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Substituent effects in a double rhodanine indoline dye on performance of zinc oxide dye-sensitized solar cell

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1. Introduction

Recently, the structures of highly efficient organic sensitizers for dye-sensitized solar cells have been focused on arylamine [1,2], dimethylfluorene [3], carbazole [4], and indoline dyes [5-10]. Among these organic sensitizers, a double rhodanine indoline dye named D149 has been reported to show highest solar-to-electricity conversion efficiency (η) 9.0% on titanium oxide [11]. More recently, D205, the N-octyl derivative of D149 was reported to show even higher efficiency of 9.4% [12]. In the case of zinc oxide, indoline dyes also displayed high conversion efficiency among the organic sensitizers. In order to exhibit high conversion efficiency, it is important to obtain high incident photon-to-current efficiency (IPCE), which can reflect high short-circuit photocurrent density (I_{sc}) . In principle, the reduction potential of sensitizers should be at a greater negative level than the conduction band level of the semiconductor, whilst, at the same time, the oxidation potential level should be more positive than the I^-/I_3^- redox level of the

ABSTRACT

The solar-light-to-electricity conversion efficiency of substituted indoline dyes depended on short-circuit photocurrent density which is affected by maximum incident photon-to-current efficiency. The oxidation potential of the double rhodanine indoline dyes needed to be > 0.2 V vs Fc/Fc⁺ in acetonitrile to show high incident photon-to-current efficiency in a zinc oxide, dye-sensitized solar cell. To make a molecular design of highly efficient indoline dyes, the HOMO energy level should be more negative than ~ -4.9 eV by the DFT calculations.

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electrolyte. This paper concerns the relationship among these energy levels in double rhodanine indoline dyes.

2. Results and discussion

2.1. Synthesis

Indoline dyes **21–26** were synthesized as shown in Scheme 1. Compound **1** was allowed to react with aromatic bromides **2–7** to give *N*-aryl derivatives **8–13**, followed by formylation to afford **14–19**, which were allowed to react with a double rhodanine **20** in the presence of piperidine to give **21–26**.

2.2. UV-vis absorption and fluorescence spectra

The UV–vis absorption and fluorescence spectra of **21–26** are shown in Fig. 1. The results are also listed in Table 1. The absorption maxima (λ_{max}) were observed in the range of 516–555 nm with molar absorption coefficients (ε) in the range of 56 200–78 300. As the double rhodanine indoline dyes show intramolecular charge-transfer chromophoric system from indoline to rhodanine moiety, electron-donating substituent such as dimethylamino, diphenylamino, and methoxy groups, on the indoline moiety can cause

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Scheme 1. i) 2–7 (1.0 eq), K₂CO₃ (3.0 eq) or *t*-BuOK (1.3 eq), Pd(OAc)₂ (cat), (*t*-Bu)₃P (0.1 eq), ii) POCl₃ (2.0 eq), DMF, -10 °C to rt (1 day) or -10 °C to 60 °C (3 h), iii) 20 (1.0 eq), piperidine (cat), BuOH, reflux, 3 h.

bathochromic shift [13]. The fluorescence maximum (F_{max}) was observed in the range of 578–712 nm. Interestingly, the fluorescence intensity drastically changed by the kinds of substituent.

2.3. Electrochemical properties

The oxidation potential (E_{ox}) of **21–26** was measured in acetonitrile by cyclic voltammetry. Fig. 2 shows the voltammogram of **23** in the presence of ferrocene as an internal standard. There are three distinct redox waves observed in the voltammogram. The first



Fig. 1. UV–vis absorption and fluorescence spectra of 21-26 in chloroform. Measured on $1.0\,\times\,10^{-5}$ mol dm $^{-3}$ of substrate at 25 $^\circ$ C.

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Physical properties of indoline dyes.

Compd	$\lambda_{\max} (\varepsilon)^a / nm$	F _{max} ^a /nm	RFI ^b	$E_{\rm ox}^{\rm c}/{\rm V}$	$E_{\rm ox} - E_{\rm 0-0}^{\rm c}/{\rm V}$
21	396 (24 300), 555 (56 200)	712	5	-0.11	-2.13
22	386 (26 500), 549 (66 500)	700	20	+0.15	-1.88
23	387 (27 500), 546 (78 300)	633	217	+0.30	-1.80
24	385 (21 800), 538 (65 600)	608	100	+0.40	-1.75
25	381 (24 000), 521 (68 800)	584	48	+0.51	-1.73
26	383 (27 700), 516 (68 200)	578	40	+0.53	-1.73

 $^a\,$ Measured on 1 \times 10 $^{-5}\,$ mol dm $^{-3}$ of substrate in chloroform at 25 $^\circ C.$

^b Relative fluorescence intensity.

^c vs Fc/Fc⁺ in acetonitrile.

oxidative wave (I) at +0.38 V was due to the oxidation of the internal standard of ferrocene, whereas the second wave (II) near +0.71 V vs AgQRE was due to the electrochemical oxidation of **23**, respectively. The third oxidative wave (III) at 1.25 V may arise from the further oxidation of **23**. The oxidation peak potential (E_{pa}) for **23** can therefore be calculated to be +0.33 V vs Fc/Fc⁺ in acetonitrile. Although the standard E_{ox} are usually not easily obtained experimentally, it can be approximately estimated from the cyclic voltammetric peak potential, which equals to ($E_{pa} - 29$ mV) if the electrochemical oxidation is a reversible step [14]. Hence, the E_{ox} for **23** was estimated to be +0.30 V vs Fc/Fc⁺ in this study. The I⁻/I₃ redox level was estimated as -0.05 V vs Fc/Fc⁺.

No reduction peak was observed for indoline dyes. Therefore, the $E_{0x}-E_{0-0}$ level, where E_{0-0} represents the intersection of normalized absorption and the fluorescence spectra in chloroform, was calculated. This is considered to correspond to the reduction potential [15]. The E_{0-0} of **23** was observed at 590 nm, corresponding to 2.10 eV. Therefore, the $E_{0x}-E_{0-0}$ level of **23** is calculated to be $-1.80 \text{ V vs Fc/Fc}^+$ in acetonitrile. The E_{0x} and $E_{0x}-E_{0-0}$ levels of the other indoline dyes were obtained in the same way. The results are also listed in Table 1.



Fig. 2. Electrochemical measurement of **23**. Measured in acetonitrile (2 ml) containing tetrabutylammonium perchlorate (0.1 mol dm⁻³) and ferrocene (*ca*. 1 mmol dm⁻³). AgQRE was used as a reference electrode. Platinum wire was used as the working and counter electrodes. The scan rate was 100 mV s⁻¹.

2.4. Photoelectrochemical properties of indoline dyes and MO calculations

In all cases, addition of cholic acid (CA) during dye-adsorption process improved the cell performance. The UV–vis absorption and photon-to-current action spectra on zinc oxide in the presence of CA are shown in Figs. 3 and 4, respectively. Fig. 3 shows that the order of bathochromicity of indoline dyes on zinc oxide is similar to that in chloroform. Indoline dyes substituted with electron-donating group were more bathochromic than those with electron-withdrawing group. To discuss the substituent effect, IPCE was used because of similar absorbance (2.33–2.50) of dyes on zinc oxide.

Fig. 4 indicates that the maximum IPCE was in the order of dyes: **24** (80.8), **26** (79.3), **23** (79.1), **25** (78.8) > **22** (50.8) > **21** (9.3). This order is also similar to that of J_{sc} : **23** (10.29), **24** (9.80), **25** (8.36), **26** (8.31) > **22** (5.83) > **21** (0.96). The solar-light-to-electricity conversion efficiency (η) was larger in the following order: **23** (4.08), **24** (4.07) > **25** (3.58), **26** (3.34) > **22** (2.12) > **21** (0.22). The values of open-circuit voltage (V_{oc}) except for **21** and **22** were in the range of 0.61–0.63, there being no remarkable difference. Thus, it is clear that the maximum IPCE value mainly affects the η value.

The energy level of dyes measured in solution differs from that of adsorbed one. Unfortunately, indoline dyes and ferrocene on zinc oxide coated ITO electrode did not give the distinct redox responses. Therefore, the energy level of indoline dyes measured in acetonitrile was used to discuss thermodynamic electron transfer in the solar cell. In the case of titanium oxide, the energy gap of 0.2–0.3 V is required to proceed the electron transfer [15,16]. To obtain high IPCE, the reduction potential should be more negative



Fig. 3. UV-vis absorption spectra of 21-26 on zinc oxide.



Fig. 4. Photon-to-current action spectra of 21-26 on zinc oxide.

Table	2			
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hotoelectrochemical	properties	of indo	line dyes.°
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Compd	$\lambda_{\max}\left(\varepsilon\right)/nm$	Absorbance	IPCE/%	$J_{\rm sc}/{\rm mA}~{\rm cm}^{-2}$	$V_{\rm oc}/V$	ff	$\eta/\%$
21	529	2.50	9.3	0.96	0.42	0.55	0.22
22	517	2.41	50.8	5.83	0.56	0.65	2.12
23	516	2.33	79.1	10.29	0.61	0.65	4.08
24	519	2.43	80.8	9.80	0.61	0.68	4.07
25	479	2.38	78.8	8.36	0.63	0.69	3.58
26	486	2.46	79.3	8.31	0.61	0.66	3.34

^a In all cases, two molar amounts of cholic acid for dye was used during adsorption process. Photoelectrochemical measurements were performed under AM 1.5 irradiation (100 mW cm⁻²).



Fig. 5. Relationship among maximum IPCE, *E*_{ox}, and calculated HOMO level of indoline dyes.

than the conduction band level of semiconductor. All the indoline dyes showed sufficiently negative $E_{ox}-E_{0-0}$ level compared to the conduction band level of zinc oxide as shown in Table 1. For example, the $E_{ox}-E_{0-0}$ level of **23** was calculated to be -1.80 V vs Fc/Fc⁺. This level is much more negative than the conduction band level of zinc oxide (*ca.* -0.95 V vs Fc/Fc⁺), the energy gap being *ca.* 0.85 V. Even in the case of **26**, whose $E_{ox}-E_{0-0}$ level was -1.73 V, the energy gap was 0.78 V. Therefore, it is more important to examine the E_{ox} level of indoline dyes to obtain highly efficient derivatives. The relationship among maximum IPCE values, E_{ox} , and calculated HOMO level of substituted indoline dyes are shown in Fig. 5. High IPCE value was obtained for **23**, **24**, **25**, and **26**, whose E_{ox} is more positive than *ca.* 0.2 V vs Fc/Fc⁺ in acetonitrile.

To make a molecular design of indoline dyes, it is of significance to predict the E_{ox} level. The structures od indoline dyes were optimized by the B3LYP/3-21G level. Then, the HOMO energy level was calculated by the B3LYP/6-31G (d,p) level. The result is also shown in Fig. 5. Good correlation was observed between E_{ox} and HOMO energy level. It was found that the HOMO energy level of indoline dyes should be more stable than *ca*. -4.9 eV, which corresponds to the E_{ox} level more positive than *ca*. 0.2 V *vs* Fc/Fc⁺, to design high IPCE sensitizers. Table 2.

3. Conclusions

The substituent effect in double rhodanine indoline dyes was examined to clarify the relationship among IPCE, oxidation and reduction potential energy levels of indoline dyes, semiconductor conduction band level, and I^-/I_3^- redox level. The reduction potential level of indoline dye was sufficiently negative compared with the conduction band level of zinc oxide. However, the E_{ox} level

was required more positive than *ca*. 0.2 V vs Fc/Fc^+ in acetonitrile to show high IPCE. To make a molecular design of indoline dyes, the HOMO level should be more negative than *ca*. -4.9 eV by the DFT calculations.

4. Experimental

4.1. Instruments

Melting points were measured with a Yanaco MP-13 micromelting-point apparatus. NMR spectra were obtained by a JEOL ECX 400P spectrometer. MS spectra were recorded on a JEOL MStation 700 spectrometer. UV–vis absorption and fluorescence spectra were recorded on Hitachi U-3500 and F-4500 spectrophotometers, 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

1,2,3,3*a*,4,8*b*-Hexahydrocyclopenta[*b*]indole (**1**) and double rhodanine acetic acid (**20**) were obtained from Chemicrea Co., Ltd. 1-Bromo-4-(dimethylamino)benzene (**2**), 1-bromo-4-(diphenylamino)benzene (**3**), 1-bromo-4-methoxybenzene (**4**), phenyl bromide (**5**), 1-bromo-4-(trifluoromethyl)benzene (**6**), and 1-bromo-4-cyanobenzene (**7**) were purchased from Tokyo Kasei Co., Ltd.

4.3. Synthesis of 8-13

In the cases of 8-11, to toluene (37 ml) were added 1,2,3,3a,4,8bhexahydrocyclopenta[*b*]indole (1, 1.59 g, 10 mmol), aromatic bromides 2–5 (10 mmol), potassium tert.-butoxide (1.68 g, 13 mmol), palladium acetate (12 mg, 5.4×10^{-2} mmol), and tritert.-butylphosphine (caution: Pyrophoric. Spontaneously flammable in air. Air sensitive; 192 mg, 1 mmol). In the cases of **12** and 13, to toluene (37 ml) was added 1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (1, 1.59 g, 10 mmol), aromatic bromides 6 and 7 (10 mmol), potassium carbonate (2.07 g, 30 mmol), palladium acetate (12 mg, 5.4×10^{-2} mmol), and tri-*tert*.-butylphosphine (192 mg, 1 mmol). The mixture was refluxed for 3 days under an argon atmosphere. After the reaction was complete, the mixture was filtered and the filtrate washed with saturated aqueous ammonium chloride (20 ml \times 3). After drying the filtrate over anhydrous sodium sulfate, the solvent was removed in vacuo. The crude product was purified by silica gel column chromatography (8; $CH_2Cl_2:AcOEt = 40:1$, 9, 10, 11, 12; $CH_2Cl_2:C_6H_{14} = 1:3$, 13; $CH_2Cl_2:C_6H_{14} = 2:1$). The physical and spectral data are shown below.

4.3.1. 4-[4-(Dimethylamino)phenyl]-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole (**8**)

Yield 85%; mp 88–90 °C; ¹H NMR (DMSO- d_6) δ = 1.44–1.45 (m, 1H), 1.57–1.72 (m, 4H), 1.94–2.03 (m, 1H), 2.87 (s, 6H), 3.73–3.77 (m, 1H), 4.67–4.71 (m, 1H), 6.49 (d, *J* = 7.6 Hz, 1H), 6.54 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 2H), 6.90 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 8.2 Hz, 2H); EI-MS (70 eV) *m*/*z* (rel intensity) 278 (M⁺, 100), 249 (60).

4.3.2. 4-[4-(Diphenylamino)phenyl]-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole (**9**)

Yield 92%; mp 155–157 °C; ¹H NMR (DMSO- d_6) δ = 1.31–1.41 (m, 1H), 1.60–1.64 (m, 1H), 1.77–1.89 (m, 3H), 1.97–2.07 (m, 1H), 3.30–3.84 (m, 1H), 4.74–4.77 (m, 1H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.97–7.02 (m, 7H), 7.04 (d, *J* = 8.7 Hz, 2H),

6.96–7.05 (m, 9H), 7.11 (d, *J* = 7.5 Hz, 1H), 7.25–7.29 (m, 6H); EI-MS (70 eV) *m*/*z* (rel intensity) 402 (M⁺, 100), 249 (25).

4.3.3. 4-(4-Methoxyphenyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole (**10**)

Yield 76%; oil; ¹H NMR (CDCl₃) δ = 1.51–2.05 (m, 6H), 3.79–3.83 (m, 1H), 3.81 (s, 3H), 4.68–4.72 (m, 1H), 6.65 (t, *J* = 7.8 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.99 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 2H); EI-MS (70 eV) *m/z* (rel intensity) 265 (M⁺, 84), 278 (100).

4.3.4. 4-Phenyl-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole (11)

Yield 74%; oil; ¹H NMR (CDCl₃) δ = 1.49–1.59 (m, 1H), 1.61–1.70 (m, 1H), 1.80–1.96 (m, 3H), 2.00–2.09 (m, 1H), 3.82–3.86 (m, 1H), 4.73–4.78 (m, 1H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.96 (t, *J* = 7.2 Hz, 1H), 7.02–7.05 (m, 2H), 7.12 (d, *J* = 7.2 Hz, 1H), 7.27–7.35 (m, 4H); EI-MS (70 eV) *m/z* (rel intensity) 235 (M⁺, 50), 206 (100).

4.3.5. 4-[4-(Trifluoromethyl)phenyl]-1,2,3,3a,4,8b-

hexahydrocyclopenta[b]indole (12)

Yield 70%; mp 69–70 °C; ¹H NMR (CDCl₃) δ = 1.43–1.54 (m, 1H), 1.63–1.71 (m, 1H), 1.87–1.97 (m, 3H), 2.01–2.11 (m, 1H), 3.85–3.90 (m, 1H), 4.69–4.74 (m, 1H), 6.83 (t, *J* = 7.1 Hz, 1H), 7.08–7.17 (m, 3H), 7.32 (d, *J* = 9.0 Hz, 2H), 7.53 (d, *J* = 9.0 Hz, 2H); EI-MS (70 eV) *m*/*z* (rel intensity) 303 (M⁺, 49), 274 (100).

4.3.6. 4-(4-Cyanophenyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole (**13**)

Yield 85%; mp 75–76 °C; ¹H NMR (CDCl₃) δ = 1.41–1.50 (m, 1H), 1.64–1.72 (m, 1H), 1.87–2.11 (m, 4H), 3.88–3.92 (m, 1H), 4.64–4.69 (m, 1H), 6.89 (t, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.2 Hz, 2H), 7.55 (d, *J* = 7.2 Hz, 2H); EI-MS (70 eV) *m*/*z* (rel intensity) 260 (M⁺, 50), 231 (100).

4.4. Synthesis of 14–19

To DMF (15 ml) was added phosphoryl chloride (caution: Reacts violently with water. Incompatible with many metals, alcohols, amines, phenol, DMSO, strong bases; 920 mg, 5.9 mmol) at -10 °C with stirring. To this mixture was added a DMF solution of **8**–**13** (3 mmol) at -5 °C. The mixture was stirred for 1 h at -10 °C. Then, the mixture was stirred for 1 day at room temperature. In the cases of **18** and **19**, the mixture was heated at 60 °C for 3 h. After the reaction was completed, to the mixture was added water (50 ml). The mixture was neutralized with 1 N hydrochloric acid. The product was extracted with dichloromethane (150 ml × 3). After the extract was dried over anhydrous sodium sulfate, the solvent was removed *in vacuo*. The product was purified by column chromatography (SiO₂, CH₂Cl₂). The physical and spectral data are shown below.

4.4.1. 4-[4-(Dimethylamino)phenyl]-1,2,3,3a,4,8b-

hexahydrocyclopenta[b]indole-7-carbaldehyde (14)

Yield 67%; mp 139–141 °C; ¹H NMR (DMSO- d_6) δ = 1.32–1.45 (m, 1H), 1.57–1.76 (m, 4H), 1.97–2.09 (m, 1H), 2.91 (s, 6H), 3.79–3.83 (m, 1H), 4.87–4.91 (m, 1H), 6.43 (d, *J* = 8.3 Hz, 1H), 6.79 (d, *J* = 9.0 Hz, 2H), 7.17 (d, *J* = 9.0 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 1H), 7.51 (s, 1H), 9.58 (s, 1H); EI-MS (70 eV) *m*/*z* (rel intensity) 306 (M⁺, 100), 277 (48).

4.4.2. 4-[4-(Diphenylamino)phenyl]-1,2,3,3a,4,8b-

hexahydrocyclopenta[b]indole-7-carbaldehyde (15)

Yield 76%; mp 173–174 °C; ¹H NMR (CDCl₃) δ = 1.31–1.43 (m, 1H), 1.64–1.65 (m, 1H), 1.74–1.79 (m, 3H), 2.00–2.10 (m, 1H), 3.83–3.87 (m, 1H), 4.93–4.99 (m, 1H), 6.79 (d, *J* = 8.2 Hz, 1H),

7.62–7.07 (m, 8H), 7.29–7.33 (m, 6H), 7.54–7.57 (m, 2H), 9.65 (s, 1H); EI-MS (70 eV) *m/z* (rel intensity) 430 (M⁺, 100), 401 (18).

4.4.3. 4-(4-Methoxyphenyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole-7-carbaldehyde (**16**)

Yield 86%; oil; ¹H NMR (CDCl₃) δ = 1.52–1.54 (m, 2H), 1.67–1.70 (m, 2H), 1.86–1.88 (m, 2H), 2.03–2.07 (m, 1H), 3.84 (s, 3H), 4.83–4.86 (m, 1H), 6.55 (d, *J* = 8.3 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 1H), 7.61 (s, 1H), 9.67 (s, 1H); EI-MS (70 eV) *m/z* (rel intensity) 293 (M⁺, 100), 264 (94).

4.4.4. 4-Phenyl-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole-7-carbaldehyde (**17**)

Yield 70%; mp 120–122 °C; ¹H NMR (CDCl₃) δ = 1.49–1.55 (m, 1H), 1.65–1.78 (m, 2H), 1.86–1.91 (m, 2H), 2.04–2.08 (m, 1H), 3.81–3.86 (m, 1H), 4.91–4.94 (m, 1H), 6.82 (d, *J* = 8.3 Hz, 1H), 7.13 (t, *J* = 8.3 Hz, 1H), 7.28–7.31 (m, 2H), 7.37–7.39 (m, 2H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.63 (s, 1H), 9.70 (s, 1H); EI-MS (70 eV) *m/z* (rel intensity) 263 (M⁺, 57), 234 (100).

4.4.5. 4-[4-(Trifluoromethyl)phenyl]-1,2,3,3a,4,8bhexahydrocyclopenta[b]indole-7-carbaldehyde (**18**)

Yield 70%; mp 85–87 °C; ¹H NMR (CDCl₃) δ = 1.42–1.56 (m, 1H), 1.68–1.76 (m, 1H), 1.83–1.96 (m, 3H), 2.06–2.14 (m, 1H), 3.86–3.91 (m, 1H), 4.92–4.96 (m, 1H), 7.05 (d, *J* = 8.3 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.69 (s, 1H), 9.80 (s, 1H); EI-MS (70 eV) *m/z* (rel intensity) 331 (M⁺, 59), 302 (100).

4.4.6. 4-(4-Cyanophenyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole-7-carbaldehyde (**19**)

Yield 74%; mp 161–163 °C; ¹H NMR (CDCl₃) δ = 1.42–1.54 (m, 1H), 1.69–1.77 (m, 1H), 1.87–2.00 (m, 3H), 2.07–2.14 (m, 1H), 3.90–3.93 (m, 1H), 4.87–4.91 (m, 1H), 7.15 (d, *J* = 8.2 Hz, 1H), 7.38 (d, *J* = 9.2 Hz, 2H), 7.61–7.66 (m, 3H), 7.71 (s, 1H), 9.80 (s, 1H); EI-MS (70 eV) *m*/*z* (rel intensity) 288 (M⁺, 58), 259 (100).

4.5. Synthesis of dyes 21-26

To 1-butanol (40 ml) were added **14–19** (1.0 mmol) and double rhodanine acetic acid **20** (1.0 mmol). The mixture was refluxed for 20 min. Then, to the mixture was added piperidine (1 mg), which was refluxed for 3 h. After the reaction was completed, the solvent was removed *in vacuo*. The product was purified by column chromatography (SiO₂, CHCl₃:MeOH = 10:1). The physical and spectral data are shown below.

4.5.1. Dye 21

Yield 30%; mp 236–238 °C; ¹H NMR (CDCl₃) δ = 1.18 (t, J = 6.9 Hz, 3H), 1.37–1.43 (m, 1H), 1.62–1.79 (m, 4H), 2.04–2.09 (m, 1H), 2.98 (s, 6H), 3.87–3.91 (m, 1H), 4.05 (q, J = 6.9 Hz, 2H), 4.77 (s, 2H), 4.93–4.95 (m, 1H), 6.59 (d, J = 6.7 Hz, 1H), 6.79 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.2 Hz, 2H), 7.37–7.39 (m, 2H), 7.70 (s, 1H); FABMLMS (NBA) m/z 607.1462 (MH⁺), calcd for C₃₀H₃₁N₄O₄S₃: 607.1507.

4.5.2. Dye 22

Yield 61%; mp 268–270 °C; ¹H NMR (CDCl₃) δ = 1.18 (t, *J* = 7.3 Hz, 3H), 1.35–1.43 (m, 1H), 1.60–1.70 (m, 1H), 1.75–1.85 (m, 3H), 2.05–2.12 (m, 1H), 3.93–3.95 (m, 1H), 4.03 (q, *J* = 7.3 Hz, 2H), 4.67 (br s, 2H), 5.00–5.04 (m, 1H), 6.95 (d, *J* = 8.7 Hz, 1H), 7.02–7.07 (m, 8H), 7.29–7.36 (m, 6H), 7.43–7.48 (m, 2H), 7.72 (s, 1H); FABMLMS (NBA) *m*/*z* 731.1769 (MH⁺), calcd for C₄₀H₃₅N₄O₄S₃: 731.1820.

4.5.3. Dye 23

Yield 31%; mp > 300 °C; ¹H NMR (DMSO- d_6) δ = 1.19 (t, *J* = 7.1 Hz, 3H), 1.24–1.80 (m, 6H), 3.78 (s, 3H), 3.39–3.93 (m, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 4.71 (s, 2H), 4.98–5.03 (m, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 7.01 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.43 (s, 1H), 7.72 (s, 1H); FABMLMS (NBA) *m*/*z* 594.1216 (MH⁺), calcd for C₂₉H₂₈N₃O₅S₃: 594.1191.

4.5.4. Dye 24

Yield 61%; mp 272–274 °C; ¹H NMR (DMSO- d_6) δ = 1.18 (t, J = 6.9 Hz, 3H), 1.36–1.43 (m, 1H), 1.64–1.83 (m, 5H), 3.91–3.95 (m, 1H), 4.06 (q, J = 6.9 Hz, 2H), 4.78 (s, 2H), 5.06–5.09 (m, 1H), 7.00 (d, J = 8.2 Hz, 1H), 7.14 (t, J = 6.9 Hz, 1H), 7.37–7.49 (m, 6H), 7.75 (s, 1H); FABMLMS (NBA) m/z 564.1085 (MH⁺), calcd for C₂₈H₂₆N₃O₄S₃: 564.1088.

4.5.5. Dye 25

Yield 42%; mp 265–266 °C; ¹H NMR (DMSO- d_6) δ = 1.17 (t, J = 7.1 Hz, 3H), 1.31–1.41 (m, 1H), 1.66–1.70 (m, 1H), 1.72–1.77 (m, 1H), 1.83–1.86 (m, 1H), 1.89–1.98 (m, 1H), 2.09–2.18 (m, 1H), 3.94–3.99 (m, 1H), 4.05 (q, J = 7.1 Hz, 2H), 4.79 (s, 2H), 5.04–5.08 (m, 1H), 7.30 (d, J = 9.2 Hz, 1H), 7.51–7.53 (m, 2H), 7.57 (d, J = 8.7 Hz, 2H), 7.78 (s, 1H); FABMLMS (NBA) m/z 632.0927 (MH⁺), calcd for C₂₉H₂₅F₃N₃O₄S₃: 632.0959.

4.5.6. Dye 26

Yield 58%; mp 276–278 °C; ¹H NMR (CDCl₃) δ = 1.18 (t, J = 6.9 Hz, 3H), 1.32–1.40 (m, 1H), 1.66–1.76 (m, 2H), 1.81–1.87 (m, 1H), 1.93–2.03 (m, 1H), 2.09–2.17 (m, 1H), 3.58–4.00 (m, 1H), 4.05 (q, J = 6.9 Hz, 2H), 4.76 (s, 2H), 5.02–5.07 (m, 1H), 7.38 (d, J = 7.3 Hz, 1H), 7.52–7.55 (m, 4H), 7.80–7.81 (m, 3H); FABMLMS (NBA) m/z 589.1072 (MH⁺), calcd for C₂₉H₂₅N₄O₄S₃: 589.1038.

4.6. Electrochemical measurements

Electrochemical measurement of indoline dyes was performed in acetonitrile. The oxidation potential (E_{ox}) was measured by using small-size three electrodes. Ag *quasi* reference electrode (QRE) was used as a reference. Platinum wire was used as the working and counter electrodes. All electrode potentials were calibrated with respect to ferrocene(Fc)/ferrocenium (Fc⁺) redox couple. An acetonitrile solution (2 ml) of dyes containing tetrabutylammonium perchlorate (0.1 mol dm⁻³) and ferrocene (*ca*. 1 mmol dm⁻³) was prepared. The electrochemical measurement was performed at the scan rate of 100 mV s⁻¹.

4.7. Film preparation

An aqueous potassium chloride solution (300 ml, 0.1 mol dm^{-3}) was electrolyzed at -1.0 V vs SCE with bubbling an oxygen gas at 70 °C for 30 min. Platinum was used as a counter electrode. To the pre-electrolyzed film was added an aqueous solution of zinc chloride. The concentration of zinc chloride was adjusted to 5 mmol dm⁻³. Then, the film was electro-deposited again in the solution at -1.0 V vs SCE at 70 °C for 20 min with bubbling an oxygen gas. To the electro-deposited film was added an aqueous solution of eosin Y (50 μ mol dm⁻³). The film was electro-deposited at -1.0 V vs SCE at 70 °C for 30 min with bubbling an oxygen gas. The film was kept in a diluted aqueous potassium hydroxide solution (pH 10.5) for 24 h to remove adsorbed eosin Y. The film was dried at 100 °C for 1 h. The film was immersed in an acetonitrile-*tert*.-butyl alcohol 1:1 mixed solution of dye $(0.5 \text{ mmol dm}^{-3})$ containing cholic acid $(1.0 \text{ mmol dm}^{-3})$ at room temperature. Then, the film was washed with an acetonitrile-tert.-butyl alcohol 1:1 mixed solution. Acetonitrile-ethylenecarbonate (v/v = 1:4) containing tetrabutylammonium iodide (0.5 mol dm^{-3}) and iodine (0.05 mol dm^{-3}) was used as an electrolyte.

4.8. Photoelectrochemical measurements

An action spectrum was measured under monochromatic light with a constant photon number (5×10^{15} photon cm⁻² s⁻¹). I–V characteristics were measured under illumination with AM 1.5 simulated sun light (100 mW cm⁻²) through a shading mast (5.0 mm × 4.0 mm) by using a Bunko-Keiki CEP-2000 system.

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