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Highly efficient substituted triple rhodanine indoline dyes in zinc oxide dye-sensitized solar cell

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ABSTRACT

Substituited triple rhodanine indoline dyes showed higher performance than known triple rhodanine derivative (D150). A few triple rhodanine indoline derivatives showed comparable conversion efficiency to D149.

1. Introduction

Highly efficient organic sensitizers for dye-senisitized solar cell have been focused on coumarin,[1] carbazole,[2] dimethylfluorene,[3] arylamine,[4] and indoline dyes.[5] Among them, indoline dyes have been reported to show excellent cell performance.[5g,h] Recently, arylamine sensitizers having isophorone,[6] cyclohexadienyl,[7] furyl,[8] and thiophene linkers[3a,4b,9] have been reported to show good performance. In the reported sensitizers, most anchor moiety is cyanoacrylic group. Therefore, it is of interest to examine the other anchor groups, which can cause bathochromic shift in the UV–vis absorption band. Because the bathochromic shift can increase short-circuit photocurrent density (J_{sc}) to improve solar-light-to-electricity conversion efficiency (η). Three series of indoline dyes having cyanoacrylic acid (D131), single rhodanine (D102), and double rhodanine acetic acid (D149) as an anchor moiety are known. Among the series, the double rhodanine derivatives show the highest efficiency. Triple rhodanine indoline dyes are more bathochromic than the double rhodanine derivative due to increased conjugation. Only one triple rhodanine indoline dye named D150 has been reported to show η 5.9% on titanium oxide.[10] We considered that substituted triple rhodanine indoline dyes could show high conversion efficiency. In a series of our study on survey of sensitizers, we report herein the use of substituted triple rhodanine indoline dyes in a zinc oxide dye-sensitized solar cell.

2. Results and discussion

Triple rhodanine indoline dyes **30**–**35** were synthesized as shown in Scheme 1. Single rhodanines **1**–**4** were allowed to react with alkyl isothiocyanates **5**–**8** and ethyl bromoacetate (**9**) in the presence of DBU to afford double rhodanines **10**–**15**, which were again allowed to react with ethyl isothiocyanatoacetate (**16**) and **9** in the presence of DBU to give triple rhodanine ethyl acetates **17**–**22**. These compounds were hydrolyzed to produce the corresponding triple rhodanine acetic acids **23**–**28**. An indoline-7-carbaldehyde **29** was allowed to react with **23**–**28** to give **30**–**35**. Dye **30** is D150. D149 was also prepared as a reference compound.

The UV–vis absorption and fluorescence spectra of **30**–**35** are shown in Figure 1. The results are also listed in Table 1. The first and second absorption maxima (λ_{max}) of **30**–**35** were observed at around 570 and 450 nm, respectively. As expected, the λ_{max} were more bathochromic than those of D149 (550 and 395 nm), respectively. The molar absorption coefficients (ε) of **30**–**35** (60,700–101,200) at first λ_{max} were slightly larger than that of D149 (69,700). The fluorescence maxima (F_{max}) of **30**–**35** (649–662 nm) were more

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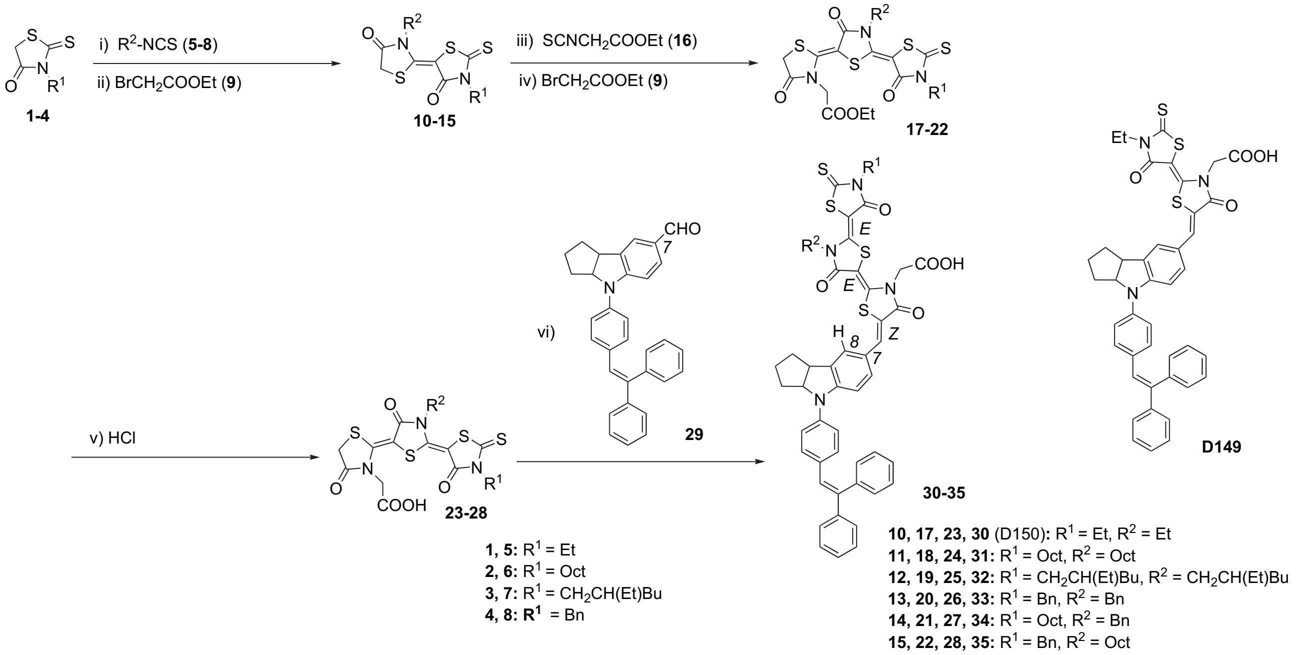

Scheme 1. Reagents and conditions: (i) **1**–**4** (1.0 equiv), **5**–**8** (1.0 equiv), DBU (1.0 equiv), MeCN, 30 min, reflux, (ii) **9** (2.0 equiv), rt to reflux, 4 h, (iii) **10**–**15** (1.0 equiv), **16** (1.0 equiv), DBU (1.0 equiv), MeCN, rt to reflux, 4 h, (iv) **9** (2.0 equiv), rt to reflux, 4 h, (v) **17**–**22** (1.0 equiv), concd HCl (300 equiv), AcOH, reflux, 4 h, (vi) **23**–**28** (1.0 equiv), **29** (1.1 equiv), AcNH$_4$ (4.9 equiv), reflux, 4 h.

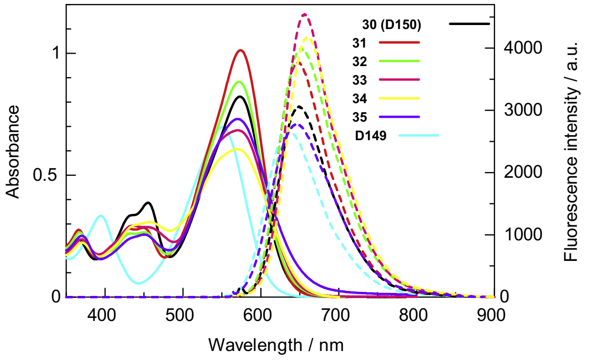

Figure 1. UV–vis absorption and fluorescence spectra of **30**–**35** and D149. Measured on 1×10^{-5} mol dm^{-3} of substrate in chloroform at 25 °C. Solid and dotted lines represent UV–vis absorption and fluorescence spectra, respectively.

Table 1
Properties of indoline dyes

Compd	λ_{max} (ε)[a]/nm	F_{max}/nm[a]	RFI[b]	E_{ox}/V[c]	$E_{ox}-E_{0-0}$/V[d]	HOMO/eV[e]	LUMO/eV[e]	f[f]
30 (D150)	455 (38,700), 573 (82,200)	649	100	+0.33	−1.70	—	—	—
31	440 (28,400), 574 (101,200)	650	123	+0.33	−1.70	−4.79	−2.34	−1.63
32	450 (26,600), 572 (88,300)	652	130	+0.33	−1.70	—	—	—
33	435 (29,300), 571 (68,400)	656	148	+0.33	−1.69	—	—	—
34	457 (30,800), 570 (60,700)	659	136	+0.34	−1.67	—	—	—
35	451 (25,700), 570 (73,000)	662	91	+0.33	−1.67	—	—	—
D149	395 (33,300), 550 (69,700)	635	87	+0.4	−1.70	−5.07	−2.37	−1.61

[a] Measured on 1.0×10^{-5} mol dm^{-3} of substrate in chloroform at 25 °C.
[b] Relative fluorescence intensity.
[c] Versus Fc/Fc$^+$ in DMF.
[d] Calculated on the basis of E_{ox} and λ_{int}.
[e] Calculated by the B3LYP/6-31G(d,p)//B3LYP/3–21 G level.
[f] Oscillator strength calculated by the INDO/S method.

bathochromic than that of D149 (635). The fluorescence of **30**–**35** (RFI=91–148) was slightly more intense than that of D149 (87).

The most stable structure of triple rhodanine indoline dyes was examined. In the case of **31**, as there are three olefinic bonds in the molecule, eight *E*/*Z* structural isomers are considerable. In addition, *syn*- and *anti*-conformers between the carbonyl group in the inner rhodanine moiety and aromatic-hydrogen at the 8-position are considerable. Consequently, sixteen structural isomers are considerable for **31**. The structures were optimized by the AM1 method. The results are shown in Figure S1 in supplementary data. Among the isomers, the structure of dye **31** indicated in Scheme 1 was most stable. Two olefinic bonds in the triple rhodanine moiety are *E*-form. The olefinic bond on the 7-position is *Z*-form. The carbonyl-oxygen and aromatic-hydrogen at the 8-position forms *anti*-conformer. The most stable structure was calculated again by the B3LYP/3-21 G level. Then, the HOMO and LUMO energy levels were calculated by the B3LYP/6-31G(d,p) level as shown in Figure S2 in supplementary data. The first absorption band of the optimized **31** was attributed to HOMO to LUMO transition. The HOMO and LUMO energy levels of **31** were calculated to be −4.97 and −2.34 eV, respectively. Thus, the HOMO level of **31** was less stable than that of D149 (−5.07 eV). The LUMO level of **31** (−2.34) was slightly less stable than that of D149 (−2.37).

The oxidation potential of **30**–**35** was measured by cyclic voltammetry. The voltammogram of **31** versus Ag *quasi* reference electrode (QRE) in the presence of ferrocene as an internal standard is shown in Figure 2. Three characteristic redox waves were observed in the voltammogram. The first oxidative wave (I) at +0.73 V and the second wave (II) at +1.09 V versus AgQRE were attributed to the oxidation of ferrocene and **31**, respectively. The third oxidative wave (III) at around 1.2 V may arise from the further oxidation of **31**. Therefore, the oxidation peak potential (E_{pa}) for **31** is calculated to be +0.36 V versus Fc/Fc$^+$ in DMF. Although the standard oxidation potential (E_{ox}) are not easily obtained experimentally, it can be approximately estimated from the cyclic voltammetric peak potential, which equals to (E_{pa}−29 mV), when the electrochemical oxidation is a reversible step.[11] Therefore, the E_{ox} of **31** was estimated to be +0.33 V versus Fc/Fc$^+$. The I$^-$/I$_3^-$ redox level was estimated at −0.05 V versus Fc/Fc$^+$. As the reduction levels of **31** were not observed by the electrochemical measurement, the potential level of E_{ox}−E_{0-0}, where E_{0-0} represents the intersection of normalized absorption and the fluorescence spectra in solution was calculated.[12] The λ_{int}, which represents the intersection wavelength in the normalized UV–vis absorption and fluorescence spectra of **31** was observed at 611 nm, corresponding to E_{0-0} 2.03 V. Therefore, the E_{ox}−E_{0-0} level of **31** was calculated to be −1.70 V versus Fc/Fc$^+$. The E_{ox} and E_{ox}−E_{0-0} of D149 were obtained in the same way. The results are listed in Table 1.

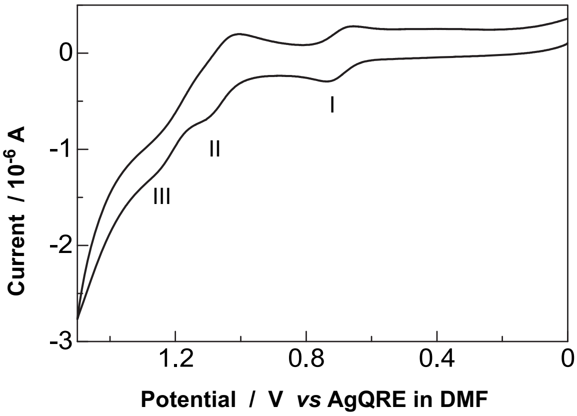

Figure 2. Cyclic voltammogram of **31** in the presence of ferrocene. Measured in DMF versus AgQRE at scan rate 100 mV s^{-1}.

The results of photoelectrochemical properties of **30**–**35** and D149 are shown in Figure 3 and Table 2. Figure 3a depicts that the first λ_{max} of triple rhodanine indoline dyes **30**–**35** on zinc oxide were observed in the range of 540–560 nm, which were slightly hypsochromic compared with those in chloroform (570–574 nm). This is a general tendency for double rhodanine indoline dyes, such as D149 on zinc oxide, which may come from decrease in electron-withdrawing ability of the rhodanine moiety on zinc oxide. As expected, the first λ_{max} of **30**–**35** (540–560) on zinc oxide were more bathochromic than that of D149 (516). The UV–vis absorption spectra on zinc oxide were broad compared with those in chloroform, indicating aggregates formation. The IPCE values of **30**–**35** (71–77%) were significantly lower than that of D149 (82) as shown in Figure 3b. The E_{ox}−E_{0-0} levels of **30**–**35** (−1.67 to −1.70 V) were sufficiently negative compared to the conduction band level of zinc oxide (−0.95 V), there being the energy gap ca. 0.75 V. Meanwhile, the energy gap between the E_{ox} level of **30**–**35** (+0.33 V) and I$^-$/I$_3^-$ redox level (−0.05 V) is 0.38 V. In the case of titanium oxide, the energy gap of 0.2–0.3 V is required to proceed the electron transfer.[12,13] Therefore, the E_{ox} level is more important factor than the E_{ox}−E_{0-0} level to improve the performance of indoline dyes. The E_{ox} of triple rhodanine dyes **30**–**35** (+0.33 V vs Fc/Fc$^+$) were more negative than that of double rhodanine dye D149 (+0.40). In our previous paper, the relationship between the IPCE and E_{ox} level of indoline dyes was examined.[5a] It was found when the E_{ox} level is more positive than 0.2 V versus Fc/Fc$^+$, high IPCE was obtained. Therefore, it is reasonable that triple indoline dyes **30**–**35** show the IPCE in the range of 71–77%, which are slightly small compared to that of D149 (82%). However, as triple rhodanine dyes **30**–**35** exhibit sensitization at around 670 nm as shown in Figure 3b, no marked differences in J_{sc} were observed between **30**–**35** (9.83–11.19 mA cm^{-2}) and D149 (11.04). Interestingly, the open-circuit photovoltage (V_{oc}) of substituted triple rhodanine indoline dyes **31**–**35** (0.60–0.67 V) were significantly higher than that of known **30** (D150, 0.56) as shown in Figure 3c. Introduction of medium normal alkyl groups into the rhodanine rings was effective to increase V_{oc}. In the case of double rhodanine indoline dyes, the octyl derivative (D205) has been reported to show higher V_{oc} than the ethyl derivative (D149), which can result from inhibition of

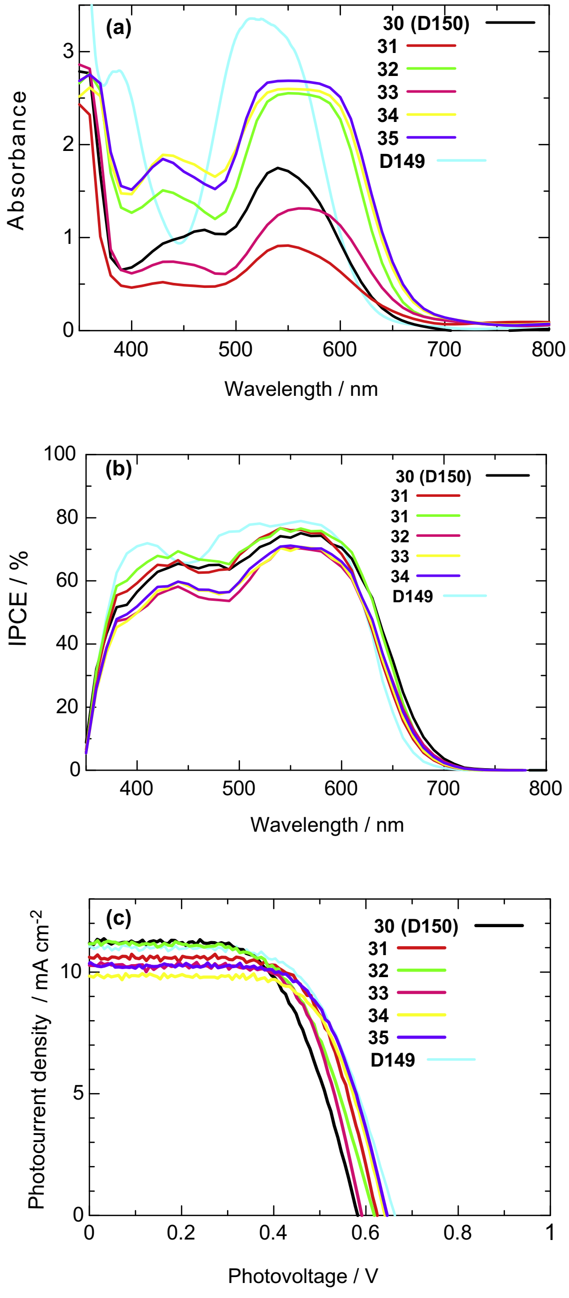

Figure 3. (a) UV–vis absorption spectra on zinc oxide, (b) IPCE action spectra, and (c) I–V curve of **30**–**35** and D149 on zinc oxide.

back electron transfer from semiconductor surface to triidodide anions.[5d,f,14] The fill factors (*ff*) of **31** (0.66), **33** (0.67), **34** (0.65), and **35** (0.66) were larger than those of **30** (0.62) and D149 (0.61). Consequently, all of substituted triple rhodanine indoline dyes **31**–**35** showed higher conversion efficiency (4.09–4.36%) than known **30** (D150, 3.92). The conversion efficiency of **31** (4.36) and **34** (4.35) were comparable to that of D149 (4.48).

Table 2
Photoelectrochemical properties of indoline dyes

Compd	λ_{max}/nm	Abs	IPCE/%	J_{sc}/mA cm^{-2}	V_{oc}/V	*ff*	η /%
30 (D150)	540	1.75	75	11.19	0.56	0.62	3.92
31	550	0.92	77	10.61	0.62	0.66	4.36
32	550	2.55	77	11.16	0.62	0.60	4.12
33	560	1.31	71	10.28	0.59	0.67	4.09
34	550	2.69	71	10.36	0.65	0.65	4.35
35	550	2.60	71	9.83	0.64	0.66	4.15
D149	516	33.6	82	11.04	0.66	0.61	4.48

In summary, the substituted triple rhodanine indoline dyes significantly showed better performance than known triple rhodanine indoline dye D150. A few triple rhodanine indoline dyes showed comparable performance to D149.

3. Experimental

3.1. General

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 taken 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.

3.2. Materials

Single rhodanines **1** and **4**, benzylisothiocyanate (**8**), and ethyl bromoacetate (**9**) were purchased from Tokyo Kasei Co., Ltd. Ethyl isothiocyanate (**5**) and octyl isothiocyanate (**6**) were purchased from KANTO CHEMICAL CO., INC. and Wako Pure Chemical Industries Ltd., respectively. Single rhodanines **2** and **3**, 2-ethylhexyl isothiocyanate (**7**), and ethyl isothiocyanatoacetate (**16**) were synthesized as described in our previous paper.[5c]

3.3. Synthesis of double rhodanines 10–15

To an acetonitrile solution (30 ml) of monorhodanine derivatives **1**–**4** (18 mmol) and isothiocyanates **5**–**8** (18 mmol) was added DBU (2.74 g, 18 mmol) at room temperature. The mixture was stirred for 30 min. Then, to the mixture was added ethyl bromoacetate **9** (6.01 g, 36 mmol). The mixture was stirred for 30 min and then refluxed for 4 h. After the reaction was completed, the mixture was concentrated and dissolved in chloroform. Aqueous 2 N hydrochloric acid (100 ml) was added to the mixture. The pH value was adjusted below 3.0. The product was extracted with chloroform (80 ml×3) and purified by column chromatography (SiO_2, $CHCl_3$).

*3.3.1. Double rhodanine **10***. Yield 43%; mp 183–185 °C; ^{1}H NMR ($CDCl_3$) δ=1.28 (t, *J*=7.1 Hz, 3H), 1.33 (t, *J*=7.1 Hz, 3H), 3.81 (s, 2H), 3.96 (q, *J*=7.1 Hz, 2H), 4.17 (q, *J*=7.1 Hz, 2H); FABMS (NBA) *m*/*z* 289 (MH^+).

*3.3.2. Double rhodanine **11***. Yield 18%; mp 60–61 °C; IR (KBr) ν=1735, 1666, 1528 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.87 (t, *J*=6.9 Hz, 3H), 0.88 (t, *J*=6.9 Hz, 3H), 1.20–1.43 (m, 20H), 1.65 (quin, *J*=7.8 Hz, 2H), 1.72 (quin, *J*=7.8 Hz, 2H), 3.81 (s, 2H), 3.85 (t, *J*=7.8 Hz, 2H), 4.08 (t, *J*=7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=14.2×2, 22.7×2, 26.5, 26.91, 26.93, 29.16×2, 29.21×2, 29.5, 31.6, 31.79, 31.85, 44.9, 45.1, 93.8, 151.5, 167.7, 173.0, 190.3; FABMS (NBA) *m*/*z* 457 (MH^+).

*3.3.3. Double rhodanine **12***. Yield 15%; mp 65–67 °C; IR (KBr) ν=1731, 1657, 1513 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.82–1.00 (m, 12H), 1.16–1.46 (m, 16H), 1.85 (sep, *J*=7.8 Hz, 1H), 2.08 (sep, *J*=7.8 Hz, 1H), 3.81 (d, *J*=7.8 Hz, 2H), 3.82 (s, 2H), 4.00 (d, *J*=7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=10.2, 10.7, 14.07, 14.12, 22.9, 23.09, 23.12, 24.0, 28.0, 28.5, 29.5, 30.6, 31.4, 37.0, 38.7, 48.8, 48.9, 94.1, 151.7, 168.3, 173.3, 190.6; FABMS (NBA) *m*/*z* 457 (MH^+).

*3.3.4. Double rhodanine **13***. Yield 48%; mp 195–197 °C; IR (KBr) ν=1734, 1663, 1530 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.93 (s, 2H), 5.16 (s, 2H), 5.23 (s, 2H), 7.12–7.16 (m, 2H), 7.27–7.39 (m, 6H), 7.44–7.48 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=31.4, 47.6, 47.7, 94.7, 125.9, 128.2, 128.4, 128.6, 129.2, 129.3, 133.7, 134.9, 151.1, 168.0, 173.1, 190.4; FABMS (NBA) *m*/*z* 413 (MH^+).

*3.3.5. Double rhodanine **14***. Yield 31%; mp 104–106 °C; IR (KBr) ν=1730, 1681, 1530 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.87 (t, *J*=6.9 Hz, 3H), 1.20–1.39 (m, 10H), 1.64 (quin, *J*=7.6 Hz, 2H), 3.94 (s, 2H), 4.02 (t, *J*=7.6 Hz, 2H), 5.17 (s, 2H), 7.12–7.17 (m, 2H), 7.28–7.42 (m, 3H); ^{13}C NMR ($CDCl_3$) δ=14.2, 22.7, 26.9×2, 29.2×2, 31.4, 31.8, 44.9, 47.7, 94.9, 125.9, 128.3, 129.3, 133.7, 150.6, 167.8, 173.1, 190.4; FABMS (NBA) *m*/*z* 435 (MH^+).

*3.3.6. Double rhodanine **15***. Yield 8%; mp 105–107 °C; IR (KBr) ν=1731, 1664, 1508 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (t, *J*=6.9 Hz, 3H), 1.21–1.41 (m, 10H), 1.64 (quin, *J*=7.6 Hz, 2H), 3.80 (s, 2H), 3.84 (t, *J*=7.6 Hz, 2H), 5.29 (s, 2H), 7.28–7.32 (m, 3H), 7.49–7.50 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=14.2, 22.7, 26.5, 26.9, 29.1, 29.5, 31.6, 31.8, 45.1, 47.7, 93.6, 128.1, 128.6, 129.2, 135.0, 151.9, 167.7, 173.0, 190.2; FABMS (NBA) *m*/*z* 435 (MH^+).

3.4. Synthesis of triple rhodanine ethyl esters 17–22

To an acetonitrile solution (30 ml) of **10**–**15** (1 mmol) and ethyl isocynatoacetate **16** (145 mg, 1 mmol) was added DBU (152 mg, 1 mmol) at room temperature. The mixture was stirred for 30 min. Ethyl bromoacetate **9** (334 mg, 2 mmol) was added to the mixture at room temperature and stirred for 30 min. Then, the mixture was refluxed for 4 h. After the reaction was completed, the mixture was concentrated in vacuo. Aqueous 2 N hydrochloric acid (200 ml) was added and the pH value was adjusted below 3. The product was extracted with chloroform (80 ml×3) and purified by column chromatography (SiO_2, CH_2Cl_2/AcOEt=20:1).

*3.4.1. Triple rhodanine ethyl ester **17***. Yield 45%; mp 262–264 °C; ^{1}H NMR ($CDCl_3$) δ=1.28 (t, *J*=7.2 Hz, 3H), 1.36 (t, *J*=7.2 Hz, 3H), 1.39 (t, *J*=7.2 Hz, 3H), 3.90 (s, 2H), 4.05 (q, *J*=7.2 Hz, 2H), 4.17 (q, *J*=7.2 Hz, 2H), 4.34 (q, *J*=7.2 Hz, 2H), 4.85 (s, 2H); FABMS (NBA) *m*/*z* 474 (MH^+).

*3.4.2. Triple rhodanine ethyl ester **18***. Yield 43%; mp 104–106 °C; IR (KBr) ν=1735, 1680, 1523, 1225 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (t, *J*=7.3 Hz, 3H), 0.89 (t, *J*=6.9 Hz, 3H), 1.22–1.47 (m, 20H), 1.38 (t, *J*=7.3 Hz, 3H), 1.64–1.75 (m, 4H), 3.89 (s, 2H), 3.93 (t, *J*=7.8 Hz, 2H), 4.07 (t, *J*=7.8 Hz, 2H), 4.33 (q, *J*=7.3 Hz, 2H), 4.85 (s, 2H); ^{13}C NMR ($CDCl_3$) δ=14.10, 14.16×2, 22.7×2, 26.6, 26.9, 27.0, 29.19×2, 29.22×2, 29.7, 31.3, 31.8, 31.9, 44.9, 45.1, 45.9, 63.0, 90.3, 92.9, 145.5, 151.6, 166.4, 166.8, 167.0, 172.8, 189.8; FABMS (NBA) *m*/*z* 642 (MH^+).

*3.4.3. Triple rhodanine ethyl ester **19***. Yield 51%; oil; IR (KBr) ν=1735, 1669, 1522, 1181 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.83–0.97 (m, 12H), 1.17–1.45 (m, 16H), 1.39 (t, *J*=7.3 Hz, 3H), 1.88 (sep, *J*=7.8 Hz, 1H), 2.07 (sep, *J*=7.3 Hz, 1H), 3.89 (s, 2H), 3.90 (d, *J*=7.8 Hz, 2H), 3.99 (d, *J*=7.3 Hz, 2H), 4.33 (q, *J*=7.3 Hz, 2H), 4.86 (s, 2H); ^{13}C NMR (CDCl$_3$) δ=10.4, 10.8, 14.07, 14.12, 14.9, 23.1×2, 24.1×2, 28.0, 28.5, 29.6, 30.1, 31.7, 36.9, 39.0, 40.6, 48.9, 49.0, 61.7, 90.3, 91.4, 146.8, 152.8, 167.4×2, 167.6, 173.0, 190.0; FABMS (NBA) *m*/*z* 642 (MH$^+$).

*3.4.4. Triple rhodanine ethyl ester **20**.* Yield 40%; mp 224–226 °C; IR (KBr) ν=1730, 1664, 1522, 1202, 1153 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.38 (t, *J*=7.3 Hz, 3H), 3.90 (s, 2H), 4.34 (q, *J*=7.3 Hz, 2H), 4.88 (s, 2H), 5.23 (s, 2H), 5.25 (s, 2H), 7.14–7.44 (m, 10H); ^{13}C NMR (CDCl$_3$) δ=14.1, 31.4, 45.9, 47.7×2, 63.1, 91.1, 92.2, 126.0, 128.1, 128.3, 128.5, 129.1, 129.3, 133.9, 135.1, 145.4, 152.4, 166.4, 166.9, 167.0, 172.8, 189.9; FABMS (NBA) *m*/*z* 598 (MH$^+$).

*3.4.5. Triple rhodanine ethyl ester **21**.* Yield 22%; mp 130–132 °C; IR (KBr) ν=1735, 1654, 1526, 1221, 1145 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.87 (t, *J*=6.9 Hz, 3H), 1.20–1.36 (m, 10H), 1.40 (t, *J*=7.3 Hz, 3H), 1.64 (quint, *J*=7.7 Hz, 2H), 3.90 (s, 2H), 4.01 (t, *J*=7.7 Hz, 2H), 4.35 (q, *J*=7.3 Hz, 2H), 4.89 (s, 2H), 5.25 (s, 2H), 7.12–7.40 (m, 5H); ^{13}C NMR (CDCl$_3$) δ=14.2, 15.0, 22.7, 26.9, 27.0, 29.2, 31.7, 31.8, 33.7, 40.6, 45.0, 47.7, 61.6, 90.9, 91.1, 126.0, 128.3, 129.3, 134.1, 146.0, 153.5, 167.1, 167.2, 169.9, 173.0, 189.8; FABMS (NBA) *m*/*z* 620 (MH$^+$).

*3.4.6. Triple rhodanine ethyl ester **22**.* Yield 27%; mp 165–167 °C; IR (KBr) ν=1735, 1672, 1513, 1192 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.88 (t, *J*=6.9 Hz, 3H), 1.21–1.44 (m, 10H), 1.36 (t, *J*=7.3 Hz, 3H), 1.68 (quint, *J*=8.0 Hz, 2H), 3.89 (s, 2H), 3.93 (t, *J*=8.0 Hz, 2H), 4.31 (q, *J*=7.3 Hz, 2H), 4.84 (s, 2H), 5.29 (s, 2H), 7.28–7.48 (m, 5H); ^{13}C NMR (CDCl$_3$) δ=14.1, 14.2, 22.7, 26.5×2, 29.2, 29.7, 31.3, 31.8, 45.2, 45.9, 47.7, 63.0, 90.1, 92.8, 128.1, 128.5, 129.1, 135.1, 145.9, 151.7, 166.4, 166.7, 169.9, 172.7, 189.7; FABMS (NBA) *m*/*z* 620 (MH$^+$).

3.5. Synthesis of triple rhodanine aceric acids 23–28

To an acetic acid solution (20 ml) of ethyl esters **17**–**22** (0.32 mmol), was added concd hydrochloric acid (8 ml). The mixture was refluxed for 4 h. After the reaction was completed, the product was extracted with chloroform (80 ml×3). The crude product was used without further purification.

*3.5.1. Triple rhodanine acetic acid **23**.* Yield 76%; mp 179–181 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ=1.29 (t, *J*=7.2 Hz, 3H), 1.33 (t, *J*=7.2 Hz, 3H), 3.90 (s, 2H), 3.96 (q, *J*=7.2 Hz, 2H), 4.17 (q, *J*=7.2 Hz, 2H), 4.90 (s, 2H); FABMS (NBA) *m*/*z* (rel intensity) 460 (MH$^+$).

*3.5.2. Triple rhodanine acetic acid **24**.* Yield 71%; mp 180–182 °C; IR (KBr) ν=3495, 1735, 1654, 1518, 1143 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.88 (t, *J*=6.9 Hz, 3H), 0.89 (t, *J*=6.9 Hz, 3H), 1.21–1.45 (m, 20H), 1.63–1.73 (m, 4H), 3.89 (s, 2H), 3.94 (t, *J*=8.2 Hz, 2H), 4.07 (t, *J*=7.8 Hz, 2H), 4.91 (s, 2H); ^{13}C NMR (CDCl$_3$) δ=14.2×2, 22.7×2, 26.5, 26.9, 27.0, 29.17×2, 29.23×2, 29.7, 31.3, 31.8, 31.9, 45.0, 45.2, 45.6, 90.6, 92.8, 145.7, 151.6, 166.7, 167.3, 168.8, 173.0, 189.6; FABMS (NBA) *m*/*z* 614 (MH$^+$).

*3.5.3. Triple rhodanine acetic acid **25**.* Yield 72%; mp 169–171 °C; IR (KBr) ν=3495, 1735, 1666, 1513, 1142 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.81–9.99 (m, 12H), 1.17–1.45 (m, 16H), 1.88 (sep, *J*=7.8 Hz, 1H), 2.08 (sep, *J*=7.4 Hz, 1H), 3.89 (s, 2H), 3.91 (d, *J*=7.8 Hz, 2H), 4.00 (d, *J*=7.4 Hz, 2H), 4.95 (s, 2H); ^{13}C NMR (CDCl$_3$) δ=10.3, 10.7, 14.06, 14.12, 23.1×2, 24.0×2, 28.0, 28.5, 29.6, 30.5, 31.3, 36.9, 39.0, 45.7, 49.0×2, 90.8, 92.7, 146.0, 151.6, 167.1, 167.8, 168.8, 173.1, 189.8; FABMS (NBA) *m*/*z* 614 (MH$^+$).

*3.5.4. Triple rhodanine acetic acid **26**.* Yield 70%; mp 170–172 °C; IR (KBr) ν=3463, 1735, 1654, 1522, 1144 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=3.90 (s, 2H), 4.94 (s, 2H), 5.24 (s, 2H), 5.26 (s, 2H), 7.12–7.16 (m, 2H), 7.27–7.43 (m, 8H); ^{13}C NMR (CDCl$_3$) δ=31.3, 45.6, 47.7, 47.8, 91.3, 92.2, 126.0, 128.1, 128.4, 128.6, 128.8, 129.3, 133.8, 134.9, 145.6, 152.5, 166.8, 167.2, 167.8, 172.9, 189.9; FABMS (NBA) *m*/*z* 570 (MH$^+$).

*3.5.5. Triple rhodanine acetic acid **27**.* Yield 78%; mp 121–123 °C; IR (KBr) ν=3448, 1735, 1654, 1534, 1137 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.87 (t, *J*=6.9 Hz, 3H), 1.20–1.37 (m, 10H), 1.64 (quint, *J*=7.8 Hz, 2H), 3.91 (s, 2H), 4.01 (t, *J*=7.8 Hz, 2H), 4.97 (s, 2H), 5.26 (s, 2H), 7.10–7.42 (m, 5H); ^{13}C NMR (CDCl$_3$) δ=14.2, 22.7, 26.88, 26.94, 29.2, 29.8, 31.4, 31.8, 40.3, 44.9, 47.7, 91.5, 92.2, 126.0, 128.4, 129.3, 133.9, 145.3, 152.4, 166.9, 167.2, 167.8, 173.2, 189.8; FABMS (NBA) *m*/*z* 592 (MH$^+$).

*3.5.6. Triple rhodanine acetic acid **28**.* Yield 77%; mp 141–143 °C; IR (KBr) ν=3448, 1735, 1654, 1507, 1154 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.88 (t, *J*=6.9 Hz, 3H), 1.21–1.45 (m, 10H), 1.68 (quint, *J*=7.9 Hz, 2H), 3.89 (s, 2H), 3.94 (t, *J*=7.9 Hz, 2H), 4.91 (s, 2H), 5.29 (s, 2H), 7.28–7.44 (m, 5H); ^{13}C NMR (CDCl$_3$) δ=14.2, 22.7, 26.45, 26.54, 29.2, 29.2, 31.3, 31.8, 45.2, 45.7, 47.7, 90.2, 92.6, 128.1, 128.6, 129.2, 135.0, 146.3, 152.1, 166.7, 167.1, 168.4, 173.0, 189.6; FABMS (NBA) *m*/*z* 592 (MH$^+$).

3.6. Synthesis of triple rhodanine indoline dyes 30–35

To an acetic acid solution (20 ml) containing **29** (75 mg, 0.17 mmol) and **23**–**28** (0.16 mmol) was added ammonium acetate (60 mg, 0.78 mmol). The mixture was refluxed for 4 h. After the reaction was completed, the mixture was concentrated in vacuo and washed with methanol. The product was purified by column chromatography (SiO$_2$, CHCl$_3$/MeOH=20:1).

*3.6.1. Triple rhodanine indoline dye **30** (D150).* Yield 44%; mp >300 °C; IR (KBr) ν=3375, 1643 cm^{-1}; ^{1}H NMR (DMSO-*d*$_6$) δ=1.17 (t, *J*=7.2 Hz, 3H), 1.28 (t, *J*=7.2 Hz, 3H), 1.30–1.37 (m, 1H), 1.59–1.70 (m, 2H), 1.76–1.84 (m, 2H), 2.04–2.11 (m, 1H), 3.85–3.90 (m, 1H), 3.94–4.08 (m, 4H), 4.87 (s, 2H), 4.95–5.00 (m, 1H), 7.02–7.06 (m, 3H), 7.09 (s, 1H), 7.15–7.18 (m, 2H), 7.21 (d, *J*=6.9 Hz, 2H), 7.27–7.37 (m, 5H), 7.40–7.49 (m, 5H), 7.67 (s, 1H); HRFABMS *m*/*z* 869.1974 (MH$^+$), calcd for $C_{47}H_{41}N_4O_5S_4$: 869.1960.

*3.6.2. Triple rhodanine indoline dye **31**.* Yield 35%; mp >300 °C; IR (KBr) ν=3402, 1647 cm^{-1}; ^{1}H NMR (DMSO-*d*$_6$) δ=0.80–0.91 (m, 6H), 1.14–1.39 (m, 21H), 1.46–1.70 (m, 6H), 1.75–1.84 (m, 2H), 2.04–2.10 (m, 1H), 3.83–3.98 (m, 5H), 4.71 (s, 2H), 4.93–4.99 (m, 1H), 7.01–7.07 (m, 3H), 7.09 (s, 1H), 7.21 (d, *J*=6.8 Hz, 2H), 7.18–7.23 (m, 2H), 7.23–7.37 (m, 5H), 7.37–7.49 (m, 5H), 7.63 (s, 1H); HRFABMS *m*/*z* 1037.3827 (MH$^+$), calcd for $C_{59}H_{65}N_4O_5S_4$: 1037.3838.

*3.6.3. Triple rhodanine indoline dye **32**.* Yield 52%; mp >300 °C; IR (KBr) ν=3395, 1647 cm^{-1}; ^{1}H NMR (DMSO-*d*$_6$) δ=0.72–0.92 (m, 12H), 1.06–1.40 (m, 17H), 1.56–1.70 (m, 2H), 1.70–1.88 (m, 3H), 1.88–2.00 (m, 1H), 2.00–2.12 (m, 1H), 3.72–3.90 (m, 5H), 4.73 (s, 2H), 4.90–4.98 (m, 1H), 7.00–7.06 (m, 3H), 7.08 (s, 1H), 7.20 (d, *J*=7.4 Hz, 2H), 7.17–7.23 (m, 2H), 7.26–7.50 (m, 10H), 7.62 (s, 1H); HRFABMS *m*/*z* 1037.3770 (MH$^+$), calcd for $C_{59}H_{65}N_4O_5S_4$: 1037.3838.

*3.6.4. Triple rhodanine indoline dye **33**.* Yield 43%; mp >300 °C; IR (KBr) ν=3402, 1651 cm^{-1}; ^{1}H NMR (DMSO-*d*$_6$) δ=1.22–1.38 (m, 1H), 1.54–1.68 (m, 2H), 1.70–1.84 (m, 2H), 1.96–2.10 (m, 1H), 3.78–3.86 (m, 1H), 4.61 (s, 2H), 4.88–4.96 (m, 1H), 5.11 (s, 2H), 5.28 (s, 2H), 6.96–7.94 (m, 28H), 7.61 (s, 1H); HRFABMS *m*/*z* 993.2192 (MH$^+$), calcd for $C_{57}H_{45}N_4O_5S_4$: 993.2273.

*3.6.5. Triple rhodanine indoline dye **34**.* Yield 41%; mp >300 °C; IR (KBr) ν=3383, 1655 cm^{-1}; ^{1}H NMR (DMSO-*d*$_6$) δ=0.84 (t,

J=6.7 Hz, 3H), 1.17–1.35 (m, 11H), 1.47–1.68 (m, 4H), 1.70–1.83 (m, 2H), 1.97–2.06 (m, 1H), 3.78–3.89 (m, 3H), 4.57 (s, 2H), 4.88–4.95 (m, 1H), 5.26 (s, 2H), 6.93–7.48 (m, 23H), 7.58 (s, 1H); HRFABMS m/z 1015.3074 (MH$^+$), calcd for $C_{58}H_{55}N_4O_5S_4$: 1015.3055.

*3.6.6. Triple rhodanine indoline dye **35**.* Yield 40%; mp >300 °C; IR (KBr) ν=3402, 1647 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ=0.84 (t, J=7.8 Hz, 3H), 1.19–1.41 (m, 11H), 1.56–1.70 (m, 4H), 1.72–1.84 (m, 2H), 1.99–2.10 (m, 1H), 3.79–3.92 (m, 3H), 4.54 (s, 2H), 4.88–4.95 (m, 1H), 5.13 (s, 2H), 6.97–7.05 (m, 3H), 7.07 (s, 1H), 7.09–7.14 (m, 2H), 7.17–7.22 (m, 2H), 7.24–7.49 (m, 15H), 7.55 (s, 1H); HRFABMS m/z 1015.3030 (MH$^+$), calcd for $C_{58}H_{55}N_4O_5S_4$: 1015.3055.

3.7. Electrochemical measurements

Electrochemical measurement of indoline dyes was performed in DMF. 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. A DMF 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}.

3.8. Film preparation

An aqueous potassium chloride solution (300 ml, 0.1 mol dm^{-3}) was electrolyzed at −1.0 V versus 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 (5 mmol dm^{-3}). Then, the film was electro-deposited again in the solution at −1.0 V versus 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 μmol dm^{-3}). The film was electro-deposited at −1.0 V versus 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 150 °C for 1 h. The film was immersed in a chloroform solution of dye (0.5 mmol dm^{-3}) containing cholic acid (0.5 mmol dm^{-3}) at room temperature for 1 h. In the case of D149, the film was immersed in an acetonitrile-*tert*-butyl alcohol (1:1) mixed solution of dye (0.5 mmol dm^{-3}) containing cholic acid (1.0 mmol dm^{-3}) at room temperature. Then, the film was washed with the 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.

3.9. Photoelectrochemical measurements

An action spectrum was measured under monochromatic light with a constant photon number (0.5×10^{16} 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 mask (5.0×4.0 mm) by using a Bunko-Keiki CEP-2000 system.

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Supplementary data

Calculated total energy of structural isomers of **31** and the LUMO and HOMO electron density of **31** calculated by the B3LYP/6-31G(d, p)//B3LYP/3-21 G level. Supplementary data associated with this article can be found online version at doi:10.1016/j.tet.2010.07.017.

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