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# *N*-(2-Alkoxyphenyl)-substituted double rhodanine indoline dyes for zinc oxide dye-sensitized solar cell

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ABSTRACT

The effect of *N*-(2-alkoxyphenyl) group in double rhodanine indoline dye on the performance of zinc oxide dye-sensitized solar cell was examined. Both $J_{sc}$ and $V_{oc}$ were improved by introducing long alkoxy group due to prevention of H-aggregates formation and inhibition of electron recombination from zinc oxide surface to electrolyte.



## 1. Introduction

Indoline dyes are known as highly efficient sensitizer in dye-sensitized solar cell.[1–5] Especially, D149 has been reported to show excellent conversion efficiency ($\eta$) 9.0% on titanium oxide.[6] The relationship between the oxidation potential ($E_{ox}$) of indoline dyes and conversion efficiency has been also clarified.[7] The X-ray crystallography of D149 ethyl ester suggests that the saturated five-membered ring can act as steric hindrance to prevent intermolecular π–π stacking.[8] D205, in which an octyl group is attached on the nitrogen atom at the terminal rhodanine ring, has been reported to show higher $V_{oc}$ than D149.[9] On the basis of these results, we considered that a long alkoxy group attached at the indoline moiety could have suitable energy level and act as steric hindrance to improve the cell performance. We report herein the effect of 2-alkoxyphenyl group at the indoline-nitrogen in double rhodanine indoline dye on the performance of zinc oxide dye-sensitized solar cell.

## 2. Results and discussion

### 2.1. Synthesis

Indoline dyes **18**–**22** were synthesized as shown in Scheme 1. Compound **1** was allowed to react with 2-alkoxybromobenzenes **2**–**6** to give *N*-(2-alkoxyphenyl) derivatives **7**–**11**, followed by formylation to afford **12**–**16**. These formyl derivatives **12**–**16** were allowed to react with double rhodanine acetic acid **17** to afford **18**–**22**.

### 2.2. UV–vis absorption and fluorescence spectra

The UV–vis absorption and fluorescence spectra of **18**–**22** are shown in Fig. 1. The results are also listed in Table 1. The indoline dyes **18**–**22** showed first and second absorption maxima ($\lambda_{max}$) at around 545 and 384 nm, respectively. The molar absorption coefficients ($\varepsilon$) of **18**–**22** at the first absorption band were observed in the range of 69,700–78,800 $dm^3\ mol^{-1}\ cm^{-1}$, there being no significant difference among them. The fluorescence maxima ($F_{max}$) of **18**–**22** were observed at around 606 nm.

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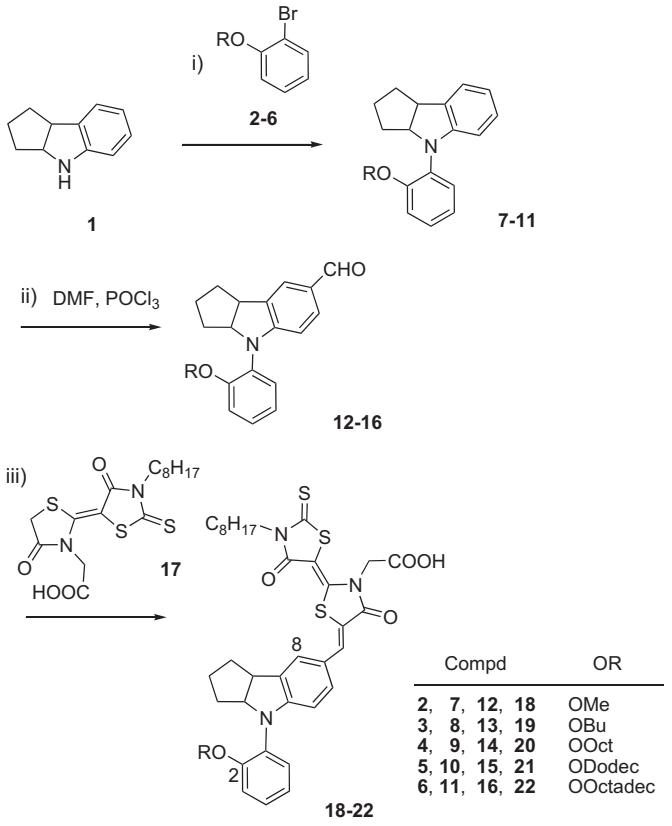


**Scheme 1.** Reagents and reaction conditions: (i) **1** (1.0 equiv), **2**–**6** (1.2 equiv), $Pd(OAc)_2$ (0.05 equiv), SPhos (0.1 equiv), *t*-BuONa (1.4 equiv), toluene, reflux, overnight; (ii) **7**–**11** (1.0 equiv), DMF, $POCl_3$ (1.0 equiv), room temperature, overnight; (iii) **12**–**16** (1.1 equiv), **17** (1.0 equiv), piperidine (0.95 equiv), BuOH, reflux, 4 h.

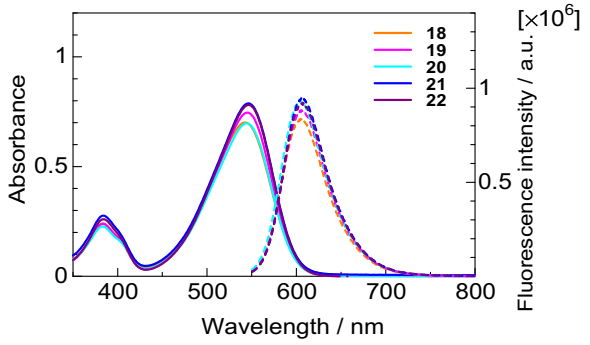


**Fig. 1.** UV–vis absorption and fluorescence spectra of **18**–**22**. Measured on $1.0\times10^{-5}$ mol dm$^{-3}$ of substrate in chloroform at 25 °C.

## 2.3. Electrochemical measurements

The oxidation potential ($E_{ox}$) of **18**–**22** was measured as described in our previous paper.[7] The results are listed in Table 1. The $E_{ox}$ of **18**–**22** was observed in the range of 0.38–0.40 V versus Fc/$Fc^+$, there being similar to that of D149 (0.39 V). The $I^-/I_3^-$ redox level was estimated to be −0.05 V versus Fc/$Fc^+$. As the reduction potential of **18**–**22** was not observed, the $E_{ox}-E_{0-0}$ level was calculated as described in our previous paper.[7] The conduction band level of zinc oxide is estimated to be −0.95 V versus Fc/$Fc^+$. Thus, the $E_{ox}$ level of **18**–**22** is ca. 0.45 V more positive than $I^-/I_3^-$ redox level. The $E_{ox}-E_{0-0}$ level of **18**–**22** is ca. 0.78 V more negative than the conduction band level. These results indicate that dyes **18**–**22** can thermodynamically act as sensitizers.

**Table 1**
Properties of indoline dyes

| Compd | $\lambda_{max}$ ($\varepsilon$)[a]/nm | $F_{max}$[a]/nm | RFI[b] | $E_{ox}$[c]/V | $E_{ox}-E_{0-0}$[d]/V | $\theta$ [e]/° | HOMO[f]/eV | LUMO[f]/eV |
|---|---|---|---|---|---|---|---|---|
| **18** | 384 (24,100), 543 (70,100) | 606 | 78 | 0.40 | −1.73 | 54.8 | −5.06 | −2.24 |
| **19** | 383 (23,900), 545 (74,600) | 607 | 96 | 0.39 | −1.74 | 54.7 | −5.04 | −2.23 |
| **20** | 383 (22,700), 545 (69,700) | 605 | 101 | 0.39 | −1.75 | 55.0 | −5.04 | −2.22 |
| **21** | 384 (27,600), 547 (78,800) | 606 | 100 | 0.38 | −1.75 | 55.5 | −5.04 | −2.22 |
| **22** | 384 (26,000), 547 (78,100) | 608 | 100 | 0.39 | −1.73 | 55.0 | −5.04 | −2.22 |

[a] Measured on $1.0\times10^{-5}$ mol dm$^{-3}$ of substrate in chloroform at 25 °C.
[b] Relative fluorescence intensity.
[c] Versus Fc/$Fc^+$ in acetonitrile.
[d] Obtained on the basis of $E_{ox}$, UV–vis absorption band, and fluorescence spectrum.
[e] Calculated dihedral angle.
[f] Calculated by the B3LYP/6–31G(d,p)//B3LYP/3-21G level.

## 2.4. DFT calculations

The optimized structure of **22** calculated by the B3LYP/3-21G(d,p) level is depicted in Fig. 2. The double bond on the 7-position is *Z*-form, coming from less steric repulsion between the hydrogen atom at the 8-position and the carbonyl-oxygen at the inner rhodanine ring. The double bond in the double rhodanine moiety is *E*-form. The dihedral angle ($\theta$) between the 2-alkoxyphenyl group on the nitrogen atom and planar chromophoric moiety in **18**–**22** is calculated to be ca. 55°, there being slightly larger than that of D149 ethyl ester (DFT calculation: 37.3°, X-ray: 35°).[8,10] This result comes from steric hindrance between the alkoxy group and indoline moiety. A side view suggests that a long alkoxy group can act as steric hindrance to prevent π–π interactions between the planar chromophores.

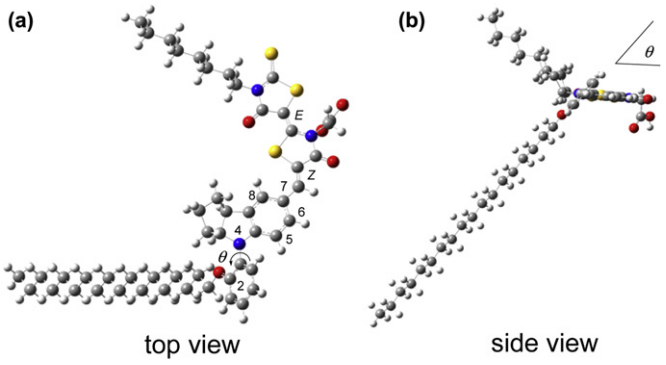


**Fig. 2.** Optimized structure of **22**.

Then, the HOMO and LUMO energy levels of the optimized structures were calculated by the B3LYP/6-31G(d,p) level. The results are shown in Table 1. The first absorption band was attributed to the HOMO–LUMO transition. No remarkable differences of respective HOMO and LUMO levels among **18**–**22** were calculated. The HOMO level of **22** was calculated to be −5.04 eV, there being similar to those of D149 (−5.07 eV).[11]

## 2.5. Photoelectrochemical properties

The UV–vis absorption spectra of **18**–**22** on zinc oxide are shown in Fig. 3a. The absorption maxima were observed at around 520 nm with absorbance in the range of 1.76–2.02, indicating that similar amounts of dyes were adsorbed on zinc oxide and more than 90% of

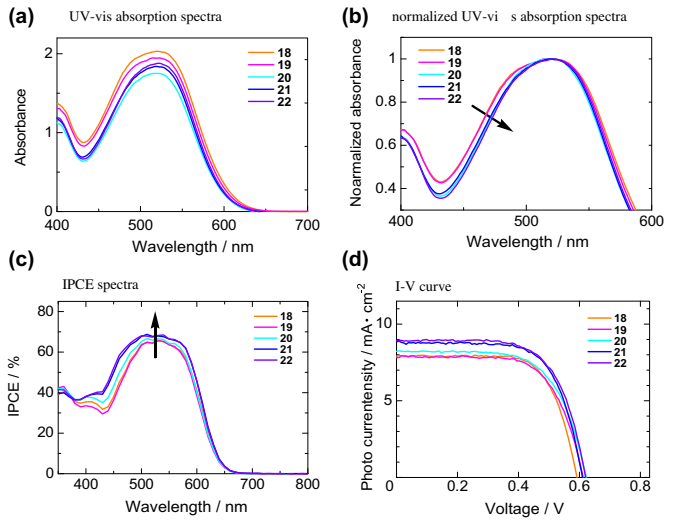


**Fig. 3.** Photoelectrochemical properties of **18**–**22**. (a) UV–vis absorption spectra on zinc oxide, (b) normalized UV–vis absorption spectra on zinc oxide, (c) IPCE spectra, and (d) *I*–*V* curve.

photon was absorbed by the sensitizers. The normalized ones shown in Fig. 3b indicate that the shoulder peak at around 480 nm is broad as shorter is the alkoxy group. This result suggests that H-aggregates are more easily formed on zinc oxide as shorter is the alkoxy group. The IPCE action spectra in Fig. 3c depict that the sensitization is significantly larger as longer is the alkoxy group. Consequently, the $J_{sc}$ value increased as longer was the alkoxy group as shown in Fig. 3d. Thus, prevention of H-aggregates formation by long alkoxy group could improve $J_{sc}$ in the indoline dyes. The data are listed in Table 2.

**Table 2**
Photoelectrochemical properties of **18**–**22**

| Run | Compd | Absorbance | IPCE/% | $J_{sc}$/mA cm$^{-2}$ | $V_{oc}$/V | ff | $\eta$/% |
|---|---|---|---|---|---|---|---|
| 1 | **18** | 2.02 | 66 | 7.92 | 0.59 | 0.70 | 3.26 |
| 2 | **19** | 1.93 | 66 | 7.82 | 0.61 | 0.67 | 3.21 |
| 3 | **20** | 1.76 | 67 | 8.23 | 0.61 | 0.65 | 3.33 |
| 4 | **21** | 1.82 | 69 | 8.85 | 0.61 | 0.68 | 3.65 |
| 5 | **22** | 1.87 | 69 | 8.94 | 0.62 | 0.67 | 3.69 |

Table 2 also indicates that the $V_{oc}$ values gradually increased from 0.59 to 0.62 as longer was the alkoxy group. As the $V_{oc}$ values are affected by the electron lifetimes, those of **18**–**22** on zinc oxide was measured. The results are shown in Fig. 4. The electron lifetime of **22** was longest, and then the lifetime decreased as shorter was the alkoxy group. Thus, the long alkyl moiety could also prevent back electron-transfer from zinc oxide surface to electrolyte to improve $V_{oc}$. This is the first report that both $J_{sc}$ and $V_{oc}$ values were improved by introducing a long alkoxy group into indoline dyes.

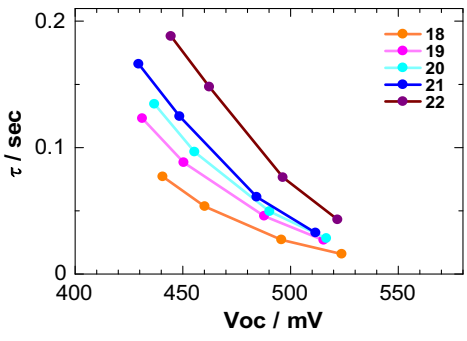


**Fig. 4.** Electron lifetime measurements of **18**–**22**.

## 3. Conclusion

Long 2-alkoxyphenyl group on the indoline ring in double rhodanine indoline dye could inhibit H-aggregates formation and prevent back electron-transfer from zinc oxide surface to electrolyte resulting in improvement of both the $J_{sc}$ and $V_{oc}$ values. Consequently, the 2-(octadecyloxy)phenyl derivative showed the highest conversion efficiency.

## 4. Experimental

### 4.1. Instruments

Melting points were measured with a Yanaco MT-6 micro-melting-point apparatus. NMR spectra were obtained by JEOL ECX-400P and ECA-600 spectrometers. Mass spectra were taken on JEOL MStation 700 spectrometer. UV–vis absorption, fluorescence, and reflection spectra were taken on Hitachi U-3500, F-4500, and U-4000 spectrophotometers, respectively.

### 4.2. Materials

2-Bromophenol (**1**) was supplied from Chemicrea Co. Ltd. 2-Bromophenol and 2-methoxybromobenzene (**2**) were purchased from Wako Pure Chemical Co. Ltd. Compound **17** was prepared as described in the literature.[11]

### 4.3. Synthesis of 2-alkoxybromobenzenes 3–6

To a DMF solution (200 ml) of **1** (2.07 g, 12.0 mmol) were added an alkyl iodide (10.8 mmol) and aqueous solution (20 ml) of sodium hydroxide (0.48 g, 12.0 mmol). The mixture was stirred for 4 h at room temperature. After the reaction was completed, the mixture was poured into water (100 ml). The product was extracted with ether (100 ml×3). The extract was dried over anhydrous sodium sulfate. The product was purified by column chromatography ($SiO_2$, $C_6H_{14}$). The physical and spectral data are shown below.

*4.3.1. 1-Bromo-2-butoxybenzene (**3**).* Yield 66%; oil; $^1$H NMR ($CDCl_3$) $\delta$=0.98 (t, $J$=7.1 Hz, 3H), 1.53 (sex, $J$=7.1 Hz, 2H), 1.81 (quin, $J$=7.1 Hz, 2H), 4.01 (t, $J$=7.1 Hz, 2H), 6.80 (t, $J$=7.9 Hz, 1H), 6.87 (d, $J$=7.9 Hz, 1H), 7.22 (t, $J$=7.9 Hz, 1H), 7.51 (d, $J$=7.9 Hz, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$=14.0, 19.4, 31.3, 68.9, 112.4, 113.3, 121.7, 128.5, 133.4, 155.6; IR (NaCl) $\nu$ 1249, 1031 cm$^{-1}$; EIMS (70 eV) $m/z$ (rel intensity) 230 ($M^+$+2, 10), 228 ($M^+$, 11), 174 (96), 172 (100); HRMS $m/z$ 228.0149 ($M^+$), calcd for $C_{10}H_{13}BrO$: 228.0150.

*4.3.2. 1-Bromo-2-octyloxybenzene (**4**).* Yield 78%; oil; $^1$H NMR ($CDCl_3$) $\delta$=0.89 (t, $J$=7.2 Hz, 3H), 1.25–1.39 (m, 8H), 1.49 (quin, $J$=7.2 Hz, 2H), 1.82 (quin, $J$=7.2 Hz, 2H), 4.00 (t, $J$=7.2 Hz, 2H), 6.79 (t, $J$=7.8 Hz, 1H), 6.86 (d, $J$=7.8 Hz, 1H), 7.22 (t, $J$=7.8 Hz, 1H), 7.51 (d, $J$=7.8 Hz, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$=14.1, 22.6, 26.0, 29.1, 29.2, 29.3, 31.8, 69.1, 112.2, 113.1, 121.5, 128.3, 133.2, 155.4; IR (NaCl) $\nu$ 1249, 1031 cm$^{-1}$; EIMS (70 eV) $m/z$ (rel intensity) 286 ($M^+$+2, 7), 284 ($M^+$, 7), 174 (98), 172 (100); HRMS $m/z$ 284.0750 ($M^+$), calcd for $C_{14}H_{21}BrO$: 284.0776.

*4.3.3. 1-Bromo-2-dodecyloxybenzene (**5**).* Yield 32%; oil; $^1$H NMR ($CDCl_3$) $\delta$=0.88 (t, $J$=7.1 Hz, 3H), 1.23–1.38 (m, 16H), 1.49 (quin, $J$=7.1 Hz, 2H), 1.82 (quin, $J$=7.1 Hz, 2H), 3.99 (t, $J$=7.1 Hz, 2H), 6.79 (t, $J$=7.8 Hz, 1H), 6.86 (d, $J$=7.8 Hz, 1H), 7.21 (t, $J$=7.8 Hz, 1H), 7.51 (d, $J$=7.8 Hz, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$=14.1, 22.7, 26.0, 29.1, 29.32, 29.35, 29.55, 29.58, 29.6, 29.7, 31.9, 69.0, 112.2, 113.1, 121.5, 128.3, 133.2, 155.4; IR (NaCl) $\nu$ 1249, 1031 cm$^{-1}$; EIMS (70 eV) $m/z$ (rel intensity)

342 ($M^+$+2, 5), 340 ($M^+$, 5), 174 (97), 172 (100); HRMS *m*/*z* 340.1383 ($M^+$), calcd for $C_{18}H_{29}BrO$: 340.1402.

*4.3.4. 1-Bromo-2-octadecyloxybenzene (**6**).* Yield 38%; mp 37–39 °C; $^1$H NMR ($CDCl_3$) $\delta$=0.88 (t, *J*=7.1 Hz, 3H), 1.24–1.33 (m, 28H), 1.49 (quin, *J*=7.1 Hz, 2H), 1.83 (quin, *J*=7.1 Hz, 2H), 4.01 (t, *J*=7.1 Hz, 2H), 6.80 (t, *J*=7.8 Hz, 1H), 6.88 (d, *J*=7.8 Hz, 1H), 7.23 (t, *J*=7.8 Hz, 1H), 7.52 (d, *J*=7.8 Hz, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$=14.1, 22.7, 26.0, 29.1, 29.3, 29.4, 29.56, 29.58, 29.66 (2C), 29.70 (6C), 31.9, 69.1, 112.2, 113.2, 121.5, 128.3, 133.3, 155.5; IR (NaCl) $\nu$ 1249, 1031 cm$^{-1}$; EIMS (70 eV) *m*/*z* (rel intensity) 426 ($M^+$+2, 2), 424 ($M^+$, 2), 174 (96), 172 (100); HRMS *m*/*z* 424.2341 ($M^+$), calcd for $C_{24}H_{41}BrO$: 424.2341.

### 4.4. Synthesis of 7–11

To a toluene solution (60 ml) of **1** (4.0 mmol) were added 2-alkoxybromobenzenes (**2**–**6**, 4.8 mmol), palladium diacetate (0.04 g, 0.2 mmol), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (SPhos, 0.16 g, 0.4 mmol), and sodium *tert*-butoxide (0.56 g, 5.6 mmol). The mixture was refluxed overnight. After the reaction was completed, the mixture was poured into water (100 ml). The product was extracted with dichloromethane (100 ml×3). The extract was dried over anhydrous sodium sulfate. The product was purified by column chromatography ($SiO_2$, $CH_2Cl_2$/$C_6H_{14}$=1:3). The physical and spectral data are shown below.

*4.4.1. 4-(2-Methoxyphenyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole (**7**).* Yield 68%; oil; $^1$H NMR ($CDCl_3$) $\delta$=1.46–1.62 (m, 3H), 1.67–1.73 (m, 1H), 1.82–1.89 (m, 1H), 1.94–2.02 (m, 1H), 3.81 (s, 3H), 3.82–3.85 (m, 1H), 4.91 (t, *J*=6.4 Hz, 1H), 6.32 (d, *J*=7.6 Hz, 1H), 6.62 (t, *J*=7.6 Hz, 1H), 6.91–6.99 (m, 3H), 7.07 (d, *J*=7.6 Hz, 1H), 7.16 (t, *J*=7.6 Hz, 1H), 7.34 (d, *J*=7.6 Hz, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$=24.2, 33.0, 35.5, 45.9, 55.6, 68.6, 107.0, 112.4, 117.2, 120.8, 124.3, 125.7, 126.7, 127.0, 131.4, 133.9, 150.1, 155.3; IR (NaCl) $\nu$ 1262, 1024 cm$^{-1}$; EIMS (70 eV) *m*/*z* (rel intensity) 265 ($M^+$, 100), 236 (78), 222 (48); HRMS *m*/*z* 265.1457 ($M^+$), calcd for $C_{18}H_{19}NO$: 265.1467.

*4.4.2. 4-(2-Butoxyphenyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole (**8**).* Yield 57%; oil; $^1$H NMR ($CDCl_3$) $\delta$=0.88 (t, *J*=7.1 Hz, 3H), 1.36 (sep, *J*=7.1 Hz, 2H), 1.45–1.54 (m, 2H), 1.56–1.63 (m, 1H), 1.67 (quin, *J*=7.1 Hz, 2H), 1.70–1.77 (m, 1H), 1.81–1.88 (m, 1H), 1.93–2.01 (m, 1H), 3.80 (t, *J*=8.1 Hz, 1H), 3.94 (t, *J*=7.1 Hz, 2H), 4.91 (t, *J*=8.1 Hz, 1H), 6.33 (d, *J*=7.5 Hz, 1H), 6.60 (t, *J*=7.5 Hz, 1H), 6.89–6.97 (m, 3H), 7.06 (d, *J*=7.5 Hz, 1H), 7.12 (t, *J*=7.7 Hz, 1H), 7.34 (d, *J*=7.7 Hz, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$=13.7, 19.2, 24.1, 31.3, 33.1, 35.6, 45.9, 67.9, 68.7, 107.1, 113.3, 117.0, 120.6, 124.2, 125.6, 126.8, 126.9, 131.6, 133.9, 150.4, 154.8; IR (NaCl) $\nu$ 1262, 1023 cm$^{-1}$; EIMS (70 eV) *m*/*z* (rel intensity) 307 ($M^+$, 100), 278 (75), 222 (45); HRMS *m*/*z* 307.1917 ($M^+$), calcd for $C_{21}H_{25}NO$: 307.1936.

*4.4.3. 4-(2-Octyloxyphenyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole (**9**).* Yield 45%; oil; $^1$H NMR ($CDCl_3$) $\delta$=0.87 (t, *J*=6.6 Hz, 3H), 1.20–1.36 (m, 10H), 1.44–1.51 (m, 2H), 1.56–1.61 (m, 2H), 1.65–1.72 (m, 2H), 1.80–1.88 (m, 1H), 1.93–2.01 (m, 1H), 3.80 (t, *J*=7.3 Hz, 1H), 3.93 (t, *J*=6.6 Hz, 2H), 4.91 (t, *J*=7.3 Hz, 1H), 6.31 (d, *J*=7.5 Hz, 1H), 6.60 (t, *J*=7.5 Hz, 1H), 6.88–6.96 (m, 3H), 7.06 (d, *J*=7.5 Hz, 1H), 7.12 (t, *J*=7.7 Hz, 1H), 7.33 (d, *J*=7.7 Hz, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$=14.2, 22.8, 24.3, 26.1, 29.3, 29.4, 29.5, 31.9, 33.3, 35.7, 46.0, 68.4, 68.9, 107.2, 113.5, 117.2, 120.8, 124.3, 125.8, 127.1, 129.5, 131.8, 134.0, 150.6, 155.0; IR (NaCl) $\nu$ 1262, 1023 cm$^{-1}$; EIMS (70 eV) *m*/*z* (rel intensity) 363 ($M^+$, 100), 334 (24), 222 (51); HRMS *m*/*z* 363.2539 ($M^+$), calcd for $C_{25}H_{33}NO$: 363.2562.

*4.4.4. 4-(2-Dodecyloxyphenyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole (**10**).* Yield 44%; oil; $^1$H NMR ($CDCl_3$) $\delta$=0.88 (t, *J*=6.7 Hz, 3H), 1.20–1.34 (m, 18H), 1.44–1.50 (m, 1H), 1.54–1.61 (m, 2H), 1.64–1.76 (m, 3H), 1.80–1.87 (m, 1H), 1.91–2.00 (m, 1H), 3.79 (t, *J*=7.8 Hz, 1H), 3.92 (t, *J*=6.7 Hz, 2H), 4.91 (t, *J*=7.8 Hz, 1H), 6.31 (d, *J*=7.5 Hz, 1H), 6.59 (t, *J*=7.5 Hz, 1H), 6.88–6.96 (m, 3H), 7.05 (d, *J*=7.5 Hz, 1H), 7.11 (t, *J*=7.8 Hz, 1H), 7.33 (d, *J*=7.8 Hz, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$=14.3, 22.9, 24.3, 26.2, 29.48 (2C), 29.52, 29.69, 29.73, 29.80, 29.83, 32.1, 33.3, 35.8, 46.1, 68.4, 69.0, 107.2, 113.5, 117.2, 120.8, 124.4, 125.8, 127.1 (2C), 131.8, 134.0, 150.6, 155.0; IR (NaCl) $\nu$ 1262, 1023 cm$^{-1}$; EIMS (70 eV) *m*/*z* (rel intensity) 419 ($M^+$, 100), 390 (11), 222 (41); HRMS *m*/*z* 419.3203 ($M^+$), calcd for $C_{29}H_{41}NO$: 419.3188.

*4.4.5. 4-(2-Octadecaoxyphenyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole (**11**).* Yield 45%; oil; $^1$H NMR ($CDCl_3$) $\delta$=0.88 (t, *J*=6.6 Hz, 3H), 1.20–1.34 (m, 30H), 1.44–1.50 (m, 1H), 1.54–1.61 (m, 2H), 1.64–1.76 (m, 3H), 1.80–1.87 (m, 1H), 1.91–2.00 (m, 1H), 3.79 (t, *J*=7.7 Hz, 1H), 3.92 (t, *J*=6.6 Hz, 2H), 4.91 (t, *J*=7.7 Hz, 1H), 6.31 (d, *J*=7.2 Hz, 1H), 6.59 (t, *J*=7.2 Hz, 1H), 6.88–6.96 (m, 3H), 7.05 (d, *J*=7.2 Hz, 1H), 7.11 (t, *J*=7.8 Hz, 1H), 7.33 (d, *J*=7.8 Hz, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$=14.3, 22.8, 24.3, 26.1, 29.45, 29.47, 29.5, 29.68, 29.72, 29.8 (2C), 29.9 (6C), 32.1, 33.3, 35.8, 46.1, 68.4, 69.0, 107.2, 113.5, 117.2, 120.8, 124.4, 125.8, 127.0 (2C), 131.8, 134.0, 150.6, 155.0; IR (NaCl) $\nu$ 1262, 1023 cm$^{-1}$; EIMS (70 eV) *m*/*z* (rel intensity) 503 ($M^+$, 100), 250 (14), 222 (29); HRMS *m*/*z* 503.4117 ($M^+$), calcd for $C_{35}H_{53}NO$: 503.4127.

### 4.5. Synthesis of 4-(2-alkoxyphenyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole-7-carbaldehydes 12–16

To DMF (3 ml) was added phosphoryl chloride (0.46 g, 3.0 mmol). Then, to this mixture was added a DMF solution (1 ml) of **7**–**11** (1.5 mmol). The mixture was stirred overnight at room temperature. After the reaction was completed, to the mixture was poured into ice-water (ca. 10 ml) and neutralized with 1 N aqueous sodium hydroxide. The product was extracted with dichloromethane (100 ml×3). After the extract was dried over anhydrous sodium sulfate, the solvent was removed in vacuo. The product was purified by silica gel column chromatography ($SiO_2$, $CH_2Cl_2$).

*4.5.1. 4-(2-Methoxyphenyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole-7-carbaldehyde (**12**).* Yield 68%; oil; $^1$H NMR ($CDCl_3$) $\delta$=1.46–1.60 (m, 2H), 1.64–1.76 (m, 2H), 1.85–1.92 (m, 1H), 1.96–2.07 (m, 1H), 3.81 (s, 3H), 3.86 (t, *J*=7.9 Hz, 1H), 4.97 (t, *J*=7.9 Hz, 1H), 6.16 (d, *J*=8.2 Hz, 1H), 6.98–7.03 (m, 2H), 7.24–7.31 (m, 2H), 7.44 (d, *J*=8.2 Hz, 1H), 7.61 (s, 1H), 9.65 (s, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$=24.1, 32.8, 35.9, 44.9, 55.6, 70.0, 105.5, 112.5, 121.1, 125.0, 127.2, 127.9, 128.3, 128.6, 133.9, 134.7, 155.8, 156.3, 190.0; IR (KBr) $\nu$ 2740, 1262, 1024 cm$^{-1}$; EIMS (70 eV) *m*/*z* (rel intensity) 293 ($M^+$, 71), 264 (100), 248 (18); HRMS *m*/*z* 293.1423 ($M^+$), calcd for $C_{19}H_{19}NO_2$: 293.1416.

*4.5.2. 4-(2-Butoxyphenyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole-7-carbaldehyde (**13**).* Yield 67%; oil; $^1$H NMR ($CDCl_3$) $\delta$=0.86 (t, *J*=7.0 Hz, 3H), 1.25–1.36 (m, 2H), 1.47–1.60 (m, 2H), 1.62–1.70 (m, 3H), 1.74–1.80 (m, 1H), 1.86–1.93 (m, 1H), 1.98–2.03 (m, 1H), 3.86 (t, *J*=8.0 Hz, 1H), 3.96 (t, *J*=7.0 Hz, 2H), 4.96 (t, *J*=8.0 Hz, 1H), 6.15 (d, *J*=7.3 Hz, 1H), 6.95–7.02 (m, 2H), 7.23–7.28 (m, 2H), 7.43 (d, *J*=7.3 Hz, 1H), 7.61 (s, 1H), 9.66 (s, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$=13.8, 19.2, 24.1, 31.3, 32.9, 35.9, 44.9, 67.9, 70.4, 105.7, 113.2, 120.9, 124.9, 127.2, 127.9, 128.4, 128.9, 133.7, 134.6, 155.4, 156.5, 189.9; IR (KBr) $\nu$ 2740, 1262, 1023 cm$^{-1}$; EIMS (70 eV) *m*/*z* (rel intensity) 335 ($M^+$, 100), 306 (65), 250 (34); HRMS *m*/*z* 335.1876 ($M^+$), calcd for $C_{22}H_{25}NO_2$: 335.1885.

*4.5.3. 4-(2-Octyloxyphenyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole-7-carbaldehyde (**14**).* Yield 66%; oil; $^1$H NMR ($CDCl_3$) $\delta$=0.86 (t, *J*=6.7 Hz, 3H), 1.15–1.30 (m, 10H), 1.47–1.58 (m, 2H), 1.60–1.69 (m, 3H), 1.73–1.79 (m, 1H), 1.85–1.92 (m, 1H), 1.97–2.03 (m, 1H), 3.85 (t, *J*=7.7 Hz, 1H), 3.94 (t, *J*=6.7 Hz, 2H), 4.94 (t, *J*=7.7 Hz, 1H), 6.14 (d, *J*=8.2 Hz, 1H), 6.95–7.01 (m, 2H), 7.22–7.28 (m, 2H), 7.42 (d, *J*=8.2 Hz, 1H), 7.60 (s, 1H), 9.65 (s, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$=14.2, 22.7, 24.1, 26.0, 29.3 (3C), 31.8, 32.9, 35.9, 44.9, 68.3, 70.4, 105.7,

113.2, 120.9, 124.9, 127.2, 127.9, 128.4, 128.9, 133.8, 134.6, 155.4, 156.5, 189.9; IR (KBr) $\nu$ 2740, 1262, 1023 $cm^{-1}$; EIMS (70 eV) $m/z$ (rel intensity) 391 ($M^+$, 100), 362 (14), 250 (57); HRMS $m/z$ 391.2502 ($M^+$), calcd for $C_{26}H_{33}NO_2$: 391.2511.

*4.5.4. 4-(2-Dodecyloxyphenyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b] indole-7-carbaldehyde (**15**).* Yield 63%; oil; $^1H$ NMR ($CDCl_3$) $\delta$=0.88 (t, $J$=6.7 Hz, 3H), 1.16–1.34 (m, 16H), 1.47–1.57 (m, 2H), 1.58–1.71 (m, 5H), 1.73–1.79 (m, 1H), 1.86–1.92 (m, 1H), 1.97–2.06 (m, 1H), 3.85 (t, $J$=7.8 Hz, 1H), 3.94 (t, $J$=6.7 Hz, 2H), 4.95 (t, $J$=7.8 Hz, 1H), 6.14 (d, $J$=8.2 Hz, 1H), 6.95–7.01 (m, 2H), 7.23–7.28 (m, 2H), 7.42 (d, $J$=8.2 Hz, 1H), 7.60 (s, 1H), 9.65 (s, 1H); $^{13}C$ NMR ($CDCl_3$) $\delta$=14.2, 22.8, 24.1, 26.0, 29.27, 29.30, 29.4, 29.6 (2C), 29.7 (2C), 32.0, 32.9, 35.9, 44.9, 68.3, 70.4, 105.7, 113.2, 120.9, 124.9, 127.2, 127.9, 128.4, 128.9, 133.8, 134.6, 155.4, 156.5, 189.9; IR (KBr) $\nu$ 2740, 1262, 1023 $cm^{-1}$; EIMS (70 eV) $m/z$ (rel intensity) 447 ($M^+$, 100), 250 (59), 222 (24); HRMS $m/z$ 447.3134 ($M^+$), calcd for $C_{30}H_{41}NO_2$: 447.3137.

*4.5.5. 4-(2-Octadecyloxyphenyl)-1,2,3,3a,4,8b-hexahydrocyclopenta [b]indole-7-carbaldehyde (**16**).* Yield 60%; oil; $^1H$ NMR ($CDCl_3$) $\delta$=0.88 (t, $J$=6.9 Hz, 3H), 1.16–1.34 (m, 30H), 1.47–1.58 (m, 2H), 1.60–1.71 (m, 3H), 1.73–1.80 (m, 1H), 1.86–1.93 (m, 1H), 1.98–2.06 (m, 1H), 3.85 (t, $J$=7.9 Hz, 1H), 3.94 (t, $J$=6.5 Hz, 2H), 4.95 (t, $J$=7.9 Hz, 1H), 6.14 (d, $J$=8.1 Hz, 1H), 6.95–7.01 (m, 2H), 7.23–7.28 (m, 2H), 7.42 (d, $J$=8.1 Hz, 1H), 7.60 (s, 1H), 9.65 (s, 1H); $^{13}C$ NMR ($CDCl_3$) $\delta$=14.2, 22.8, 24.1, 26.0, 29.27, 29.31, 29.5, 29.61, 29.63, 29.7 (2C), 29.8 (6C), 32.0, 32.9, 35.9, 44.9, 68.3, 70.4, 105.7, 113.2, 120.9, 124.9, 127.2, 127.9, 128.4, 128.9, 133.8, 134.6, 155.4, 156.5, 189.9; IR (KBr) $\nu$ 2740, 1262, 1023 $cm^{-1}$; EIMS (70 eV) $m/z$ (rel intensity) 531 ($M^+$, 19), 250 (100), 222 (19); HRMS $m/z$ 531.4094 ($M^+$), calcd for $C_{36}H_{53}NO_2$: 531.4076.

### 4.6. Synthesis of dyes 18–22

To a butanol solution of (50 ml) of **12**–**16** (1.0 mmol) and double rhodanine acetic acid **17** (0.38 g, 0.95 mmol) was added piperidine (0.07 g, 0.9 mmol). The mixture was refluxed for 4 h. After the reaction was completed, the solvent was removed in vacuo. The resulting precipitate was purified by column chromatography ($SiO_2$, $CHCl_3$/MeOH=20:1). The physical and spectral data are shown below.

*4.6.1. Dye **18**.* Yield 52%; mp 147–149 °C; $^1H$ NMR (DMSO-$d_6$) $\delta$=0.85 (t, $J$=6.4 Hz, 3H), 1.20–1.32 (m, 10H), 1.41–1.54 (m, 2H), 1.56–1.68 (m, 4H), 1.76–1.84 (m, 1H), 2.00–2.10 (m, 1H), 3.80 (s, 3H), 3.90–4.00 (m, 3H), 4.64 (s, 2H), 5.01 (t, $J$=6.6 Hz, 1H), 6.17 (d, $J$=8.3 Hz, 1H), 7.04 (t, $J$=7.9 Hz, 1H), 7.19 (d, $J$=7.9 Hz, 1H), 7.29–7.38 (m, 3H), 7.40 (s, 1H) 7.68 (s, 1H); $^{13}C$ NMR (DMSO-$d_6$) $\delta$=14.5, 22.6, 24.2, 26.7, 26.8, 29.0, 29.1, 31.7, 32.6, 36.2, 44.7, 44.8, 46.8, 56.1, 70.0, 92.7, 107.2, 111.4, 113.5, 121.6, 122.6, 127.5, 127.9, 128.3, 128.4, 134.1, 135.8, 136.0, 147.4, 153.4, 155.7, 166.6, 166.8, 168.4, 189.6; IR (KBr) $\nu$ 1676, 1266 $cm^{-1}$; FABMS (NBA) $m/z$ 677 ($MH^+$). Anal. Found: C, 61.88; H, 5.85; N, 5.98%. Calcd for $C_{35}H_{39}N_3O_5S_3$: C, 62.01; H, 5.80; N, 6.20%.

*4.6.2. Dye **19**.* Yield 48%; mp 153–154 °C; $^1H$ NMR (DMSO-$d_6$) $\delta$=0.80 (t, $J$=7.3 Hz, 3H), 0.85 (t, $J$=6.7 Hz, 3H), 1.19–1.32 (m, 10H), 1.42–1.68 (m, 10H), 1.77–1.84 (m, 1H), 2.00–2.10 (m, 1H), 3.89–4.03 (m, 5H), 4.52 (s, 2H), 4.99 (t, $J$=6.6 Hz, 1H), 6.17 (d, $J$=8.2 Hz, 1H), 7.01 (t, $J$=7.9 Hz, 1H), 7.16 (d, $J$=7.9 Hz, 1H), 7.26–7.36 (m, 3H), 7.39 (s, 1H), 7.66 (s, 1H); $^{13}C$ NMR (DMSO-$d_6$): $\delta$=14.1, 14.5, 19.1, 22.6, 22.8, 24.1, 26.7, 26.8, 29.05, 29.06, 31.3, 31.7, 32.7, 36.2, 44.1, 45.0, 47.8, 67.9, 70.3, 92.6, 107.4, 111.8, 114.0, 121.4, 122.6, 127.3, 128.0, 128.3, 128.5, 133.8, 135.7, 135.8, 147.9, 153.4, 155.1, 166.6, 166.8, 168.1, 189.7; IR (KBr) $\nu$ 1684, 1266 $cm^{-1}$; FABMS (NBA) $m/z$ 719 ($MH^+$). Anal. Found: C, 63.11; H, 5.96; N, 6.11%. Calcd for $C_{38}H_{45}N_3O_5S_3$: C, 63.39; H, 6.30; N, 5.84%.

*4.6.3. Dye **20**.* Yield 52%; mp 184–185 °C; $^1H$ NMR (DMSO-$d_6$) $\delta$=0.76 (t, $J$=6.9 Hz, 3H), 0.85 (t, $J$=6.6 Hz, 3H), 1.03–1.32 (m, 20H), 1.44–1.67 (m, 8H), 1.76–1.84 (m, 1H), 2.00–2.09 (m, 1H), 3.89–4.02 (m, 5H), 4.73 (s, 2H), 4.98 (t, $J$=6.6 Hz, 1H), 6.13 (d, $J$=8.7 Hz, 1H), 7.02 (t, $J$=8.3 Hz, 1H), 7.15 (d, $J$=8.3 Hz, 1H), 7.26–7.37 (m, 3H), 7.39 (s, 1H) 7.69 (s, 1H); $^{13}C$ NMR (DMSO-$d_6$) $\delta$=14.39, 14.44, 22.57, 22.61, 24.1, 26.0, 26.7, 26.8, 28.99, 29.02, 29.16, 29.2, 29.3, 31.67, 31.69, 32.8, 36.2, 44.7, 45.0, 46.5, 68.2, 70.6, 92.6, 107.5, 110.9, 113.9, 121.4, 122.4, 127.4, 128.1, 128.42, 128.48, 134.0, 135.6, 136.3, 147.2, 153.6, 155.2, 166.5, 166.7, 168.6, 189.4; IR (NaCl) $\nu$ 1675, 1266 $cm^{-1}$; FABMS (NBA) $m/z$ 775 ($MH^+$). Anal. Found: C, 65.29; H, 6.82; N, 5.39%. Calcd for $C_{42}H_{53}N_3O_5S_3$: C, 65.00; H, 6.88; N, 5.41%.

*4.6.4. Dye **21**.* Yield 50%; mp 182–183 °C; $^1H$ NMR ($CDCl_3$) $\delta$=0.83–0.90 (m, 6H), 1.14–1.40 (m, 28H), 1.48–1.59 (m, 2H), 1.61–1.79 (m, 6H), 1.87–1.94 (m, 1H), 1.99–2.11 (m, 1H), 3.89 (t, $J$=7.7 Hz, 1H), 3.95 (t, $J$=6.4 Hz, 2H), 4.09 (t, $J$=7.8 Hz, 2H), 4.92 (s, 2H), 4.99 (t, $J$=7.7 Hz, 1H), 6.22 (d, $J$=8.2 Hz, 1H), 6.95–7.01 (m, 2H), 7.22–7.28 (m, 3H), 7.35 (s, 1H), 7.76 (s, 1H); $^{13}C$ NMR ($CDCl_3$) $\delta$=14.17, 14.21, 22.7, 22.8, 24.1, 26.1, 27.0 (2C), 29.2 (3C), 29.27, 29.34, 29.4, 29.6 (2C), 29.7 (2C), 31.9, 32.0, 32.8, 36.2, 45.1, 45.2, 68.3, 70.4, 93.2, 107.2, 110.2, 113.2, 120.9, 122.5, 127.4, 127.8, 128.0, 128.7, 134.5, 135.6, 137.5, 146.4, 154.0, 155.1, 167.0, 167.2, 169.3, 188.8; IR (KBr) $\nu$ 1674, 1266 $cm^{-1}$; FABMS (NBA) $m/z$ 831 ($MH^+$). Anal. Found: C, 66.40; H, 7.61; N, 4.89%. Calcd for $C_{46}H_{61}N_3O_5S_3$: C, 66.39; H, 7.39; N, 5.05%.

*4.6.5. Dye **22**.* Yield 47%; mp 177–178 °C; $^1H$ NMR ($CDCl_3$) $\delta$=0.88 (t, $J$=7.0 Hz, 6H), 1.15–1.39 (m, 40H), 1.49–1.59 (m, 2H), 1.63–1.78 (m, 6H), 1.87–1.94 (m, 1H), 2.00–2.10 (m, 1H), 3.89 (t, $J$=7.7 Hz, 1H), 3.95 (t, $J$=7.0 Hz, 2H), 4.09 (t, $J$=7.0 Hz, 2H), 4.92 (s, 2H), 4.96 (t, $J$=7.7 Hz, 1H), 6.22 (d, $J$=8.2 Hz, 1H), 6.95–7.01 (m, 2H), 7.22–7.28 (m, 3H), 7.36 (s, 1H), 7.75 (s, 1H); $^{13}C$ NMR ($CDCl_3$) $\delta$=14.18, 14.22, 22.7, 22.8, 24.1, 26.1, 27.0 (2C), 29.2 (3C), 29.29, 29.34, 29.5, 29.7 (2C), 29.76 (2C), 29.81 (6C), 31.9, 32.0, 32.8, 36.2, 45.06, 45.14, 68.3, 70.4, 93.2, 107.3, 110.3, 113.2, 120.9, 122.5, 127.4, 127.8, 128.0, 128.7, 134.4, 135.6, 137.5, 146.5, 154.0, 155.1, 167.0, 167.2, 169.2, 188.9; IR (KBr) $\nu$ 1675, 1266 $cm^{-1}$; FABMS (NBA) $m/z$ 916 ($MH^+$). Anal. Found: C, 68.24; H, 8.33; N, 4.42%. Calcd for $C_{52}H_{73}N_3O_5S_3$: C, 68.16; H, 8.03; N, 4.59%.

### 4.7. Film preparation

The electrodes were formed by the screen printing of zinc oxide (0.28 $cm^2$) films on F-doped tin-oxide-coated (FTO) glass plates (Nippon Sheet Glass, Solar, 4 mm thick) with zinc oxide pastes prepared from nanoparticle ZnO-410 (Sumitomo Osaka Cement Co., Ltd). The thickness of zinc oxide layer was 12 μm. An acetonitrile/*tert*-butyl alcohol (v/v, 1:1) mixed solution of dye (0.5 mM) containing cholic acid (1.0 mM) was prepared. The zinc oxide electrodes were immersed into the solution and kept at room temperature for 90 min. Platinum (6 μm thick) sputtered FTO glass plates were used as the counter electrode. The dye-adsorbed zinc oxide electrode and platinum counter electrode were assembled into a sealed sandwich-type cell by heating with a hot melt type ionomer film (HIMILAN, 35 μm thick, DuPont), which served as a spacer between the electrodes. A drop of the electrolyte solution was placed on a drilled hole in the counter electrode of the assembled cell, and was driven into the cell by means of vacuum backfilling method. The electrolyte composed of 1.0 M tetrapropylammonium iodide and 0.1 M iodine in acetonitrile/ethylene carbonate (v/v, 1:4) mixture. Finally, the hole was sealed using additional HIMILAN and a cover glass.

### 4.8. Photoelectrochemical measurements

Action spectrum was obtained under monochromatic light with a constant photon number ($0.05\times10^{16}$ photon $cm^{-2}$ $s^{-1}$). *I*–*V* characteristics were measured under illumination with AM 1.5 simulated sun light (100 mW $cm^{-2}$) by using a Bunko-Keiki CEP-2000 system.

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## Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2012.03.060.

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