **I** was obtained as a crystalline form in a 28 % yield.

The heteronuclear multiple bond coherence (HMBC) spectrum of **I** is shown in Figure 1. The spectrum indicates that the H^5 peak correlates with the C^7, C^5, and COO peaks. The H^7 peak correlates with the C^5, C^{3a}, and COO peaks. The H^4 peak correlates with the C^6, C^{7a}, and C^3 peaks. Thus, compound **I** was identified as ethyl indan-3-dicyanovinilidene-1-one-6-carboxylate. The hydrolysis of ester moiety of **I** afforded the carboxyl derivative **2e**. Compound **H** was allowed to react with 4.0 molar amounts of malononitrile to give **J** in a 78 % yield. The hydrolysis of the ester moiety of **J** provided a carboxylic acid **2f**. Finally, an indoline carboaldehyde **1** was allowed to react with **2a**, **2b**, **2c**, **2d**, **2e**, and **2f** to afford **3a**, **3b**, **3c**, **3d**, **3e**, and **3f**, respectively.

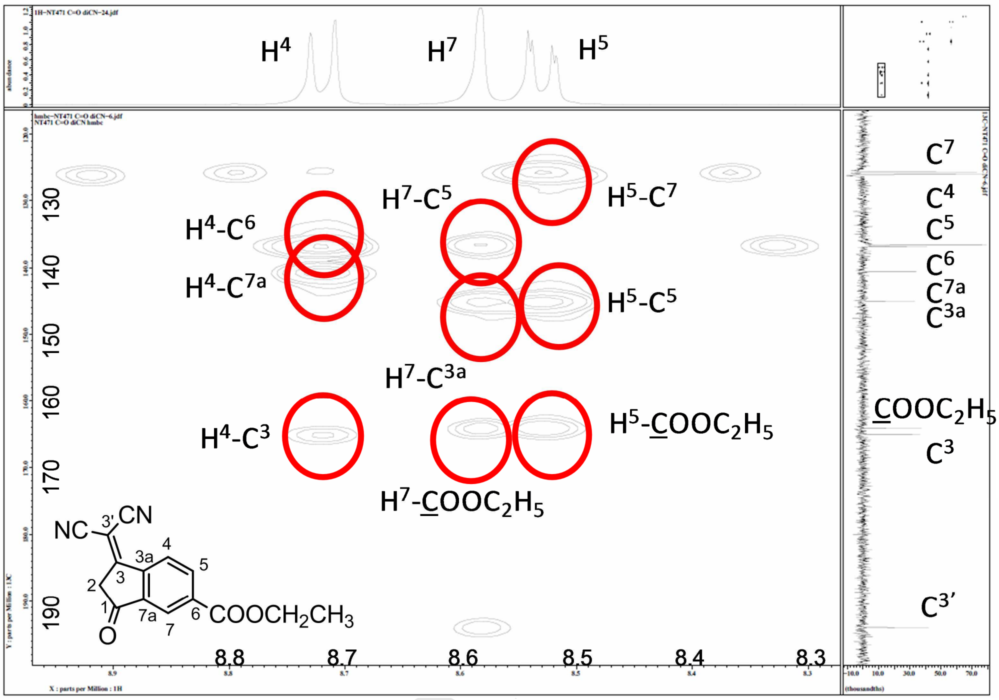
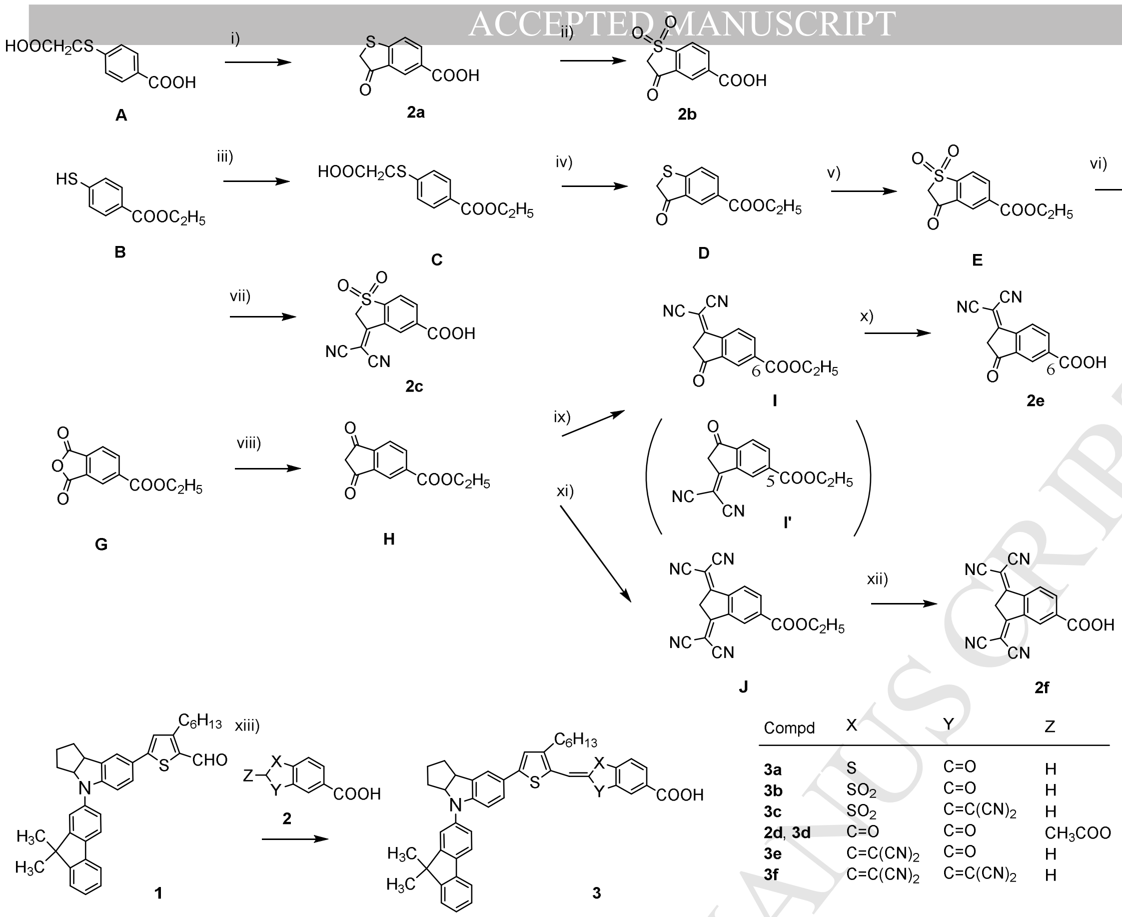


Figure 1. HMBC spectrum of **I**.



Compd	X	Y	Z
3a	S	C=O	H
3b	SO_2	C=O	H
3c	SO_2	$C=C(CN)_2$	H
2d, **3d**	C=O	C=O	CH_3COO
3e	$C=C(CN)_2$	C=O	H
3f	$C=C(CN)_2$	$C=C(CN)_2$	H

Scheme 1. Reagents and conditions: i) **A** (1.0 molar amount), $SOCl_2$ (excess), $AlCl_3$ (4.0 molar amounts), CH_2ClCH_2Cl, 0 °C, 20 min then rt, 18 h, ii) **2a** (1.0 molar amount), oxone (2.0 molar amounts), 1,4-dioxane-water (5/1), rt, 3 h, iii) $CH_2ClCOOH$ (1.5 molar amounts), K_2CO_3 (2.0 molar amounts), MeCN, rt, 3 h, then **B** (1.0 molar amount), 60 °C, 3 h, iv) **C** (1.0 molar amount), $SOCl_2$ (5 molar amounts), reflux, 30 min, then, $AlCl_3$ (4.0 molar amounts), CH_2ClCH_2Cl, 0 °C, 30 min, then rt, 21 h, v) **D** (1.0 molar amount), oxone (2.0 molar amounts), 1,4-dioxane-water (5/1), rt, 23 h, vi) **E** (1.0 molar amount), $CH_2(CN)_2$ (2.5 molar amounts), AcONa (1.0 molar amount), EtOH, reflux, 17 h, vii) **F** (1.0 molar amount), Me_3SiOK (1.0 molar amount), THF, rt, 21 h, then 10 % HCl, viii) **G** (1.0 molar amount), $AcCH_2COOEt$ (1.0 molar amount), Et_3N, (6.0 molar amounts), Ac_2O, 70 °C, 30 min, ix) **H** (1.0 molar amount), $CH_2(CN)_2$ (3.0 molar amounts), AcONa (1.0 molar amount), EtOH, reflux, 1 h, x) **I** (1.0 molar amount), Me_3SiOK (3.0 molar amounts), rt, 24 h, xi) **H** (1.0 molar amount), $CH_2(CN)_2$ (4.0 molar amounts), AcONa (1.0 molar amount), EtOH, reflux, 17 h, xii) **J** (1.0 molar amount), H_2O (excess), LiOH (7.0 molar amounts), THF, rt, 24 h, xiii) **1** (1.0 molar amount), **2a**, **2b, 2c** (1.3 molar amounts), AcOH, $AcONH_4$ (cat.), 120 °C. 2–4 h, or **1** (1.0 molar amount), **2d**, **2e**, **2f** (1.0 molar amount), AcOH, 55–100 °C, 3–4 h.

2.2. UV-Vis absorption and fluorescence spectra

The UV-Vis absorption and fluorescence spectra of **3a**, **3b**, **3c**, **3d**, **3e**, and **3f** in chloroform are shown in Figure 2 and the results are summarized in Table 1. The λ_{max} was more bathochromic in the order of dyes: **3f** (821 nm) > **3c** (750 nm) > **3e** (709 nm) > **3b** (614 nm), **3d** (610 nm) > **3a** (561 nm). The molar absorption coefficients (ε) were observed in the range of 39,000 to 65,800 dm^3 mol^{-1} cm^{-1}. Dyes **3a**, **3b**, and **3d** were fluorescent, showing the fluorescence maximum (F_{max}) at 713, 742, and 731 nm with fluorescence quantum yield (Φ_f) of 0.06, 0.10, and 0.21, respectively. Dyes **3c** and **3e** were very weak fluorescent compounds, having Φ_f lower than 0.01. Dye **3f** was non-fluorescent.

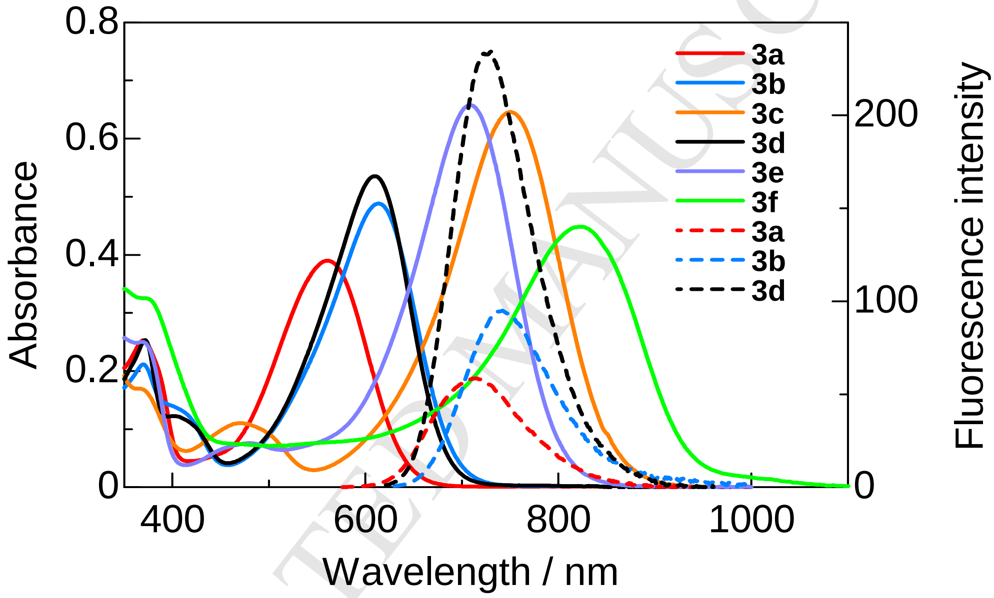


Figure 2. UV-Vis absorption and fluorescence spectra of **3a**, **3b**, **3c**, **3d**, **3e**, and **3f** (1.0×10^{-5} mol dm^{-3}) in chloroform. Solid and dotted lines represent the UV-Vis and fluorescence spectra, respectively.

Table 1 Physical data of **3a**, **3b**, **3c**, **3d**, **3e**, and **3f**

Dye	λ_{max} (ε)^a / nm	F_{max}^{a} / nm	Φ_f^{a}	τ_f^{a} / ns	E_{ox}^{b} / V	E_{red}^{b} / V
3a	370 (25,300), 561 (39,000)	713	0.06	0.70	0.87	–1.05
3b	371 (21,100), 412 (sh), 614 (48,800)	742	0.10	0.66	0.98	–0.83
3c	371 (sh), 471 (11,000), 750 (64,600)	901	< 0.01	-^{c}	0.99	–0.24
3d	371 (25,300), 412 (sh), 610 (53,500)	731	0.21	1.29	1.22	–0.60
3e	366 (25,000), 709 (65,800)	819	< 0.01	-^{c}	0.97	–0.73
3f	375 (sh), 821 (44,800)	-^{c}	-^{c}	-^{c}	0.97	–0.17^d

[a] Measured on 1.0 × 10^{-5} mol dm^{-3} of substrate in chloroform.
[b] *vs*. NHE in DMF.
[c] Not measured.
[d] Calculated on the basis of E_{ox} and onset peak.

The fluorescence decay curves of **3a**, **3b**, and **3d** are indicated in Figure 3. The fluorescence lifetime (τ_f) was determined by fitting the curve with a one-component exponential function. The τ_f of **3a**, **3b**, and **3d** were observed to be 0.70, 0.66, and 1.29 ns, respectively. The fluorescence of **3c** and **3e** was too weak to measure τ_f.

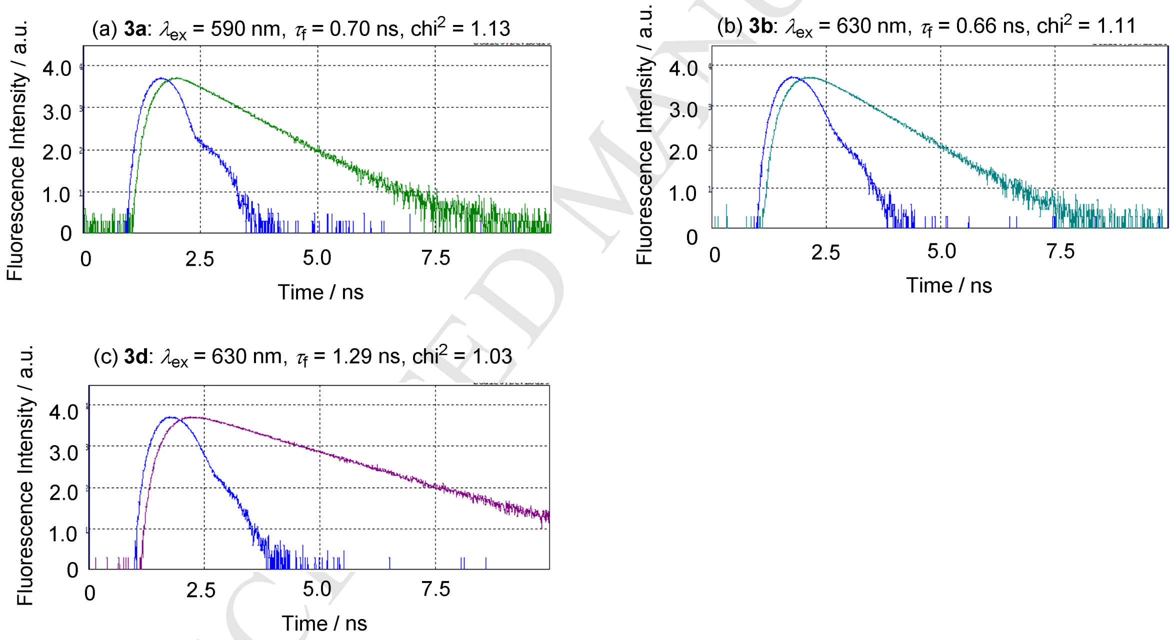


Figure 3. Fluorescence decay curve of **3a**, **3b**, and **3d** (1.0 × 10^{-5} mol dm^{-3}) in chloroform.

2.3.Electrochemical measurements

Figure 4 shows the cyclic voltammogram of **3a**, **3b**, **3c**, **3d**, **3e**, and **3f** *vs.* Ag *quasi* reference electrode (QRE) in DMF in the presence of ferrocene (Fc). In Figure 4b, the oxidation potential (E_{ox}) of Fc and **3d** and the reduction potential (E_{red}) of **3d** were observed at +0.99, +1.58, and –0.24 V, respectively. Then, the E_{ox} and E_{red} of **3d** were calculated to be +0.59 and –1.23 V *vs.* Fc/Fc$^+$, respectively. Therefore, the E_{ox} and E_{red} of **3d** were calculated to be +1.22 and –0.60 V *vs.* NHE, respectively.[10] In a similar way, the E_{ox} and E_{red} levels of **3a**, **3b**, **3c**, and **3e** were obtained. As the reduction peak of **3f** was not observed by the electrochemical measurements, the E_{red} level was calculated on the basis of the onset peak of the UV-Vis absorption band. The E_{ox} and E_{red} of **3a**, **3b**, **3c**, **3d**, **3e**, and **3f** are also listed in Table 1.

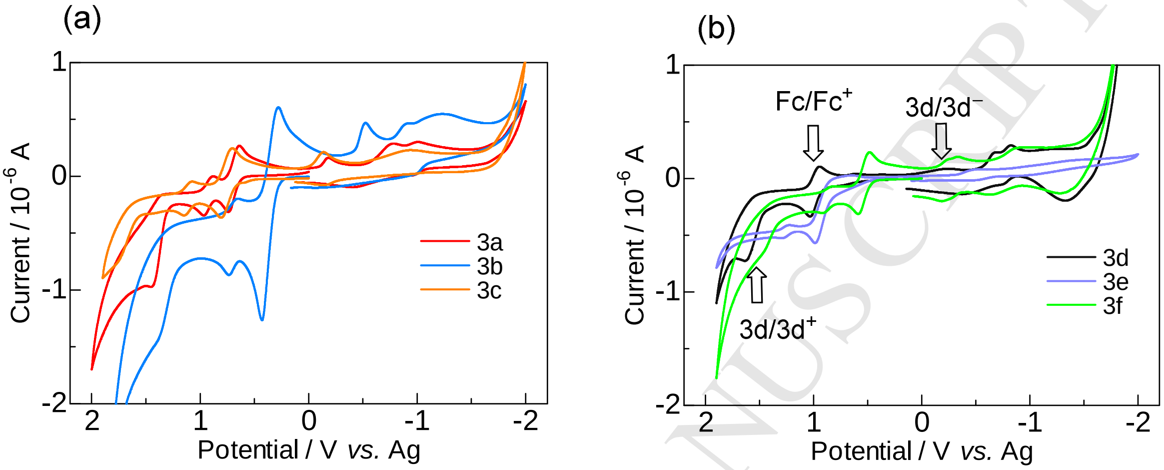


Figure 4. Cyclic voltammogram of (a) **3a**, **3b**, and **3c**, and (b) **3d**, **3e**, and **3f** measured *vs.* Ag *quasi* reference electrode in DMF in the presence of ferrocene (scan rate: 50 mV sec^{-1}).

2.4.DFT calculations

The optimized structures of **3a**, **3b**, **3c**, **3d**, **3e**, and **3f** by the DFT calculations (B3LYP/3-21G level) are shown in Figure S1. The *E*- and *Z*-configurations at the double bond between the hexylthiophene and indan-1,3-dione ring analogue are considerable for the indoline dyes. Furthermore, *s-trans* and *s-cis* conformations between the hexylthienyl ring and indan-1,3-dione analogue moiety are considerable for the respective *E*- and *Z*-configurations. Thus, four stereo isomers are considerable. Consequently, the *E*- and *s-trans* form was calculated to be most stable for **3d**. For the other derivatives, the stereo isomer having the least electronic repulsion between the hexylthienyl moiety and the substituent at the 1- or 3-position in the indan-1,3-dione analogue was most stable.

The single-point energy calculations were performed for the optimized structures by the B3LYP/6-31G(d,p) level. The calculated absorption maximum, main orbital transition, and oscillator strength of **3a**, **3b**, **3c**, **3d**, **3e**, and **3f** are shown in Table 2. The HOMO to LUMO transition was the main contribution (62–71 %) for the first absorption band, indicating that the HOMO and LUMO levels are important for the indoline dyes.

Table 2 Absorption maxima (λ_{max}), main orbital transition, and oscillator strengths (*f*) of **3a**, **3b**, **3c**, **3d**, **3e**, and **3f** calculated by TDDFT at the B3LYP/6-31G(d,p)//B3LYP/3-21G level

Dye	Transition	$\lambda_{max}{}^{a}$ / nm	Main orbital transition	*f*
3a	S_0 to S_1	548	HOMO to LUMO (0.70)	1.03
	S_0 to S_2	424	HOMO−1 to LUMO (0.66), HOMO−2 to LUMO (0.13), HOMO to LUMO+2 (0.17)	0.26
3b	S_0 to S_1	491	HOMO to LUMO (0.70)	0.92
	S_0 to S_2	451	HOMO to LUMO+1 (0.70)	0.18
3c	S_0 to S_1	673	HOMO to LUMO (0.70)	0.98
	S_0 to S_2	498	HOMO to LUMO+1 (0.69)	0.30
	S_0 to S_3	479	HOMO−1 to LUMO+1 (0.69), HOMO to LUMO+2 (0.10)	0.22
3d	S_0 to S_1	567	HOMO to LUMO (0.71)	0.94
	S_0 to S_2	489	HOMO to LUMO+1 (0.69)	0.20
3e	S_0 to S_1	623	HOMO to LUMO (0.69)	1.00
	S_0 to S_2	568	HOMO to LUMO+1 (0.69)	0.27
	S_0 to S_3	451	HOMO−1 to LUMO (0.69), HOMO to LUMO+2 (0.11)	0.27
3f	S_0 to S_1	700	HOMO to LUMO (0.62), HOMO to LUMO+1 (0.33)	0.35
	S_0 to S_2	643	HOMO to LUMO+1 (0.62)	0.74
	S_0 to S_3	507	HOMO−1 to LUMO (0.69)	0.07

Figure 5 shows the surface isodensity plots of HOMO–1, HOMO, LUMO, and LUMO+1 together with the energy levels in **3a**, **3b**, **3c**, **3d**, **3e**, and **3f**. These dyes showed intramolecular charge-transfer from the indoline to carboxylated indan-1,3-dione analogues in the first absorption band. The HOMO levels of **3a**, **3b**, **3c**, **3d**, **3e**, and **3f** were calculated to be 0.87, 0.98, 0.99, 1.22, 0.97, and 0.97, respectively. That of **D205** has been reported to be –5.06 eV.[4b] Thus, the E_{ox} levels are low enough to accept electrons from I^-/I_3^- electrolyte.

The LUMO levels of **3a**, **3b**, **3c**, **3d**, **3e**, and **3f** were calculated to be –2.37, –2.77, –3.20, –2.53, –2.93, and –3.27, respectively. That of **D205** has been reported to be –2.36 eV.[4b] The DFT calculations predict that the LUMO levels of **3c** and **3f** are low compared with the other analogues.

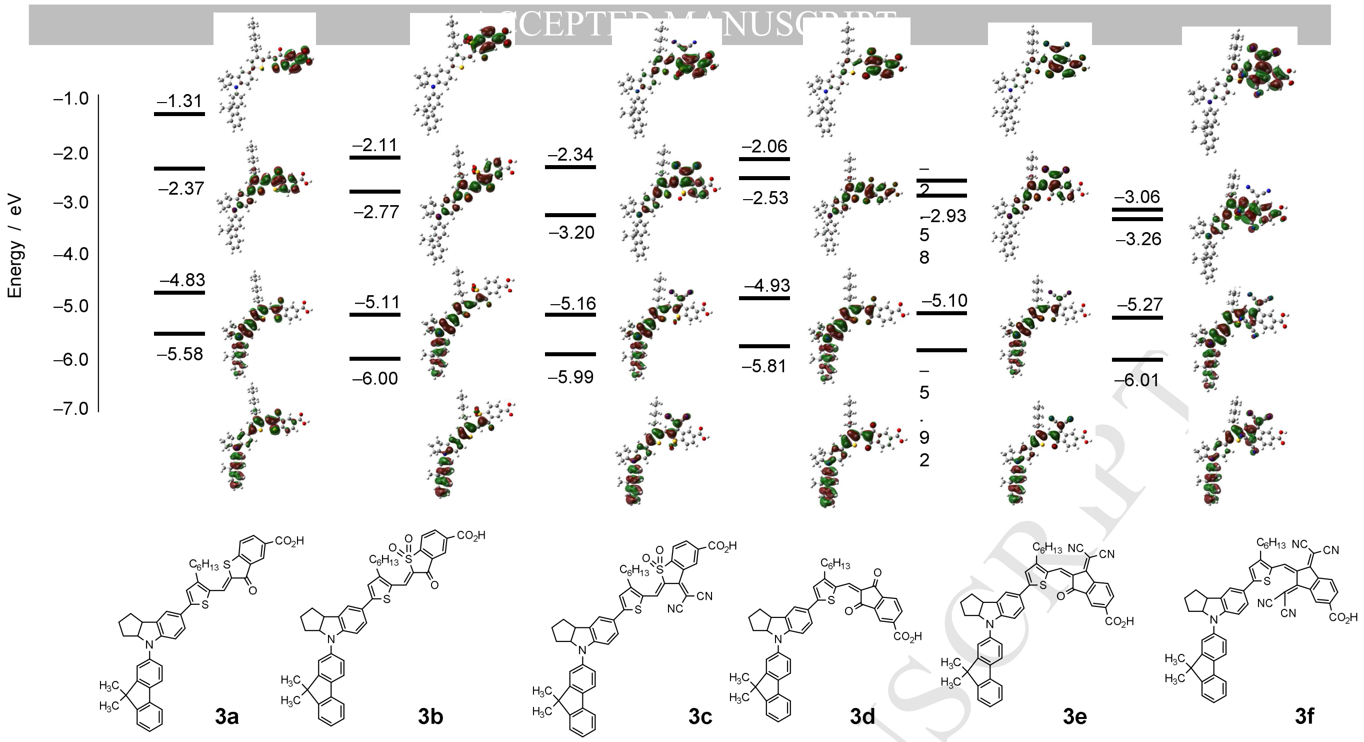


Figure 5. Surface isodensity plots and energy levels of **3a**, **3b**, **3c**, **3d**, **3e**, and **3f**.

2.5.Photoelectrochemical properties

The UV-Vis absorption spectra on titanium dioxide, IPCE spectra, and I-V curve of **3a**, **3b**, **3c**, **3d**, **3e**, and **3f** are shown in Figure 6, and the results are summarized in Table 3. Figure 6a shows that the UV-Vis absorption bands are broad compared with those in chloroform due to the aggregate formation on titanium dioxide. Figure 6b indicates that the maximum IPCE value of **3d** was higher than 70 % in the range of 500 to 650 nm, resulting in the highest short-circuit photocurrent (J_{sc}) among them. The I-V curve is shown in Figure 6c. Dye **3d** exhibited the J_{sc} and open-circuit photovoltage (V_{oc}) of 14.9 mA cm^{-2} and 0.621 V, respectively. The J_{sc} value was significantly higher than that of **D205**. Thus, dye **3d** showed the highest conversion efficiency of 5.55 % among **3a**, **3b**, **3c**, **3d**, **3e**, **3f**, and **D205**.

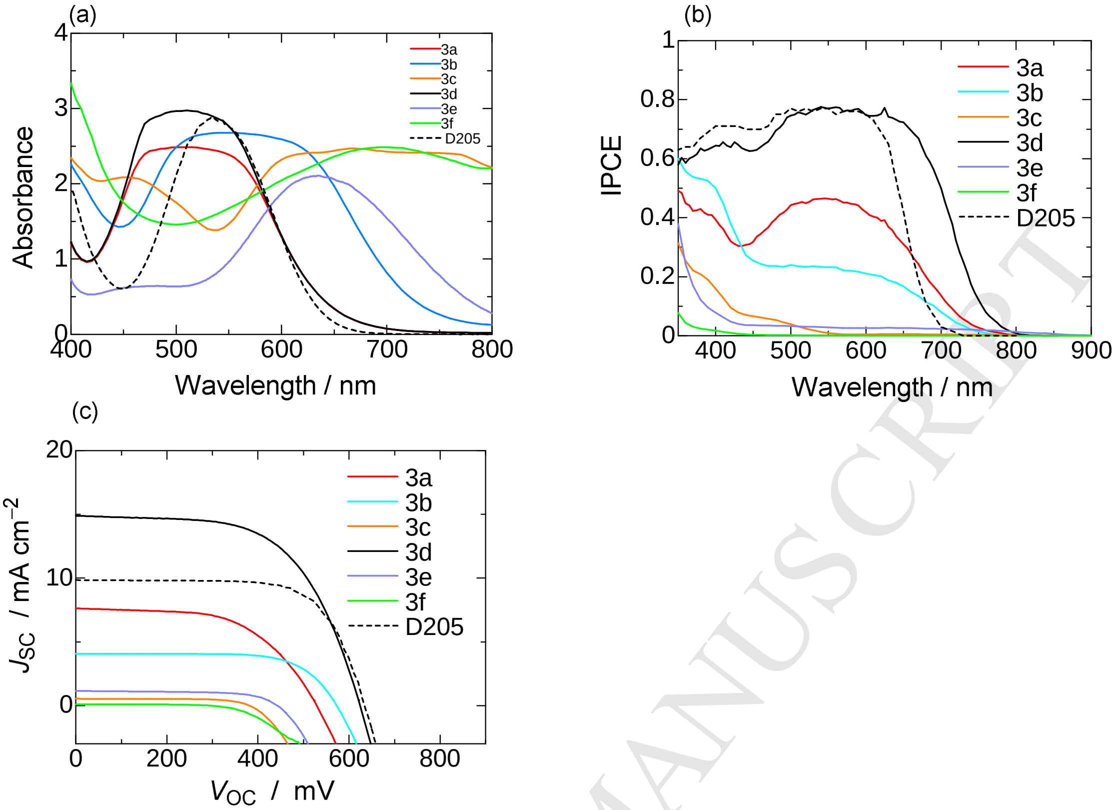


Figure 6. (a) UV-Vis absorption spectra on titanium dioxide, (b) IPCE spectra, and (c) I-V curve of **3a**, **3b**, **3c**, **3d**, **3e**, **3f**, and **D205**.

Table 3 Photoelectrochemical properties of **3a**, **3b**, **3c**, **3d**, **3e**, **3f**, and **D205**

Dye	J_{sc} / mA cm^{-2}	V_{oc} / V	*ff*	η / %
3a	7.63	0.523	0.57	2.29
3b	5.16	0.566	0.71	2.06
3c	0.68	0.381	0.70	0.18
3d	14.9	0.621	0.60	5.55
3e	1.15	0.433	0.67	0.33
3f	0.11	0.291	0.54	0.02
D205	9.85	0.630	0.69	4.33

The UV-Vis absorption band, energy levels, and excited-state lifetime drastically change by the kinds of indane-1,3-dione analogue moiety. As the indoline dyes have the intramolecular push–pull chromophoric system, the stronger the electron-withdrawing ability of the indan-1,3-dione analogues, the more bathochromic the λ_{max}. As expected, the λ_{max} on titanium dioxide was more bathochromic in the order of dyes: **3f**, **3c** > **3e** > **3b** > **3d**, **3a**, which is in consistent with that in chloroform. Comparing **3d** and **D205**, the UV-Vis absorption edge of **3d** and **D205** on titanium dioxide are observed at *ca*. 720 and 800 nm, respectively. The IPCE spectra clearly indicate that **3d** can act as a sensitizer in the range of 700 to 800 nm, which reflects higher J_{sc} value of **3d** than that of **D205**.

The I^-/I_3^- redox level and conduction band (CB) level of titanium dioxide *vs*. NHE have been reported to be *ca*. –0.5 and +0.4 V, respectively.[11] The E_{ox} levels of **3a**, **3b**, **3c**, **3d**, **3e**, and **3f** were lower than +0.4 V, indicating that the indoline dyes can accept electrons from I^-/I_3^- redox pair. The E_{red} level of **3a** (–1.05 V *vs*. NHE), **3b** (–0.83 V *vs*. NHE), **3d** (–0.60 V *vs*. NHE), and **3e** (–0.73 V *vs*. NHE) are higher than –0.5 V, suggesting that these dyes can inject electrons from the excited state to the CB. Meanwhile, those of **3c** (–0.24 V *vs*. NHE) and **3f** (–0.17 V *vs*. NHE) were lower than the CB level. Thus, both the electrochemical measurements and DFT calculations indicated that dyes **3c** and **3f** could not thermodynamically sensitize titanium dioxide.

Organic sensitizers should have long excited-state lifetime to inject electrons from the excited state to the CB of semiconductors. The τ_f of **3a**, **3b**, and **3d** in chloroform were observed to be 0.70, 0.66, and 1.29 ns, respectively. We have proposed that the τ_f value for the efficient indoline dye should be larger than *ca*. 0.8 ns.[12] Thus, the τ_f measurements suggest that dye **3d** can act as a highly efficient indoline sensitizer.

The color of **3c** and **3e** adsorbed on titanium dioxide changed from green and blue to yellow during I-V measurements, indicating that these dyes are not stable enough for electrochemical redox process.

Consequently, dye **3d** exhibited the highest conversion efficiency among the analogues and **D205**. It should be noted that such an improved performance of **3d** can be explained by the bathochromic UV-Vis absorption band, suitable energy levels, and a sufficiently long excited-state lifetime that allows for favored charge separation.

3. Conclusions

Six kinds of indoline dyes having a carboxylated indan-1,3-dione analogues linked with a hexylthiophene ring were synthesized and evaluated as the sensitizers. The indoline dye having the indan-1,3-dione exhibited the highest conversion efficiency of 5.55 % in DSSC among the analogues and **D205**. This result originates from the bathochromic UV-Vis absorption band, suitable energy levels, good stability for redox process, and sufficiently long lifetime in the excited state.

4. Experimental section

4.1.General

Melting points were measured with a Yanagimoto MP-S2 micro-melting-point apparatus. IR spectra were taken on a Shimadzu Affinity-1 spectrophotometer. NMR spectra were taken with a JEOL JNM-ECX 400P spectrometer. Mass spectra were taken on a JEOL MStation 700 spectrometer. Elemental analysis was performed with a Yanaco MT-6 CHN analyzer. UV-Vis absorption and fluorescence spectra were taken on Hitachi U-4100 and JASCO FP-8600 spectrophotometers, respectively. Fluorescence quantum yields and fluorescence lifetime were measured by Hamamatsu Photonics Quantaurus-QY and Quantaurus-Tau instruments, respectively. Electrochemical measurement was carried out using an EG&G Princeton Applied Research Potentiostat/Galvanostat (Model 263A) driven by the M270 software package.

4.2.Materials

Compound **B** was prepared by the reaction of 4-mercaptobenzoic acid with ethanol in the presence of conc. sulfuric acid. Compounds **G** was prepared as described in literature.[13] Compounds **1** and **2d** were supplied from Chemicrea Inc.

*4.3.Synthesis of **2b***

To a 1,4-dioxane-water (5 : 1) mixed suspension (24 mL) of **2a** (650 mg, 3.3 mmol) was added oxone (4.0 g, 6.6 mmol). The suspension was stirred at room temperature for 3 h. After the reaction was complete, the solid was filtered. The filtrate was concentrated *in vacuo*. The resulting precipitate was recrystallized from ether. Yield 15 %; mp 230–232 °C; IR (KBr) ν = 3468, 1740, 1717, 1319, 1196 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ = 4.68 (s, 2H), 8.28 (d, J = 8.3 Hz, 1H), 8.36 (s, 1H), 8.52 (d, J = 8.3 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ = 57.56, 122.25, 124.55, 133.57, 136.50, 137.58, 149.81, 165.28, 187.16; EIMS (70 eV) *m/z* (rel intensity) 226 (M$^+$, 70), 162 (100); Anal. Calcd for $C_9H_6O_5S$: C, 47.79; H, 2.67. Found: 47.57; H, 2.72.

*4.4.Synthesis of **C***

To an acetonitrile solution (55 mL) of chloroacetic acid (4.3 g, 45 mmol) was added potassium carbonate (8.3 g, 60 mmol). The mixture was stirred at room temperature for 10 min. Then, to the mixture was added **B** (5.5 g, 30 mmol) and stirred at 60 °C for 3 h. After the reaction was complete, to the mixture was added dichloromethane (150 mL) and water (100 mL). Water layer was acidified with 10 % hydrochloric acid. The resulting precipitate was filtered and purified by column chromatography (SiO_2, CH_2Cl_2) to give white powder. Yield 88 %; mp 117–119 °C; IR (KBr) ν = 1705 cm^{-1} ; ^{1}H NMR (DMSO-d_6) δ= 1.31 (t, J = 7.1 Hz, 3H), 3. (s, 2H95), 4.29 (q, J = 7.1 Hz, 2H), 7.41 (d, J = 8.7 Hz, 2H), 7.86 (d, J = 8.7 Hz, 2H); ^{13}C NMR (DMSO-d_6) δ = 14.17, 39.08, 60.66, 126.04 (2C), 126.52, 129.54 (2C), 143.08, 165.36, 170.18; EIMS (70 eV) *m/z* (rel intensity) 240 (M^+, 100), 195 (93); Anal. Calcd for $C_{11}H_{12}O_4S$: C, 54.99; H, 5.03. Found: C, 54.68; H, 5.01.

4.5.Synthesis of ***D***

To thionylchloride (5 mL) was added **C** (1.0 g, 4.2 mmol) and refluxed for 30 min. Then, the excess thionylchloride was removed *in vacuo*. The product was dissolved in 1,2-dichroloethane (5 ml) and cooled to 0 °C. To the solution was added anhydrous aluminum (III) trichloride (2.2 g, 16.8 mmol). The mixture was stirred at 0 °C for 30 min and then at room temperature for 21 h. After the reaction was complete, to the mixture was added ice-water. The product was extracted with dichloromethane (50 mL × 3). The organic layer was dried over anhydrous sodium sulfate, concentrated, and purified by column chromatography (SiO_2, CH_2Cl_2). Yield 81 %; mp 66–68 °C; IR (KBr) ν = 1717, 1686 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.40 (t, *J* = 7.1 Hz, 3H), 3.87 (s, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 1H), 8.21 (dd, *J* = 8.4 and 1.8 Hz, 1H), 8.42 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 14.27, 39.85, 61.36, 124.44, 127.51, 127.95, 130.98, 136.14, 159.27, 165.37, 198.96; EIMS (70eV) *m/z* (rel intensity) 222 (M^+, 80), 177 (100); Anal. Calcd for $C_{11}H_{10}O_3S$: C, 59.44; H, 4.53. Found; C, 59.29; H, 4.38.

4.6.Synthesis of ***E***

To a 1,4-dioxane-water (5 : 1) mixed suspension of **D** (752 mg, 3.4 mmol) was added oxone (4.2 g, 6.8 mmol). The suspension was stirred at room temperature for 23 h. After the reaction was complete, the solid was filtered. The filtrate was concentrated and purified by column chromatography (SiO_2, $CHCl_3$) to give a pink powder. Yield 49 %; mp 142–144 °C; IR (KBr) ν = 1732, 1601, 1312, 1196 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.45 (t, *J* = 7.0 Hz, 3H), 4.17 (s, 2H), 4.47 (q, *J* = 7.0 Hz, 2H), 8.07 (d, *J* = 8.2 Hz, 1H), 8.59 (d, *J* = 8.2 Hz, 1H), 8.65 (s, 1H); ^{13}C NMR ($CDCl_3$) δ

= 14.19, 57.57, 62.44, 122.01, 125.96, 133.38, 136.34, 137.90, 150.54, 163.77, 185.92; EIMS *m/z* 254 (M^+, 59), 209(100); Anal. Calcd for $C_{11}H_{10}O_5S$: C, 51.96; H, 3.96. Found: C, 51.75; H, 4.06.

*4.7.Synthesis of **F***

To an ethanol suspension (4 mL) of **E** (200 mg, 0.79 mmol) were added malononitrile (130 mg, 2.0 mmol) and anhydrous sodium acetate (65 mg, 0.79 mmol). The mixture was refluxed for 17 h. After the reaction was complete, to the mixture was added water (4 mL) and acidified by 10 % hydrochloric acid. The product was extracted with dichloromethane (10 mL × 3), dried over anhydrous sodium sulfate, and purified by column chromatography (SiO_2, CH_2Cl_2) to give pink powder. Yield 91 %; mp 166–168 °C; IR (KBr) ν = 2230, 1717, 1327, 1165 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.45 (t, *J* = 7.2 Hz, 3H), 4.49 (q, *J* = 7.2 Hz, 2H), 4.61 (s, 2H), 8.04 (d, *J* = 8.2 Hz, 1H), 8.56 (d, *J* = 8.2 Hz, 1H), 9.33 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 14.07, 56.56, 62.76, 83.45, 110.99, 111.11, 123.08, 127.43, 129.58, 136.85, 137.27, 146.57, 156.73, 163.27; EIMS (70 eV) *m/z* (rel intensity) 302 (M^+, 30), 274 (92), 257 (100); Anal. Calcd for $C_{14}H_{10}N_2O_4S$: C, 55.62; H, 3.33; N, 9.27. Found: C, 55.11; H, 3.14; N, 8.98 %.

*4.8.Synthesis of **2c***

To a THF solution (25 mL) of **F** (300 mg, 1.0 mmol) was added potassium trimethylsilanolate (255 mg, 2.0 mmol). The mixture was stirred at room temperature for 21 h. After the reaction was complete, the mixture was concentrated and acidified with aqueous 10 % hydrochloric acid. The product was extracted with dichloromethane (30 mL × 3), dried over anhydrous sodium sulfate, and purified by column chromatography (SiO_2, CH_2Cl_2 : MeOH = 25 : 1) to give pale pink powder. Yield 48 %; mp 210–212 °C; IR (KBr) ν = 3428, 2237, 1705, 1323, 1162 cm^{-1}; ^1H NMR (acetone-d_6) δ = 5.00 (s, 2H), 8.23 (d, *J* = 7.9 Hz, 1H), 8.63 (d, *J* = 7.9 Hz, 1H), 9.35 (s, 1H); ^{13}C

NMR (acetone-d_6) δ = 57.37, 83.57, 112.66, 112.99, 123.79, 128.17, 131.15, 137.37, 137.98, 148.02, 159.11, 165.23; EIMS (70 eV) *m/z* (rel intensity) 274 (M^+, 100), 165 (51); Anal. Calcd for $C_{12}H_6N_2O_4S$: C, 52.55; H, 2.21; N, 10.21. Found: 52.24; H, 2.52; N, 9.95.

*4.9.Synthesis of **H***

To acetic anhydride (10 mL) were added **G** (1.5 g, 6.8 mmol), ethyl acetoacetate (889 mg, 6.8 mmol), and triethylamine (4.1 g, 40.8 mmol). The mixture was heated at 70 °C for 30 min. After the reaction was complete, the mixture was poured into water (120 mL) containing conc. sulfuric acid (12 mL). The resulting precipitate was filtered, dried, dissolved in acetonitrile, and refluxed for 1 h. After cooling, the product was purified by column chromatography (SiO_2, $CHCl_3$: MeOH = 100 : 1) to give an orange powder. Yield 71 %; mp 60–62 °C; IR (KBr) ν = 1753, 1713 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.45 (t, *J* = 7.1 Hz, 3H), 3.33 (s, 2H), 4.46 (q, *J* = 7.1 Hz, 2H), 8.04 (d, *J* = 8.1 Hz, 1H), 8.51 (d, *J* = 8.1 Hz, 1H), 8.63 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 14.21, 45.41, 62.15, 123.30, 124.50, 136.38, 137.11, 143.33, 145.68, 164.63, 196.49, 196.74; FABMS (NBA) *m/z* 219 (MH^+); Anal. Calcd for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 66.15; H, 4.68.

*4.10. Synthesis of **I***

To an ethanol suspension (20 mL) of **H** (1.95 g, 8.9 mmol) were added malononitrile (1.77 g, 26.8 mmol) and anhydrous sodium acetate (689 mg, 8.9 mmol). The mixture was refluxed for 1 h. After the reaction was complete, the reaction mixture was poured into water (50 mL). The solution was acidified with 10 % aqueous hydrochloric acid. The product was extracted with chloroform (50 mL × 3) and dried over anhydrous sodium sulfate. Red and blue spots were observed on silicagel TLC. The red component (a mixture of **I** and **I’**, R_f = 0.35, $CHCl_3$: MeOH = 3 : 1) was isolated by column chromatography (SiO_2, $CHCl_3$: MeOH = 25 : 1) and recrystallized from ethanol to give **I** as a pale yellow solid. Yield 28 %; mp 190–192 °C; IR (KBr) ν = 2234, 1734, 1717 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.45 (t, *J* = 7.0 Hz, 3H), 3.81 (s, 2H), 4.47 (q, *J* = 7.0 Hz, 2H), 8.53 (d, *J* = 8.5 Hz, 1H), 8.58 (s, 1H), 8.72 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 14.19, 43.46, 62.35, 80.98, 111.70, 111.79, 125.63, 125.99, 136.62, 136.84, 140.61, 145.08, 164.09, 165.03, 193.97; FABMS (NBA) *m/z* 267 (MH^+); Anal. Found: C, 67.58; H, 3.61; N, 10.48 %. Calcd for $C_{15}H_{10}N_2O_3$: C, 67.67; H, 3.79; N, 10.5 2%. The blue component (R_f = 0.50, $CHCl_3$: MeOH = 3 : 1) was isolated by column chromatography (SiO_2, $CHCl_3$: MeOH = 25 : 1) to give **J** (28 %) as a blue solid.

*4.11. Synthesis of **2e***

To a THF solution (20 mL) of **I** (500 mg, 1.9 mmol) was added potassium trimethylsilanolate (723 mg, 5.6 mmol). The mixture was stirred at room temperature for 24 h. After the reaction was complete, the mixture was acidified with 10 % aqueous hydrochloric acid. The product was extracted with chloroform (50 mL × 4), dried over anhydrous sodium sulfate, and purified by column chromatography (SiO_2, CH_2Cl_2 : MeOH = 20 : 1) to give orange powder. Yield 99 %; mp 239–241°C; IR (KBr) ν = 1717 cm^{-1}; ^{1}H NMR (acetone-*d*$_6$) δ = 4.00 (s, 2H), 8.44 (s, 1H), 8.61 (d, *J* = 8.3 Hz, 1H), 8.72 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (acetone-*d*$_6$) δ = 44.42, 80.67, 113.08, 113.29, 125.39, 126.66, 137.09, 137.28, 141.97, 146.44, 165.71, 167.80, 195.58; FABMS (NBA) *m/z* 239 (MH^+); Anal. Calcd for $C_{13}H_6N_2O_3$: C, 65.55; H, 2.54; N, 11.76. Found: C, 65.37; H, 2.46; N, 11.58.

*4.12. Synthesis of **J***

To an ethanol suspension (10 mL) of **H** (800 mg, 3.7 mmol) were added malononitrile (975 mg, 14.6 mmol) and anhydrous sodium acetate (283 mg, 3.7 mmol). The mixture was refluxed for 17 h. After the reaction was complete, the mixture was poured into water (50 mL) and acidified with 10%

aqueous hydrochloric acid. The product was extracted with chloroform (70 mL × 3), dried over anhydrous sodium sulfate, and purified by column chromatography (SiO_2, $CHCl_3$: MeOH = 25 : 1) to give blue precipitate. Yield 78%; mp 206–208 °C; IR (KBr) ν = 2226, 1719 cm^{-1}; ^1H NMR (acetone-d_6) δ = 1.42 (t, J = 7.1 Hz, 3H), 4.47 (q, J = 7.1 Hz, 2H), 4.69 (s, 2H), 8.61 (d, J = 8.2 Hz, 1H), 8.71 (d, J = 8.2 Hz, 1H), 9.20 (s, 1H); ^{13}C NMR (acetone-d_6) δ = 14.34, 43.16, 62.90, 79.69, 80.60, 112.76, 112.82, 112.98 (2C), 127.40, 127.56, 136.83, 137.41, 141.96, 144.61, 164.61, 167.25, 167.57; FABMS (NBA) *m/z* 315 (MH^+); Anal. Calcd for $C_{11}H_{12}O_4S$: C, 68.79; H, 3.21; N, 17.8. Found: C, 69.06; H, 3.33, N, 17.52.

*4.13. Synthesis of **2f***

To a THF solution (2 mL) of **J** (100 mg, 0.32 mmol) were added water (1 mL) and lithium hydroxide (54 mg, 2.24 mmol). The mixture was stirred at room temperature for 24 h. After the reaction was complete, the mixture was concentrated and acidified with 10 % hydrochloric acid. The product was extracted with dichloromethane (20 mL × 5), dried over anhydrous sodium sulfate, and washed with hexane to give blue powder. Yield 98 %; mp >300 °C; IR (KBr) ν = 3406, 2199, 1724 cm^{-1}; ^1H NMR (acetone-d_6) δ = 4.70 (s, 2H), 8.65 (d, J = 8.3 Hz, 1H), 8.73 (d, J = 8.3 Hz, 1H) , 9.24 (s, 1H); ^{13}C NMR (acetone-d_6) δ = 43.19, 79.66, 80.59, 112.78, 112.83, 113.01 (2C), 127.39, 127.84, 137.16, 137.59, 141.98, 144.63, 165.41, 167.23, 167.57; FABMS (NBA) *m/z* 287 (MH^+); Anal. Calcd for $C_{16}H_6N_4O_2$: C, 67.14; H, 2.11; N, 19.57. Found: C, 66.95; H, 2.05; N, 19.49.

*4.14. Synthesis of **3a***

To an acetic acid solution (2 mL) of **2a** (50 mg, 0.26 mmol) and **1** (140 mg, 0.26 mmol) was added ammonium acetate (3 mg). The mixture was heated at 120 °C for 2 h. After the reaction was complete, water was added to the mixture. The resulting precipitate was filtered and purified by column chromatography (SiO_2, $CHCl_3$: MeOH = 100 : 1). Yield 35 %; mp 158–160 °C; IR (KBr) ν = 3429, 1690 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ = 0.87 (t, J = 6.2 Hz, 3H), 1.27–1.31 (m, 4H), 1.34–1.38, (m, 2H), 1.42–1.44 (m, 1H), 1.47 (s, 6H), 1.63–1.67 (m, 3H), 1.78–1.80 (m, 1H), 1.86–1.92 (m, 2H), 2.07–2.14 (m, 1H), 2.80 (t, J = 7.6 Hz, 2H), 3.87–3.89 (m, 1H), 5.01–5.04 (m, 1H), 6.99 (d, J = 8.2 Hz, 1H), 7.27–7.34 (m, 3H), 7.48–7.53 (m, 4H), 7.57 (s, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.93 (d, J = 8.2 Hz, 1H), 8.09 (s, 1H), 8.17 (d, J = 8.2 Hz, 1H), 8.27 (s, 1H); ^{13}C NMR (DMSO-d_6) δ = 13.96, 22.05, 24.09, 26.85, 26.98, 28.47, 28.51, 30.43, 31.02, 33.06, 34.80, 44.41, 46.55, 68.69, 79.17, 107.58, 114.19, 118.75, 119.45, 120.95, 122.21, 122.66, 122.96, 124.66, 124.79, 124.95, 125.95, 126.52, 126.62, 127.04, 128.58, 129.14, 130.94, 132.93, 135.10, 136.19, 138.45, 141.03, 148.07, 148.97, 151.32, 152.95, 153.09, 154.77, 166.37, 185.61; FABMS (NBA) *m/z* 722 (MH^+); Anal. Calcd for $C_{46}H_{43}NO_3S_2$: C, 76.53; H, 6.00; N, 1.94. Found: 76.20; H, 5.85; N, 1.92.

4.15. Synthesis of ***3b***

To an acetic acid solution (2 mL) of **2b** (50 mg, 0.22 mmol) and **1** (120 mg, 0.22 mmol) was added ammonium acetate (3 mg). The mixture was heated at 120 °C for 2 h. After the reaction was complete, water was added to the reaction mixture. The resulting precipitate was filtered and purified by column chromatography (SiO_2, $CHCl_3$: MeOH = 100 : 1). Yield 37 %; mp 175–177 °C; IR (KBr) ν = 1728, 1377, 1157 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ = 0.87 (t, J = 6.9 Hz, 3H), 1.28–1.33 (m, 4H), 1.36–1.39 (m, 2H), 1.42–1.47 (m, 1H), 1.47 (s, 3H), 1.48 (s, 3H), 1.66–1.69 (m, 3H), 1.77–1.79 (m, 1H), 1.84–1.91 (m, 2H), 2.10–2.15 (m, 1H), 2.91 (t, J = 7.6 Hz, 2H), 3.90–3.92 (m, 1H), 5.09–5.11 (m, 1H), 7.00 (d, J = 8.2 Hz, 1H), 7.29 (t, J = 7.2 Hz, 1H), 7.32–7.35 (m, 2H), 7.54 (d, J = 7.5 Hz, 1H), 7.56 (d, J = 2.0 Hz, 1H), 7.61 (dd, J = 7.2 and 2.0 Hz, 1H), 7.67 (s, 1H), 7.69–7.71 (m, 1H), 7.78 (d, J = 7.5 Hz, 1H), 7.84 (d, J = 8.2 Hz, 1H), 8.14 (s, 1H), 8.29 (d, J = 8.3 Hz, 1H), 8.42 (s, 1H), 8.51 (d, J = 8.3 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ = 13.97, 22.05, 24.06, 26.81, 26.97, 28.47, 28.81, 30.67, 30.97, 30.88, 35.00, 44.24, 46.62, 68.99, 79.19, 107.59, 114.96, 119.51, 119.62, 121.04, 121.44, 121.61, 122.08, 122.71, 123.01, 124.38, 125.19, 125.45, 126.72, 127.10, 127.55, 131.72, 132.42, 133.64, 136.51, 136.93, 138.35, 140.40, 146.11, 149.65, 153.21, 154.84, 158.99, 161.44, 165.43, 176.82; FABMS (NBA) *m/z* 754 (MH^+); Anal. Calcd for $C_{46}H_{43}NO_5S_2$: C, 73.28; H, 5.75; N, 1.86. Found: 73.44; H, 5.52; N, 1.78.

*4.16. Synthesis of **3c***

To an acetic acid solution (3 mL) of **2c** (100 mg, 0.36 mmol) and **1** (200 mg, 0.36 mmol) was added ammonium acetate (3 mg). The mixture was heated at 120 °C for 4 h. After the reaction was complete, water was added to the reaction mixture. The resulting precipitate was filtered and purified by column chromatography (SiO_2, $CHCl_3$: MeOH = 100 : 1). Yield 28 %; mp 179–181 °C; IR (KBr) ν = 3433, 2210, 1732, 1396, 1177 cm^{-1}; ^1H NMR (DMSO-d_6) δ = 0.87 (m, 3H), 1.27–1.30 (m, 4H), 1.38–1.44 (m, 3H), 1.47 (s, 3H), 1.48 (s, 3H), 1.66–1.71 (m, 3H), 1.76–1.78 (m, 1H), 1.84–1.89 (m, 2H), 2.09–2.15 (m, 1H), 2.90 (t, *J* = 7.9 Hz, 2H), 3.90–3.93 (m, 1H), 5.13–5.15 (m, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.33–7.35 (m, 2H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.58 (s, 1H), 7.66 (d, *J* = 9.0 Hz, 1H), 7.71 (s, 1H), 7.76 (s, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 1H), 8.25 (d, *J* = 8.7 Hz, 1H), 8.44 (d, *J* = 8.7 Hz, 1H), 8.86 (s, 1H), 9.30 (s, 1H); ^{13}C NMR (DMSO-d_6) δ = 14.33, 22.40, 24.37, 27.15, 27.30, 29.10, 29.51, 31.36 (2C), 33.12, 35.39, 44.53, 47.02, 67.42, 69.72, 108.07, 115.91, 116.06, 116.47, 120.10, 120.41, 120.47, 121.45, 122.44, 122.62, 123.10, 123.83, 126.08 (2C), 127.23, 127.31, 127.49, 128.90, 129.68, 131.84, 134.60, 136.02, 136.88, 137.18, 138.63, 140.32, 141.27, 150.35, 150.99, 153.65, 155.27, 162.71, 163.44, 165.69; FABMS (NBA) *m/z* 802 (MH^+); Anal. Calcd for $C_{49}H_{43}N_3O_4S_2$: C, 73.38; H, 5.40; N, 5.24. Found: 73.63; H, 5.53; N, 5.01.

*4.17. Synthesis of **3d***

To an acetic acid solution (3 mL) of **1** (110 mg, 0.2 mmol) was added **2d** (50 mg, 0.2 mmol). The mixture was heated at 100 °C for 4 h. After the reaction was complete, the mixture was poured into water (3 mL). The resulting precipitate was purified by column chromatography (SiO_2, $CHCl_3$: MeOH = 100 : 1). Yield 55 %; mp 152–154 °C; IR (KBr) ν = 3429, 1724 cm^{-1}; ^1H NMR (DMSO-d_6) δ = 0.85 (t, J = 6.5 Hz, 3H), 1.26–1.29 (m, 4H), 1.32–1.34 (m, 2H), 1.40–1.43 (m, 1H), 1.47 (s, 3H), 1.48 (s, 3H), 1.61–1.65 (m, 3H), 1.75–1.77 (m, 1H), 1.83–1.90 (m, 2H), 2.07–2.13 (m, 1H), 2.80 (t, J = 7.2 Hz, 2H), 3.82–3.85 (m, 1H), 5.00–5.02 (m, 1H), 6.93 (dd, J = 8.2 and 6.2 Hz, 1H), 7.26–7.29 (m, 2H), 7.32 (t, J = 7.6 Hz, 1H), 7.48 (s, 1H), 7.52–7.53 (m, 3H), 7.57 (s, 1H), 7.74 (d, J = 6.8 Hz, 1H), 7.78–7.80 (m, 2H), 7.84 (t, J = 7.6 Hz, 1H), 8.18 (d, J = 5.5 Hz, 1H), 8.27 (t, J = 8.6 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ = 13.93, 22.05, 24.08, 26.83, 26.97, 28.61, 28.95, 30.60, 31.00, 32.97, 34.86, 44.33, 46.58, 68.88, 107.54, 114.58, 119.15, 119.51, 119.70, 120.94, 122.40, 122.65 (2C), 122.83, 125.00, 126.62, 127.06, 128.59, 131.52, 132.27, 133.36, 135.48, 136.24, 138.40, 139.49, 140.63, 141.20, 142.13, 143.81, 149.02, 153.16, 154.78, 157.45, 160.51, 166.15, 187.89, 189.05; FABMS (NBA) *m/z* 718 (MH^+); Anal. Calcd for $C_{47}H_{43}NO_4S$: C, 78.63; H, 6.04; N, 1.95. Found: 78.66; H, 6.27; N, 1.92.

*4.18. Synthesis of **3e***

To an acetic anhydride solution (3 mL) of **1** (137 mg, 0.25 mmol) was added **2e** (60 mg, 0.25 mmol). The mixture was stirred at 60 °C for 2 h. After the reaction was complete, the crude product was concentrated and purified by column chromatography (SiO_2, $CHCl_3$: MeOH = 100 : 1). Yield 20 %; mp 253–255 °C; IR (KBr) ν = 3426, 2214, 1705 cm^{-1}; ^1H NMR (DMSO-d_6) δ = 0.87 (brs, 3H), 1.30 (brs, 4H), 1.38 (brs, 2H), 1.47 (s, 3H), 1.49 (s, 3H), 1.49 (brs, 1H), 1.67 (brs, 3H), 1.79 (brs, 1H), 1.87 (brs, 2H), 2.12 (brs, 1H), 2.88 (brs, 2H), 3.90 (brs, 1H), 5.13 (brs, 1H), 6.97 (d, J = 9.0 Hz, 1H), 7.29–7.34 (m, 3H), 7.51–7.58 (m, 2H), 7.66–7.72 (m, 3H), 7.79 (d, J = 6.9 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 8.17 (s, 1H), 8.36 (d, *J* = 7.9 Hz, 1H), 8.53 (d, *J* = 7.9 Hz, 1H), 8.75 (s, 1H); ^{13}C NMR (DMSO-d_6) δ = 14.38, 22.47, 24.44, 27.22, 27.38, 29.13, 29.98, 31.23, 31.42, 33.24, 35.39, 44.64, 47.96, 69.60, 108.03, 115.71, 115.84, 116.21, 118.68, 120.10, 120.23, 1221.48, 122.87, 123.15 (2C), 123.33, 123.82, 124.74, 126.22, 127.22, 127.54, 128.59, 129.99, 131.96, 134.40, 135.89, 136.80, 137.03, 138.75, 140.57, 142.48, 142.95, 150.58, 153.67, 155.29, 161.95, 163.98, 166.23, 172.57, 187.50; FABMS (NBA) *m/z* 766 (MH$^+$); Anal. Calcd for $C_{50}H_{43}N_3O_3S$: C, 78.40; H, 5.66; N, 5.49. Found: 78.10; H, 5.41; N, 5.22.

*4.19. Synthesis of **3f***

To an acetic anhydride solution (4 mL) of **1** (95 mg, 0.17 mmol) was added **2f** (50 mg, 0.17 mmol). The mixture was stirred at 50 °C for 2 h, then at 55 °C for 1 h. After the reaction was complete, to the mixture was added water (4 mL). The product was extracted with chloroform. The extract was dried over anhydrous sodium sulfate, concentrated *in vacuo*, and purified by column chromatography (SiO_2, $CHCl_3$: MeOH = 100 : 1). Yield 39 %; mp 179–181°C; IR (KBr) ν = 3622, 2210, 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.90 (t, *J* = 7.2 Hz, 3H), 1.33–1.35 (m, 4H), 1.45–1.48 (m, 2H), 1.50 (s, 3H), 1.52 (s, 3H), 1.54–1.61 (m, 1H), 1.74–1.79 (m, 3H), 1.82–1.87 (m, 1H), 1.96–1.98 (m, 2H), 2.13–2.17 (m, 1H), 2.89 (t, *J* = 7.9 Hz, 2H), 3.90–3.93 (m, 1H), 5.05–5.07 (m, 1H), 6.89 (d, *J* = 8.9 Hz, 1H), 7.20 (s, 1H), 7.25–7.26 (m, 1H), 7.31–7.35 (m, 2H), 7.37 (d, *J* = 2.1 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.47 (s, 1H), 7.52 (dd, *J* = 8.6 and 1.8 Hz, 1H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 8.36 (d, *J* = 8.3 Hz, 1H), 8.62 (d, *J* = 8.3 Hz, 1H), 8.89 (s, 1H), 9.21 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 14.07, 22.52, 24.26, 27.10, 27.28, 29.14, 30.73, 31.27, 31.52, 33.12, 35.39, 44.75, 47.00, 70.60, 107.99, 114.51, 114.78 (3C), 116.20, 119.73, 120.81, 120.84, 120.94, 122.17, 122.60, 124.28, 124.61, 125.04, 125.82, 127.16 (2C), 129.69, 132.87, 133.26, 134.77, 135.06, 136.05, 137.11, 137.65, 138.44, 139.52, 152.55, 153.44, 155.31, 158.55, 158.92, 163.15, 165.94, 168.84, two carbon peaks are missing due to overlapping with those of chloroform;

FABMS (NBA) *m/z* 814 (MH^+); Anal. Calcd for $C_{53}H_{43}N_5O_2S$: C, 78.20; H, 5.32; N, 8.60. Found: 77.98; H, 5.14; N, 8.47.

4.20. Preparation of TiO_2/Dye hybrid films and device assembly

F-doped SnO_2 coated glass substrates (4 mm thickness, 13 $\Omega\ \square^{-1}$, Nippon Sheet Glass) were used to prepare TiO_2 photoelectrodes. A commercial titanium dioxide paste (PST-18NR, JGC Catalysts and Chemicals Ltd.) was deposited onto the FTO glass by doctor blade technique and subsequently sintered at 500 °C for 15 min to obtain the 8 μm thick mesoporous titanium dioxide layer.[14] After immersing the TiO_2 films into 40 mM aqueous $TiCl_4$ solution at 70 °C for 30 min, the substrates were sintered at 500 °C for 30 min. The TiO_2 electrodes were then immersed in the 0.2 mM dye solution (solvent: acetonitrile/*t*-butyl alcohol = 1 : 1 (v/v)) in the presence of chenodeoxycholic acid (0.4 mM). The dye adsorption was performed under dark at 25 °C for 3 h. (**3a**, **3d**) or 6 h. (**3b**, **3c**, **3e**, and **3f**). Pt-sputtered FTO glasses were used as counter electrodes. The dyed-TiO_2 electrode and counter electrode were assembled into a sandwich-type cell (active area: 5 mm × 6 mm) with a reported method.[15] The composition of electrolyte solution was 3-methoxypropionitrile solution of 1,2-dimethyl-3-propylimidazolium iodide (0.6 M), I_2 (0.05 M), LiI (0.1 M), and 4-*t*-butylpyridine (0.05 M).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https:/doi.00000000.

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Highlights

Indoline dyes showing $\lambda_{\max}$ in the range of 561 to 821 nm.

Best indoline sensitizer among six analogues.

Importance of energy levels, fluorescence lifetime, and stability as sensitizers.