RSC Advances

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Journal:	*RSC Advances*
Manuscript ID	RA-ART-11-2015-023623.R1
Article Type:	Paper
Date Submitted by the Author:	10-Feb-2016
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Subject area & keyword:	Organic materials < Materials

Journal Name

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Long-term stability of novel double rhodanine indoline dyes having one and two anchor carboxyl group(s) in dye-sensitized solar cell

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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An indoline dye having both α-cyanoacrylic acid and rhodanine acetic acid anchor groups at the acceptor moiety exhibited improved stability under fluorescence light irradiation.

1. Introduction

Indoline dyes are one of the highly efficient organic sensitizers in dye-sensitized solar cells (DSSCs). **D149** in which a double rhodanine moiety is attached through a methine linkage at the 7-position on the indoline ring has been reported to show excellent conversion efficiency.[1,2] **D205**, the ethyl group in the terminal rhodanine ring of **D149** is substituted with an octyl group, has been reported to show improved open-circuit photovoltage (V_{oc}) to give higher conversion efficiency (η) than **D149**.[3] **DN319**, the thiocarbonyl group in the terminal rhodanine ring of **D205** is converted into a dicyanovinylidene group, has been reported to show higher η value than **D205** due to improved short-circuit photodensity (J_{sc}) coming from bathochromic absorption band.[4] **DN351**, in which the 4-(diphenylvinylidenephenylene) group of **DN319** is substituted with a 2-(9,9-dibutylfluorenyl) group, has been reported to exhibit higher η value than **DN319** because of less H-aggregate formation.[5] Thus, the conversion efficiency of indoline dyes is improving. Meanwhile, stability improvement of DSSCs is also important from the viewpoint of their practical use. Long-term outdoor and indoor stability tests of DSSCs have been reported.[6–12] The stability is affected by humidity,[13,14] light,[15] heat,[16] and semiconductors.[17] To solve this problem, use of ionic liquids and solid electrolyte has been proposed.[18–28] One of the main reasons for degradation of solar cell can come from the desorption of dye molecules from semiconductors.[29,30] However, less paper concerning long-term stability of DSSCs from the viewpoint of the molecular structure of organic sensitizers has been reported. Tanaka *et al*. have reported that the desorption of **D131**, an indoline dye having an α-cyanoacrylic acid anchor group, can come from decarboxylation of the anchor group.[31] We consider that introduction of two anchor groups in the sensitizers can improve the degradation. As the introduction of anchor group at the donor moiety of indoline dyes reduces the conversion efficiency, the anchor group must be introduced at the acceptor moiety.[32] On the basis of this point, we made a molecular design of **GU115**, **GU116**, and **GU117**, double rhodanine indoline dyes having one or two anchor groups, bathochromic absorption band, and suitable energy levels. We report herein the performance of these novel indoline dyes in titanium oxide DSSCs.

2. Results and discussion

2.1. Synthesis

GU115, **GU116**, and **GU117** were synthesized as shown in Scheme 1. Malononitrile (**1**) was allowed to react with ethyl 8-isothiocyanatooctanoate (**2**) and ethyl bromoacetate (**3**) in the presence of DBU to give a single rhodanine ethyl ester **4**, which was again allowed to react with ethyl isothiocyanatoacetate (**5**) and **3** in the presence of DBU to afford a double rhodanine diethyl ester **6a**. The ethyl ester groups of **6a** were hydrolyzed to give a double rhodanine dicarboxylic acid **7a**. This compound was allowed to react with an aldehyde **8** in the presence of ammonium acetate to provide **GU115**.

t-Butyl cyanoacetate (**9**) was allowed to react with octyl isothiocyanate (**10**) and **3** in the presence of DBU to form a single rhodanine *t*-butyl ester **11**, which reacted with **10** and **3** in the presence of DBU to give a double rhodanine mono *t*-butyl ester **6b**, whose ester moiety was deprotected with triethylsilane in the presence of TFA to afford the carboxylic acid **7b**. This compound was allowed to react with **8** in the presence of piperidine to give **GU116**.

The single rhodanine *t*-butyl ester **11** was allowed to react with *t*-butyl 8-isothiocyanatooctanoate (**12**) and **3** in the presence of

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† Electronic Supplementary Information (ESI) vailable: Fluorescence lifetime and cyclic voltammogram of **GU115**, **GU116**, and **GU117**, and 1H and 13C spectra of materials. See DOI: 10.1039/x0xx00000x

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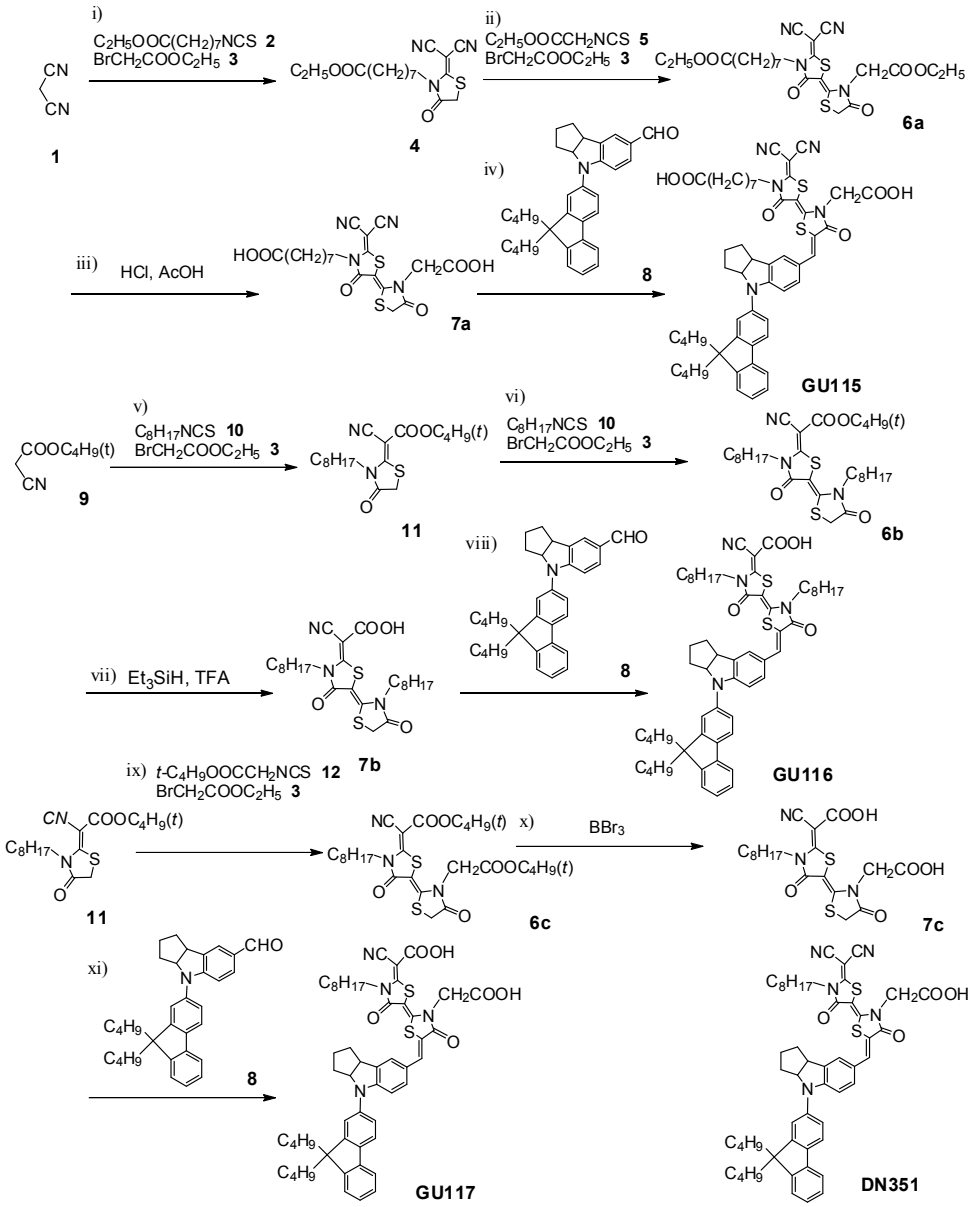

Scheme 1 Reaction conditions and reagents: i) **1** (1.0 equiv.), **2** (1.1 equiv.), DBU (1.0 equiv.), MeCN, rt, 30 min, then **3** (1.7 equiv.), rt, 1 h, then reflux, 3 h, ii) **4** (1.0 equiv.), **5** (1.8 equiv.), DBU (2.3 equiv.), MeCN, rt, 30 min, then **3** (1.7 equiv.), rt, 1 h, then reflux, 3 h, iii) **6a** (1.0 equiv.), conc. HCl, AcOH, 100°C, 3,h, iv) **7a** (1.0 equiv.), **8** (1.2 equiv.), $AcONH_4$ (cat.), AcOH, reflux, 3 h, v) **9** (1.0 equiv.), **10** (1.1 equiv.), DBU (1.0 equiv.), MeCN, rt, 30 min, then **3** (2.0 equiv.), rt, 1 h, then reflux, 3 h, vi) **11** (1.0 equiv.), **10** (1.2 equiv.), DBU (1.0 equiv.), MeCN, rt, 30 min, then **3** (1.5 equiv.), rt, 1 h, then reflux, 3 h, vii) **6b** (1.0 equiv.), Et_3SiH (5.1 equiv.), TFA, CH_2Cl_2, 0°C, 5 h, viii) **6b** (1.0 equiv.), **7** (1.2 equiv.), piperidine (1.0 equiv.), BuOH, 100°C, 1 h, ix) **11** (1.0 equiv.), **12** (1.1 equiv.), DBU (1.2 equiv.), MeCN, rt, 30 min, then **3** (1.5 equiv.), rt, 1 h, then reflux, 1 day, x) **6c** (1.0 equiv.), BBr_3 (2.1 equiv.), CH_2Cl_2, 0°C, 20 mim, xi) **7c** (1.0 equiv.), **8** (1.0 equiv.), MeOH, MeONa (2.0 equiv.), 40°C, 20 h.

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DBU to give a double rhodanine di-*t*-butyl ester **6c**, which was treated with boron tribromide to afford a double rhodanine dicarboxylic acid **7c**, which was allowed to react with **8** in the presence of piperidine to form **GU117**. Known **DN351** used as a reference compound was prepared as described in our previous paper.[5]

2.2. Physical properties

The UV-vis absorption and fluorescence spectra of **GU115**, **GU116**, **GU117**, and **DN351** in chloroform are indicated in Figure 1. The first absorption maxima (λ_{max}) of **GU115** and **DN351** were slightly more bathochromic (566 nm) than those of **GU116** and **GU117** (557 nm) due to more electron-withdrawing nature of dicyanovinylidene group than α-cyanoacrylic acid group. The molar absorption coefficients (ε) were in the range of 62,000 to 87,000 $dm^3\ mol^{-1}\ cm^{-1}$. The fluorescence maxima (F_{max}) were observed at around 650 nm. The fluorescence quantum yields (Φ_f) were in the range of 0.12 to 0.20.

The fluorescence lifetime (τ_f) of **GU115**, **GU116**, and **GU117** was measured in chloroform. The τ_f was determined by fitting the decay curve with one-component exponential function as shown in Figure S1. The results are listed in Table S1. The τ_f of **GU115**, **GU116**, and **GU117** in chloroform were calculated to be 1.48, 1.15, and 1.09 ns, respectively. That of **DN351** has been reported to be 1.51 ns in chloroform.[33] In our previous work, it was clarified that the τ_f of efficient indoline dyes should be longer than 0.9 ns in chloroform.[33] Thus, these dyes have sufficiently long excitation lifetime to inject electrons from the excited singlet state to titanium oxide.

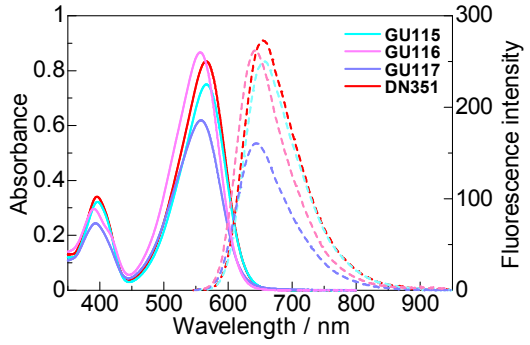

Figure 1 UV absorption and fluorescence spectra of **GU115**, **GU116**, **GU117**, and **DN351** (1.0×10^{-5} mol dm^{-3}) in chloroform.

The cyclic voltammogram of **GU115**, **GU116**, and **GU117** *vs.* Ag *quasi* reference electrode (QRE) in DMF in the presence of ferrocene as an internal standard. The results are shown in Figure S2. The oxidative waves in the range of +0.65 to +0.82 and +1.03 to +1.15 V correspond to the oxidation of ferrocene and **GU** dyes, respectively. Therefore, the oxidation potential (E_{ox}) of **GU115**, **GU116**, and **GU117** were estimated to be 0.38, 0.33 and 0.33 V *vs* Fc/Fc^+, respectively. The E_{ox} level of **GU116** and **GU117** was more negative than that of **GU115** due to electron-withdrawing dicyanovinylidene moiety. This result is consistent with the DFT calculations that the HOMO level of **GU116** (–5.08 eV) and **GU117** (–5.17 eV) are less stable than that of **GU115** (–5.24 eV). As no reduction potential peak was observed for **GU115**, **GU116**, and **GU117**, the E_{ox}–E_{0-0} level was calculated as described in our previous paper.[34,35] The E_{ox}–E_{0-0} level of **GU115**, **GU116**, and **GU117** were calculated to be –1.64, –1.72, and –1.73 V *vs.* Fc/Fc^+, respectively. The conduction band level of titanium oxide is located at around –0.95 V *vs* Fc/Fc^+. The observed E_{ox} and E_{0-0} correspond to the calculated HOMO and LUMO levels. Therefore, **GU115**, **GU116**, and **GU117** can thermodynamically sensitize titanium oxide. The I^-/I_3^- redox level is located at around –0.05 V *vs.* Fc/Fc^+. The oxidized **GU115**, **GU116**, and **GU117** can accept electrons from I^-. The Physical properties are summarized in Table 1.

2.3. DFT Calculations

The structure of **GU115** was optimized by the B3LYP/3-21G level. Figure 2 indicates that isomer **A**, whose terminal olefinic α-cyanoacrylic moiety is *E*-form, was calculated to be more stable than the *Z*-isomer **B** due to less steric repulsion between the carboxy group and adjacent octyl group in the same rhodanine ring.

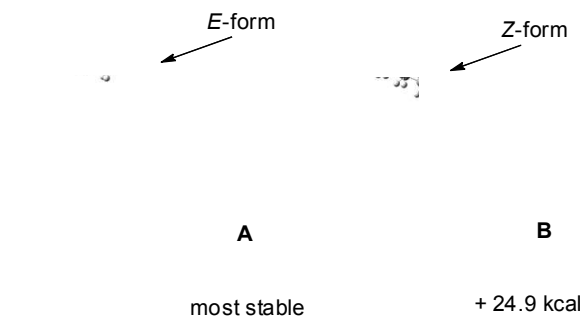

Figure 2 Optimized isomers **A**, **B**, and **C** for **GU116**.

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Table 1 Physical properties of **GU115**, **GU116**, **GU117**, and **DN351**

Compd	$\lambda_{max}(\varepsilon)^a$ nm	$F_{max}{}^a$ nm	$\Phi_f{}^a$	$\tau_f{}^b$ ns	$E_{ox}{}^c$ V	$E_{ox}–E_{0\text{-}0}{}^d$ V	HOMO^e eV	LUMO^e eV
GU115	396 (32,000), 566 (75,000)	656	0.20	1.48	0.38	−1.65	−5.24	−2.54
GU116	391 (30,000), 557 (87,000)	641	0.17	1.15	0.33	−1.72	−5.08	−2.33
GU117	393 (24,000), 558 (62,000)	645	0.12	1.09	0.33	−1.73	−5.15	−2.41
DN351	396 (34,000), 566 (83,000)	654	0.20	1.51	0.37	−1.66	−5.22	−2.52

[a]Measured on 1.0×10^{-5} mol dm^{-3} of substrate in chloroform at 25°C.
[b]Fluorescence lifetime.
[c]*vs* 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/3-21G level.

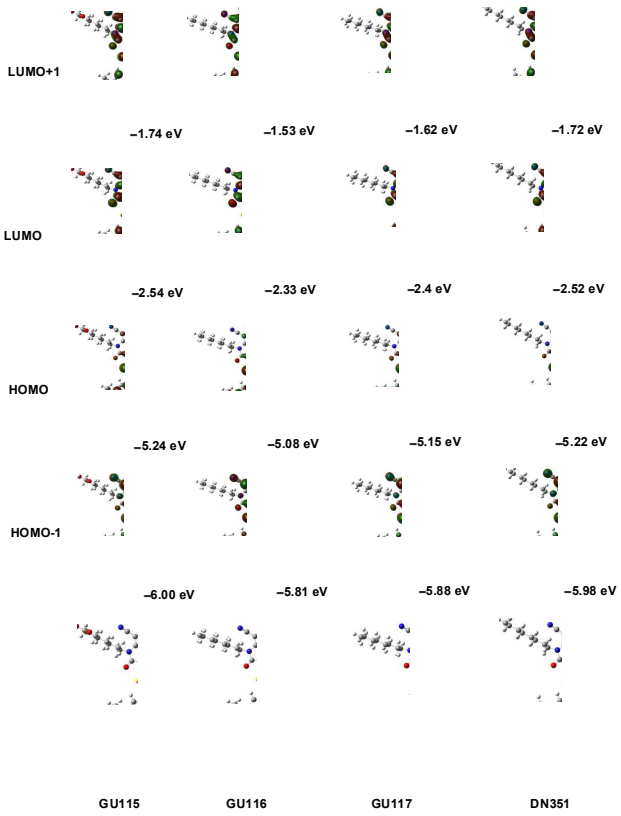


Figure 3 Isodensity surface plots and energy level of **GU115**, **GU116**, **GU117**, and **DN351**.

Table 2 Absorption maximum (λ_{max}), main orbital transition and oscillator strength calculated by TDDFT at the B3LYP/6-31G(d,p) level

Compd	Transition	λ_{max} (nm)	Main orbital transition	f
GU115	S_0 to S_1	509	HOMO to LUMO (0.70)	1.19
	S_0 to S_2	400	HOMO−1 to LUMO (0.51)	0.61
			HOMO to LUMO+1 (0.47)	
GU116	S_0 to S_1	502	HOMO to LUMO (0.70)	1.24
	S_0 to S_2	396	HOMO−1 to LUMO (0.54)	0.55
			HOMO to LUMO+1 (0.44)	
GU117	S_0 to S_1	502	HOMO to LUMO (0.70)	1.25
	S_0 to S_2	397	HOMO−1 to LUMO (0.54)	0.51
			HOMO to LUMO+1 (0.44)	
DN351	S_0 to S_1	509	HOMO to LUMO (0.70)	1.19
	S_0 to S_2	400	HOMO−1 to LUMO (0.52)	0.61
			HOMO to LUMO+1 (0.46)	

Figure 3 depicts the isodensity surface plots of **GU115**, **GU116**, **GU17**, and **DN351**. The electrons in the HOMO level are located in the indoline moiety and those in the LUMO level in the double rhodanine accepter moiety, suggesting smooth electron-transfer from the dye molecule to semiconductor.

The absorption maximum, main orbital transition, and oscillator strength of **GU115**, **GU116**, **GU117**, and **DN351** calculated by TDDFT at the B3LYP/6-31(d,p) level are shown in Table 2. The 70% of first absorption band (S_0 to S_1) in **GU115**, **GU116**, **GU117**, and **DN351** is assigned to the intramolecular

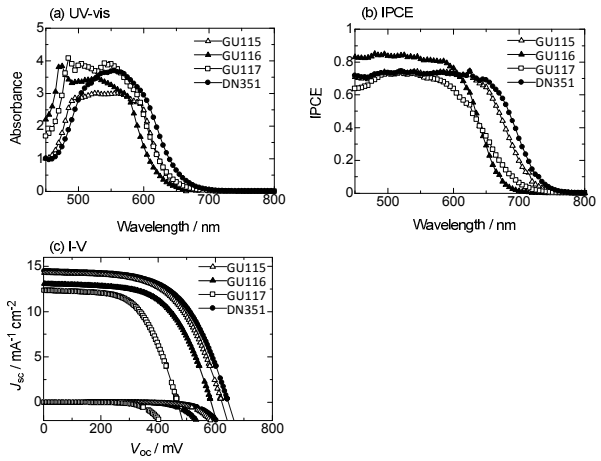


Figure 4 Performance of indoline dyes (a) UV-vis absorption spectra on titanium oxide, (b) action spectra, and (c) I-V curve.

charge-transfer HOMO to LUMO transition with large oscillator strength. The second absorption band (S_0 to S_2) is assigned to HOMO−1 to LUMO and HOMO to LUMO+1 transition. **GU115** and **DN351** show slightly bathochromic shift than **GU116** and **GU117** due to their lower LUMO level. The molar absorption coefficients of **GU115**, **GU116**, and **GU117** were predicted to be similar to that of **DN351**.

2.4. Photovoltaic Properties

The cell performance of **GU115**, **GU116**, **GU117**, and **DN351** is indicated in Figure 4 and Table 3. Figure 4a shows the UV-vis absorption spectra on titanium oxide. The λ_{max} was observed at around 550 nm. The number of adsorbed dye molecules of **GU115**, **GU116**, and **DN351** per area were in the range of 0.625 to 1.04 nm^{-2}. The amount of **GU117** was not calculated. Because **GU117** could not be extracted from titanium oxide by *N*,*N*-dimethylacetamide (DMA). This result indicates that **GU117** is very tightly attached to titanium oxide. Figure 4b indicates the IPCE spectra. **GU116** showed larger IPCE value than **GU115**, **GU117**, and **DN351** at around 550 nm. **GU115** and **DN351** exhibited larger IPCE value than **GU116** and **GU117** at *ca*. 700 nm. As the results, the J_{sc} of **DN351** and **GU115** was larger than that of **GU116** and **GU117** as shown in Figure 4c. Consequently, the η was in the order of dyes: **DN351** (5.46%) > **GU115** (5.19%) > **GU116** (4.49%) > **GU117** (3.39%).

2.5. Long-term stability of solar cells

The stability of solar cell upon fluorescence light irradiation is shown in Figure 5. No drastic difference in open-circuit photovoltage (V_{oc}) and fill factor (ff) was observed among **GU115**,

Table 3 Photovoltaic properties of **GU115**, **GU116**, **GU117**, and **DN351**

Dyes	Number of adsorbed dye[a] / number nm^{-2}	J_{sc}[b] / mA cm^{-2}	V_{oc}[b] / V	ff[b]	η[b] / %
GU115	0.625	14.3	0.619	0.587	5.19
GU116	0.714	12.7	0.584	0.605	4.49
GU117	-[c]	12.3	0.465	0.593	3.39
DN351	1.04	14.5	0.642	0.586	5.46

[a]On titanium oxide.
[b]Under AM 1.5 irradiation (100 mW cm^{-2}).
[c]Not measured.

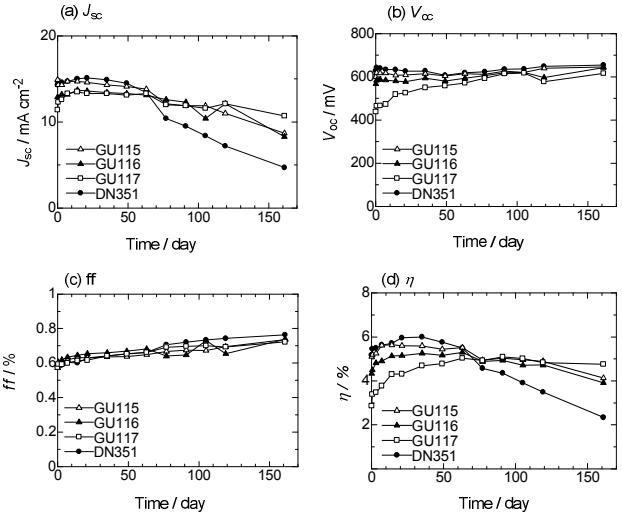


Figure 5 Change in (a) J_{sc}, (b) V_{oc}, (c) ff, and (d) η values of **GU115**, **GU116**, **GU117**, and **DN351** upon fluorescence lamp (40 W) illumination at 25°C with humidity of 28%..

GU116, **GU117**, and **DN351**. The change of η followed the change of J_{sc}. The J_{sc} value increased in the initial stage until *ca*. 20 days and then decreased. We suppose that this result can come from the removal and/or the re-alignment of dyes having weak affinity with dyes and/or titanium oxide. After 161 days, the stability was in the order of dyes: **GU117** > **GU116**, **GU115** >> **DN351**. The p*K*a values of α-cyanoacrylic acid and acetic acid are known as 1.30 and 4.76, respectively. A carboxylate group has been reported to form chelating and/or bridging linkage with titanium oxide.[36–39] Therefore, more acidic carboxylic acids can form more stable complexes with titanium oxide. Actually, **GU117** was not extracted from titanium oxide by DMA, whereas **GU115**, **GU116**, and **DN351** were completely extracted. Thus, **GU117** having both strongly acidic α-cyanoacrylic acid and rhodanine acetic acid anchor groups

in a molecule could form the most stable binding with titanium oxide to exhibit the best stability among the indoline dyes.

3. Conclusion

We have made a molecular design, synthesis, and evaluation of new indoline dyes **GU115**, **GU116**, and **GU117** in which carboxylic acid anchor group(s) are attached at the acceptor moiety. Known **DN351** was used as a standard compound. These dyes exhibited the conversion efficiency in the range of 3.39 to 5.46% at the initial stage. After 161-days fluorescence lamp irradiation, the conversion efficiency was in the order of dyes: **GU117** > **GU116**, **GU115** >> **DN351**. Thus, **GU117** having both α-cyanoacrylic acid and rhodanine acetic acids anchor groups exhibited the best stability among the indoline dyes due to the most stable binding with titanium oxide.

4. Experimental

4.1. Instruments

Melting points were measured with a Yanaco MP-S2 micro-melting-point apparatus. NMR spectra were taken with a JEOL JNM-ECX 400P spectrometer. Mass spectra were taken on a JEOL MStation 700 spectrometer. IR spectra were obtained by a Shimadzu IR Affinity-1 spectrophotometer. Elemental analysis was performed with a Yanaco MT-6 CHN corder. 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.

4.2. Materials

Malononitrile (**1**) was purchased from Kanto Chemical Co., Inc. Ethyl 8-isothiocyanatooctanoate (**2**), ethyl bromoacetate (**3**), ethyl isothiocyanatoacetate (**5**), and *t*-butyl cyanoacetate (**9**) were obtained from Tokyo Chemical Industry Co., Ltd. Octyl isothiocyanate (**10**) was purchased from Wako Pure Chemical Industries, Ltd. **D149** was supplied from Chemicrea Inc. Compounds **8**,[5] *t*-butyl 2-isothiocyanatoacetate (**12**),[40] and **DN351**[5] were synthesized as described in the literature.

*4.3. Synthesis of **4***

To an acetonitrile solution (7 mL) of malononitrile (**1**, 1.3 g, 20 mmol) and ethyl 8-isothiocyanatooctanoate (**2**, 4.9 g, 21 mmol) was added DBU (3.1 g, 20 mmol) at room temperature. The mixture was stirred for 30 min. To the mixture was added ethyl bromoacetate (**3**, 5.7 g, 34 mmol) and stirred at room temperature for 1 h and then refluxed for 3 h. After the reaction was completed, the mixture was concentrated *in vacuo*. To the mixture were added chloroform (30 mL) and an aqueous 10% hydrochloric acid (30 mL). The product was extracted with chloroform (30 mL × 3) and purified by column chromatography (SiO_2, $CHCl_3$). A pale yellow oil. Yield 6.1 g (92%); Oil; IR (KBr) ν = 2936, 2859, 2218, 1748, 1531, 1485; ^{1}H NMR ($CDCl_3$) δ = 1.26 (t, *J* = 7.2 Hz, 3H), 1.32–1.40 (m, 6H), 1.60–1.64 (m, 2H), 1.66–1.73 (m, 2H), 2.29 (t, *J* = 7.6 Hz, 2H), 4.00 (s, 2H), 4.08 (t, *J* = 7.5 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.27, 24.75. 25.67, 28.48, 28.69. 28.80, 32.29, 34.23, 45.26, 56.72, 60.24, 111.78, 112.78, 171.57 (2C), 173.74; FABMS (NBA) *m/z* 336 (MH^+); Anal. Found: C, 57.66; H, 6.34; N, 12.23%. Calcd for $C_{16}H_{21}N_3O_3S$: C, 57.29; H, 6.31; N, 12.53%.

*4.4. Synthesis of **6a***

To an acetonitrile solution (7 mL) of **4** (2.0 g, 6.0 mmol) were added and ethyl isothiocyanatoacetate (**5**, 1.6 g, 11 mmol) and DBU (2.2 g, 14 mmol) at room temperature. The mixture was stirred for 30 min. Then, to the mixture was added ethyl bromoacetate (**3**, 2.7 g, 16 mmol) at room temperature, stirred for 1 h, and refluxed for 3 h. After the reaction was completed, the mixture was concentrated *in vacuo*. To the mixture was added an aqueous 10% hydrochloric acid (30 mL). The product was extracted with chloroform (30 mL × 3) and purified by column chromatography (SiO_2, AcOEt : C_6H_{14} = 1 : 1). A pale brown solid. Yield 900 mg (18%); mp 69–71°C; IR (KBr) ν = 2940, 2855, 2214, 1740, 1686, 1539, 1524; ^{1}H NMR ($CDCl_3$) δ = 1.26 (t, *J* = 7.2 Hz, 3H), 1.36–1.40 (m, 9H), 1.60–1.63 (m, 2H), 1.71 (br s, 2H), 2.29 (t, *J* = 7.4 Hz, 2H), 3.94 (s, 2H), 4.11 (t, *J* = 7.0 Hz, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 4.33 (q, *J* = 7.0 Hz, 2H), 4.73 (s, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.13, 14.27, 24.79, 25.75, 28.62, 28.73, 28.85, 31.24, 34.25, 45.08, 45.44, 51.92, 60.21, 63.29, 88.68, 112.56, 113.49, 155.37, 164.54, 165.90, 166.02, 172.27, 173.75; FABMS (NBA) *m/z* 521 (MH^+); Anal. Found: C, 52.95; H, 5.53; N, 10.42%. Calcd for $C_{23}H_{28}N_4O_6S_2$: C, 53.06; H, 5.42; N, 10.76%.

*4.5. Synthesis of **7a***

To an acetic acid (6 mL) and conc. hydrochloric acid (3 mL) mixed solution was added **6a** (800 mg, 1.5 mmol) and stirred at 100°C for 3 h. After the reaction was completed, the mixture was cooled, poured into water, and stirred at 0°C. The resulting precipitate was filtered and purified by column chromatography (SiO_2, $CHCl_3$: CH_3OH = 5 : 1). A pale yellow solid. Yield 230 mg (31%); mp 201–203°C; IR (KBr) ν = 2932, 2866, 2210, 1694, 1682, 1574, 1535; ^{1}H NMR (DMSO-d_6) δ = 1.24–1.28 (m, 6H), 1.46–1.51 (m, 2H), 1.58–1.65 (m, 2H), 2.19 (t, *J* = 7.2 Hz, 2H), 4.01 (t, *J* = 7.6 Hz, 2H), 4.22 (s, 2H), 4.69 (s, 2H); ^{13}C NMR (DMSO-d_6) δ = 24.23, 25.25, 27.73, 28.11, 28.22, 31.13, 33.47, 44.38, 45.51, 48.60, 87.04, 113.40, 114.42, 157.45, 165.37, 165.48, 167.87, 173.25, 174.36; FABMS (NBA) *m/z* 465 (MH^+); Anal. Found: C, 48.80; H, 5.48; N, 11.86%. Calcd for $C_{19}H_{20}N_4O_6S_2$: C, 49.13; H, 5.34; N, 12.06%.

*4.6. Synthesis of **GU115***

To an acetic acid solution (8 mL) of **7a** (450 mg, 0.96 mmol) and **8** (540 mg, 1.2 mmol) was added ammonium acetate (3 mg). The mixture was refluxed for 3 h. After cooling, the resulting precipitate was filtered, washed with water, and purified by column chromatography (SiO_2, $CHCl_3$: MeOH = 100 : 1). A violet solid. Yield 220 mg (25%); mp 159–161°C; IR (KBr) ν = 2951, 2866, 2214, 1701; ^{1}HNMR ($CDCl_3$) δ = 0.62–0.74 (m, 10H), 1.04–1.15 (m, 4H), 1.38–1.40 (m, 6H), 1.51–1.57 (m, 1H), 1.60–1.66 (m, 2H), 1.71–1.82 (m, 4H), 1.91–2.00 (m, 6H), 2.11–2.16 (m, 1H), 2.36 (t, *J* = 7.2 Hz, 2H), 3.88–3.92 (m, 1H), 4.19 (t, *J* = 7.0 Hz, 2H), 4.96 (s, 2H), 5.03–5.07 (m, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 7.25–7.32 (m, 3H), 7.33–7.37 (m, 4H), 7.66–7.71 (m, 2H), 7.78 (s, 1H); ^{13}CNMR (DMSO-d_6) δ = 14.63, 14.68, 23.27 (2C), 24.70, 25.26, 26.31, 26.71, 28.79, 29.15, 29.27, 33.28, 34.49, 36.16, 40.04, 40.17, 44.86, 45.65, 46.83, 50.18, 55.59, 70.19, 80.07, 88.43, 108.26, 111.89, 114.30, 115.32, 116.81, 120.33, 120.94, 121.56, 123.66, 123.91, 127.61, 127.82, 128.34, 134.42, 136.38, 137.29, 137.53, 140.41, 141.14, 150.75, 150.95, 151.18, 152.61, 166.02, 166.09, 166.97, 168.92, 175.34; FABMS (NBA) *m/z* 910 (MH^+); Anal. Found: C, 68.31; H, 6.10; N, 7.71%. Calcd for $C_{52}H_{55}N_5O_6S_2$: C, 68.62; H, 6.09; N, 7.69%.

*4.7. Synthesis of **11***

To an acetonitrile solution (4 mL) of *t*-butyl cyanoacetate (**9**, 710 mg, 5.0 mmol) were added octyl isothiocyanate (**10**, 940 mg, 5.5 mmol) and DBU (760 mg, 5.0 mmol) at room temperature. The mixture was stirred for 30 min. Then, to the mixture was added ethyl bromoacetate (**3**, 1.7 g, 10 mmol) at room temperature, stirred for 1 h, and refluxed for 3 h. After the reaction was completed, the mixture was concentrated *in vacuo*. To the mixture were added chloroform (30 mL) and an aqueous 10% hydrochloric acid (30 mL). The product was extracted with chloroform (30 mL × 3) and purified by column chromatography (SiO_2, $CHCl_3$: C_6H_{14} = 10 : 1). A pale yellow oil. Yield 1.6 g (92%); oil; IR (KBr) ν = 2928, 2210, 1740, 1694, 1516; ^{1}H NMR ($CDCl_3$) δ = 0.88 (t, *J* = 7.3 Hz, 3H), 1.27–1.38 (m, 10H), 1.55 (s, 9H), 1.66–1.74 (m, 2H), 3.68 (s, 2H), 4.20 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.05, 22.59, 25.87, 28.10 (3C), 28.63, 29.09, 29.15, 31.04, 31.73, 45.22, 78.83, 83.38, 115.05, 164.66, 169.42, 173.05; FABMS (NBA) *m/z* 353 (MH^+); Anal. Found: C, 61.66; H, 7.89; N, 7.90%. Calcd for $C_{18}H_{28}N_2O_3S$: C, 61.33; H, 8.01; N, 7.95%.

*4.8. Synthesis of **6b***

To an acetonitrile solution (10 mL) of **11** (4.0 g, 11 mmol) were added octyl isothiocyanate (**10**, 2.3 g, 14 mmol) and DBU (1.7 g, 11 mmol) at room temperature. The mixture was stirred for 30 min. Then, to the mixture was added ethyl bromoacetate (**3**, 2.9 g, 17 mmol). The mixture was stirred for 1 h and then refluxed for 3 h. After the reaction was completed, the mixture was concentrated *in vacuo*. To the mixture were added chloroform (30 mL) and an aqueous 10% hydrochloric acid (30 mL). The product was extracted with chloroform (50 mL × 3) and purified by column chromatography (SiO_2, $CHCl_3$). A pale yellow solid. Yield 1.6 g (25%); mp 117–119°C; IR (KBr) ν = 2928, 2855, 2207, 1732, 1674, 1508; ^{1}H NMR ($CDCl_3$) δ = 0.87 (t, *J* = 7.6 Hz, 6H), 1.27–1.32 (m, 12H), 1.34–1.47 (m, 8H), 1.55 (s, 9H), 1.68–1.78 (m, 4H), 3.81 (s, 2H), 4.02 (t, *J* = 7.9 Hz, 2H), 4.31 (t, *J* = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.08, 14.10, 22.63 (2C), 25.94, 26.33, 28.17 (3C), 28.89, 29.08, 29.16, 29.21, 29.23, 29.45, 31.57, 31.70, 31.77, 45.00, 45.39, 73.72, 82.83, 92.14, 116.05, 154.33, 162.60, 165.27, 167.04, 172.99; FABMS (NBA) *m/z* 564 (MH^+); Anal. Found: C, 61.57; H, 8.33; N, 7.32%. Calcd for $C_{29}H_{45}N_3O_4S_2$: C, 61.78; H, 8.04; N, 7.45%.

*4.9. Synthesis of **7b***

To a dichloromethane solution (6 mL) of **6b** (200 mg, 0.35 mmol) were added triethylsilane (210 mg, 1.8 mmol) and TFA (4 mL). The mixture was stirred at 0°C for 5 h. After the reaction was completed, to the mixture was added ice water (20 mL). The product was extracted with chloroform (20 mL × 3) and purified by column chromatography (SiO_2, $CHCl_3$: MeOH = 50 : 1). A pale brown solid. Yield 87 mg (49%); mp 169–171°C; IR (KBr) ν = 2928, 2855, 2210, 1736, 1686, 1670, 1533; ^{1}H NMR ($CDCl_3$) δ = 0.86–0.89 (m, 6H), 1.27–1.32 (m, 16H), 1.41–1.44 (m, 4H), 1.67–1.73 (m, 2H), 1.75–1.81 (m, 2H), 3.83 (s, 2H), 4.01 (t, *J* = 7.8 Hz, 2H), 4.36 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.07 (2C), 22.59 (2C), 25.88, 26.25, 28.95, 29.03, 29.07, 29.16, 29.40, 29.68, 31.53, 31.65, 31.73, 45.29, 45.50, 70.91, 91.35, 115.39, 156.35, 164.92, 166.71, 170.23, 172.88; FABMS (NBA) *m/z* 508 (MH^+); Anal. Found: C, 59.10; H, 7.52; N, 8.23%. Calcd for $C_{25}H_{37}N_3O_4S_2$: C, 59.14; H, 7.35; N, 8.28%.

*4.10. Synthesis of **GU116***

To a butanol solution (5 mL) of **7b** (200 mg, 0.39 mmol) were added **8** (220 mg, 0.47 mmol) and piperidine (33 mg, 0.39 mmol). The mixture was stirred at 100°C for 1 h. After the reaction was completed, the mixture was concentrated. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2 : MeOH = 50 : 1) and crystallized from acetone-hexane mixed solvent. A red solid. Yield 300 mg (80%); mp 182–184°C; IR (KBr) ν = 2932, 2866, 2210, 1694, 1682; ^{1}H NMR ($CDCl_3$) δ = 0.60–0.74 (m, 10H), 0.85–0.90 (m, 6H), 1.05–1.18 (m, 4H), 1.29–1.40 (m, 16H), 1.46–1.59 (m, 5H), 1.70–1.83 (m, 6H), 1.93–2.00 (m, 6H), 2.07–2.17 (m, 1H), 3.85–3.89 (m, 1H), 4.17 (t, *J* = 7.6 Hz, 2H), 4.43 (t, *J* = 7.6 Hz, 2H), 4.98–5.02 (m, 1H), 6.91 (d, *J* = 8.9 Hz, 1H), 7.22–7.26 (m, 2H), 7.29–7.35 (m, 5H), 7.65–7.68 (m, 2H), 7.70 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 13.85, 13.91, 14.12, 14.13, 22.60, 22.63, 23.02 (2C), 24.26, 26.00 (2C), 26.08, 26.35, 28.99, 29.13 (2C), 29.16, 29.28, 29.71, 31.72, 31.78, 33.10, 35.57, 40.05, 40.15, 44.78, 45.45, 45.57, 55.10, 70.00, 70.55, 90.01, 107.67, 112.49, 115.62, 115.77, 119.28, 120.15, 120.44, 122.84, 123.58, 127.67, 126.87, 127.57, 133.72, 135.89, 136.57, 137.13, 139.90, 140.60, 150.48, 150.78, 151.76, 152.28, 16.70, 166.13, 167.37, 170.91; FABMS (NBA) *m/z* 953 (MH^+); Anal. Found: C, 72.97; H, 7.43; N, 5.67%. Calcd for $C_{58}H_{72}N_4O_4S_2$: C, 73.07; H, 7.61; N, 5.88%.

*4.11. Synthesis of **6c***

To an acetonitrile solution (40 mL) of **11** (3.7 g, 10.5 mmol) were added *t*-butyl 8-isothiocyanatooctanoate (**12**, 2.0 g, 11.6 mmol) and DBU (1.9 g, 12.6 mmol) at room temperature. The mixture was stirred for 30 min. Then, to the mixture was added ethyl bromoacetate (**3**, 2.6 g, 15.8 mmol). The mixture was stirred for 1 h and then refluxed for 1 day. After the reaction was completed, the mixture was concentrated *in vacuo*. To the mixture were added chloroform (40 mL) and an aqueous 10% hydrochloric acid (40 mL). The product was extracted with chloroform (40 mL × 3) and purified by column chromatography (SiO_2, AcOEt : C_6H_{14} = 1 : 3). A pale brown solid. Yield 1.9 g (31%); mp 71–73°C; IR (KBr) ν = 3232, 2886, 2207, 1748; ^{1}H NMR ($CDCl_3$) δ = 0.87 (t, *J* = 6.7 Hz, 3H), 1.27–1.40 (m, 10H), 1.53 (s, 9H), 1.54 (s, 9H), 1.73 (quin, *J* = 7.7 Hz, 2H), 3.88 (s, 2H), 4.28 (t, *J* = 7.7 Hz, 2H), 4.74 (s, 2H); ^{13}C NMR ($CDCl_3$) δ = 14.10, 22.62, 25.94, 27.85 (3C), 28.15 (3C), 28.91, 29.15, 29.22, 31.29, 31.77, 45.09, 46.35, 73.68, 82.86, 84.29, 93.08, 115.84, 153.45, 162.30, 165.20, 165.24, 166.77, 172.62; FABMS (NBA) *m/z* 566 (MH^+); Anal. Found: C, 57.36; H, 6.65; N, 7.23%. Calcd for $C_{27}H_{39}N_3O_6S_2$: C, 57.32; H, 6.95; N, 7.43%.

*4.12. Synthesis of **7c***

To a dichloromethane solution (7.5 mL) of **6c** (690 mg, 1.2 mmol) was slowly added a 0.1 M dichloromethane solution (2.5 mL) of boron tribromide (2.5 mmol) with stirring at 0°C. The mixture was stirred at 0°C for 20 min. Then, to the mixture was slowly added water (10 mL). The resulting precipitate was filtered and purified by column chromatography (SiO_2, $CHCl_3$: MeOH = 10 : 1). A yellow solid. Yield 459 mg (84%); mp 154–156°C; IR (KBr) ν = 3151, 2285, 2214, 1751; ^{1}H NMR (DMSO-d_6) δ = 0.86 (t, *J* = 6.7 Hz, 3H), 1.25–1.28 (m, 10H), 1.55–1.65 (m, 2H), 4.14–4.18 (m, 4H), 4.72 (s, 2H); ^{13}C NMR (DMSO-d_6) δ = 13.96, 22.05, 25.34, 28.17, 28.49 (2C), 31.00, 31.44, 44.34, 45.99, 70.83, 91.12, 116.27, 155.69, 162.89, 166.05, 166.94, 168.03, 173.42; FABMS (NBA) *m/z* 454 (MH^+); Anal. Found: C, 50.45; H, 5.27; N, 9.22%. Calcd for C19H23N3O6S2: C, 50.32; H, 5.11; N, 9.27%.

*4.13. Synthesis of **GU117***

Compound **8** (200 mg, 0.44 mmol) was dissolved in methanol (80 mL) at 60°C. Then, the temperature was set at 40°C. To the solution were added **7c** (200 mg, 0.44 mmol) and a methanol solution. After the reaction was completed, the solution was acidified by adding aqueous 10% hydrochloric acid. The product was extracted with chloroform (30 mL × 3), purified by column chromatography (SiO_2, $CHCl_3$: MeOH = 50 : 1), and recrystallized from chloroform-hexane mixed solvent. A violet solid. Yield 37 mg (10%); mp 142–144°C; IR (KBr) ν = 2955, 2932, 2856, 2207, 1767, 1690; ^{1}H NMR ($CDCl_3$) δ = 0.61–0.76 (m, 10H), 0.84 (t, *J* = 6.7 Hz, 3H), 1.04–1.17 (m, 4H), 1.23–1.44 (m, 10H), 1.52–1.59 (m, 1H), 1.72–1.84 (m, 4H), 1.93–2.04 (m, 6H), 2.09–2.17 (m, 1H), 3.89–3.93 (m, 1H), 4.30–4.32 (m, 2H), 5.03–5.07 (m, 3H), 6.94 (d, *J* = 9.0 Hz, 1H), 7.27–7.40 (m, 7H), 7.65–7.73 (m, 2H), 7.80 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 13.84, 13.92, 14.10, 22.61, 23.01, 23.04, 24.26, 25.96, 26.01, 26.10, 29.11, 29.20, 29.71, 31.75, 33.06, 35.63, 40.02, 40.19, 44.78, 45.56, 45.72, 55.15, 70.19, 70.83, 91.20, 107.71, 110.83, 114.94, 116.14, 119.37, 120.48, 120.54, 122.87, 123.32, 126.75, 126.91, 127.88, 134.13, 136.72, 137.25, 137.49, 139.72, 140.59, 150.54, 150.94, 151.33, 152.37, 164.64, 165.76, 166.65, 171.76, 173.26; FABMS (NBA) *m/z* 899 (MH^+); Anal. Found: C, 69.82; H, 6.52; N, 6.33%. Calcd for $C_{52}H_{58}N_4O_6S_2$: C, 69.46; H, 6.50; N, 6.23%.

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

F-doped tin oxide coated glass substrates (4 mm thickness, 13 Ω $\square^{-1}$, Nippon Sheet Glass) were used to prepare dyed-titanium oxide electrodes. A commercially available titanium oxide paste (PST-18NR, JGC Catalysts and Chemicals Ltd.) was coated onto the FTO glass by doctor blade technique and subsequently sintered at 500°C for 15 min as described in the paper to prepare a mesoporous titanium oxide layer (8 μm thickness).[41] At the top of titanium oxide films, a light-scattering titanium oxide layer (5 μm) was further integrated using a titanium oxide paste (PST-400C, JGC Catalysts and Chemicals Ltd.). After immersing titanium oxide plates into the 40 mM aqueous titanium tetrachloride solution at 70°C for 30 min, the substrates were sintered at 500°C for 30 min. Thus obtained titanium oxide electrodes were immersed in the 0.2 mM dye solution (solvent: acetonitrile/*t*-butyl alcohol = 1 : 1 (v/v)) and kept in a dgark at 25°C for 8 h. Pt-sputtered FTO glass plates were used as counter electrodes. The dyed-titanium oxide electrode and counter electrode were then assembled into a sandwich-type cell (5 mm × 6 mm area), for which the electrolyte solution composed of the 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) was filled into the cell with a vacuum backfilling method.[42]

4.15. Photoelectrochemical measurements and light-soaking tests

Current-voltage curves were obtained under AM 1.5 simulated sunlight (100 mW cm^{-2}) by using a Bunko-Keiki CEP-2000 system. Action spectra were measured under monochromatic light with a constant photon number (0.5×10^{16} photon cm^{-2} s^{-1}). Those measurements were carried out by regulating the active area (4 mm × 5 mm) of devices usin a mask. A light soaking test of DSSCs was carried out using a sealed box with a size of 31 cm × 31 cm × 31 cm (TOKYO GLASS KIKAI), in which temperature and humidity were maintained at around 25°C and 28%. The anode side of DSSCs was irradiated under 40 W fluorescent lamps (NEC Lighting) producing 400 nm to 716 nm light. The distance between the fluorescent lamp and DSSCs was 130 cm.

Conclusions

We have made a molecular design, synthesis, and evaluation of new indoline dyes **GU115**, **GU116**, and **GU117** in which carboxylic acid anchor group(s) are attached at the acceptor moiety. Known **DN351** was used as a standard compound. These dyes exhibited the conversion efficiency in the range of 3.39 to 5.46% at the initial stage. After 161-days fluorescence lamp irradiation, the conversion efficiency was in the order of dyes: **GU117** > **GU116**, **GU115** >> **DN351**. Thus, **GU117** having both α-cyanoacrylic acid and rhodanine acetic acids anchor groups exhibited the best stability among the indoline dyes due to the most stable binding with titanium oxide.

Acknowledgements

This work was financially supported in part by Toukai Foundation for Technology (H26-03-04-08).

Notes and references

1 T. Horiuchi, H. Miura, K. Sumioka, S. Uchida, *J. Am. Chem. Soc.*, 2004, **126**, 12218–12219.

2 T. Horiuchi, H. Miura, S. Uchida, *Chem. Commun*., 2003, 3036–3037.

3 S. Ito, H. Miura, S. Uchida, M. Takata, K. Sumioka, P. Liska, P. Comte, P. Péchy, M. Grätzel, *Chem. Commun*., 2008, 5194–5196.

4 S. Higashijima, H. Miura, T. Fujita, Y. Kubota, K. Funabiki, T. Yoshida, M. Matsui, *Tetrahedron*, 2011, **67**, 6289–6293.

5 S. Higashijima, Y. Inoue, H. Miura, Y. Kubota, K. Funabiki, T. Yoshida, M. Matsui, *RSC Adv*., 2012, **2**, 2721–2724.

6 Y. Tian, C. Hu, X. Wu, Q. Wu, C. Cao, *Solar Energy Mater Solar Cells*, 2012, **98**, 83–87.

7 N. Kato, K. Higuchi, H. Tanaka, J. Nakajima, T. Sano, T. Toyoda, *Solar Energy Mater Solar Cells*, 2011, **95**, 301–305.

8 E. Leonardi, S. Penna, T.M. Brown, A. Di Carlo, A. Reale, *J. Non-Cryst Solids*, 2010, **356**, 2049–2052.

9 J. M. Kroon, N. J. Bakker, H. I. P. Smit, P. Liska, K. R. Thampi, P. Wang, S. M. Zakeeruddin, M. Grätzel, A. Hinsch, S. Hore, U. Würfel, R. Sastrawan, J. R. Durrant, E. Palomares, H. Pettersson, T. Gruszecki, J. Walter, K. Skupien, G. E. Tulloch, *Prog. Photovolt. Res. Appl*., 2007, **15**, 1–18.

10 L. Wang, X. Fang, Z. Zhang, *Renew. Sustain. Energy Rev*., 2010, **14**, 3178–3184.

11 T. Toyoda, T. Sano, J. Nakajima, S. Doi, S. Fukumoto, A. Ito, T. Tohyama, M. Yoshida, T. Kanagawa, T. Motohiro, T. Shiga, K. Higuchi, H. Tanaka, Y. Takeda, T. Fukano, N. Katoh, A. Takeuchi, K. Takeuchi, M. Shiozawa, *J. Photochem. Photobiol, A, Chemistry*, 2004, **164**, 203–207.

12 H. Pettersson, T. Gruszecki, *Solar Energy Mater Solar Cells*, 2001, **70**, 203–212.

13 H. L. Lu, Y. H. Lee, S. T. Huang, C. Su, T. C. K. Yang, *Solar Energy Mater Solar Cells*, 2011, **95**, 158–162.

14 H. Greijer-Agrell, J. Lindgren, A. Hagfeldt, *Sol. Energy*, 2003, **75**, 169–180.

15 F. Nour-Mohhamadi, S. D. Nguyen, G. Boschloo, A. Hagfeldt, T. Lund, *J. Phys. Chem. B*, 2005, **109**, 22413–22419.

16 P. M. Sommeling, M. Späth, H. J. P. Smit, N. J. Bakker, J. M. Kroon, *J. Photochem. Photobiol. A*, 2004, **164**, 137–144.

17 W. Guo, L.-Q Wu, Z. Chen, G. Boschloo, A. Hagfeldt, T.-L. Ma, *J. Photochem. Photobiol. A, Chemistry*, 2011, **219**, 180–187.

18 S. Venkatesan, S-C. Su, S-C. Kao, H. Teng, Y.-L. Lee, *J. Power Sources*, 2015, **274,** 506–511.

19 J. Gao, A. M. Bhagavathi, L. Kloo, *Chem. Commun*., 2015, **50**, 6249–6251.

20 M. Giannouli, G. Syrrokostas, P. Yianoulis, *Prog. Ptotovolt. Res. Appl*., 2010, **18**, 128–136.

21 N. Kato, Y. Takeda, K. Hihuchi, A. Takeuchi, E. Sudo, H. Tanaka, T. Motohiro, T. Sano, T. Toyoda, *Solar Energy Mater Solar Cells*, 2009, **93**, 893–897.

22 Y. Bai, Y. Cao, J. Zhang, M. Wang, R. Li, P. Wang, S. M. Zakeeruddin, M. Grätzel, *Nat. Materials*, 2008, **7**, 626–630.

23 D. Shi, N. Pootrakulchote, R. Li, J. Guo, Y. Wang, S. M. Zakeeruddin, M. Grätzel, P. Wang, *J. Phys. Chem. C*, 2008, **112**, 17046–17050.

24 D. Kuang, C. Klein, S. Ito, J.-E. Moser, R. Humphry-Baker, N. Evans, F. Duriaux, C. Grätzel, S. M. Zakeeruddin, M. Grätzel, *Adv. Mater*., 2007, **19**, 1133–1137.

25 J. Xia, F. Li, C. Huang, J. Zhai, L. Jiang, *Solar Energy Mater Solar Cells*, 2006, **90**, 944–952.

26 S. Nakade, T. Kanzaki, S. Kambe, Y. Wada, S. Yanagida, *Langmuir*, 2005, **21**, 11414–11417.

27 P. Wang, S. M. Zakeeruddin, J. E. Moser, M. K. Nazeeruddin, T. Sekiguchi, M. Grätzel, *Nat. Materials*, 2003, **2**, 402–407.

28 H. Tributsch, *Coord.Chem. Rev*., 2004, **248**, 1511–1530.

29 N. Heo, Y. Jun, J. H. Park, *Scientific Reports*, 2013, **3**, 1712–1720.

30 J. Lim, Y.-S. Kwon, T. Park, *Chem. Commun*., 2011, **47**, 4147–4149.

31 H. Tanaka, A. Takeuchi, K. Higuchi, T. Motohiro, M. Tanaka, N. Hirota, J. Nakajima, T. Toyoda, *Solar Energy Mater Solar Cells*, 2009, **93**, 1143–1148.

32 M. Matsui, A. Ito, M. Kotani, Y. Kubota, K. Funabiki, J. Jin, T. Yoshida, H. Minoura, H. Miura, *Dyes Pigm*., 2009, **80**, 233–238.

33 M. Matsui, R. Aoki, Y. Kubota, K. Funabiki, J. Jin, T. Yoshida, S. Higashijima, H. Miura, RSC Adv, 2015, 5, 57721–57724.

34 M. Matsui, Y. Asamura, Y. Kubota, K. Funabiki, J. Jin, T. Yoshida, H. Miura, *Tetrahedron*, 2010, **66**, 7405–7410.

35 T. Dentani, Y. Kubota, K. Funabiki, J. Jin, T. Yoshida, H. Minoura, H. Miura, M. Matsui, *New J. Chem*., 2009, **33**, 93–101.

36 Z.-S. Wang, K. Hara, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, H. Arakawa, H. Sugihara, *J. Phys. Chem. B*, 2005, **109**, 3907–3914.

37 C. Klein, M. K. Nazeeruddin, D. D. Censo, P. Liska, M. Grätzel, *Inorg. Chem*., 2004, **43**, 4216–4236.

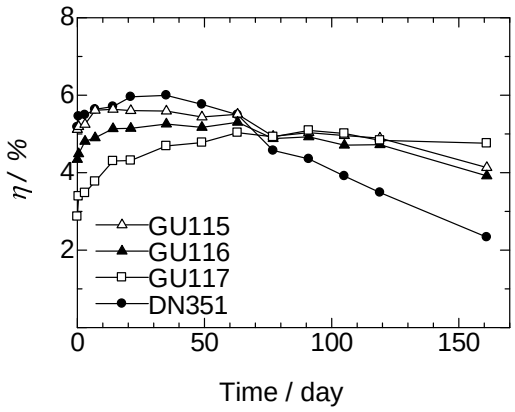
38 K. Hara, T. Sato, R. Katoh, A. Furube, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Sugihara, H. Arakawa, *J. Phys. Chem. B*, 2003, **107**, 597–606.

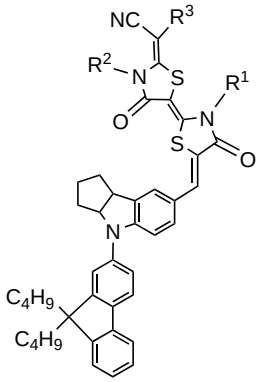
39 N. W. Duffy, K. D. Dobson, K. C. Gordon, B. H. Robinson, A. J. M. Quillan, *Chem. Phys. Lett*., 1997, **266**, 451–455.

40 S. Fuse, S. Sugiyama, M. Maitani, M. Masato, Y. Wada, Y. Ogomi, S. Hayase, R. Katoh, T. Kaiho, T. Takahashi, *Chem. Eur. J*., 2014, **20**, 10685–10694.

41 S. Ito, S.-M. Zakeeruddin, R. Humphry-Baker, P. Liska, R. Charvet, P. Comte, M.-K. Nazeeruddin, P. Péchy, M. Takata, H. Miura, S. Uchida, M. Grätzel, *Adv. Maters*, 2006, **18**, 1202–1205.

42 K. Manseki, Y. Kondo, T. Ban, T. Sugiura, T. Yoshida, *Dalton Trans*., 2013, **42**, 3295–3299.





	R^1	R^2	R^3
GU115	CH_2COOH	$(CH_2)_7COOH$	CN
GU116	C_8H_{17}	C_8H_{17}	COOH
GU117	CH_2COOH	C_8H_{17}	COOH
DN351	CH_2COOH	C_8H_{17}	CN

An indoline dye having both α-cyanoacrylic and rhodanine acetic acid anchor groups at the acceptor moiety exhibited improved stability upon fluorescence lamp irradiation.