



**Importance of fluorescence lifetime for efficient indoline dyes in dye-sensitized solar cell**

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## Importance of fluorescence lifetime for efficient indoline dyes in dye-sensitized solar cell

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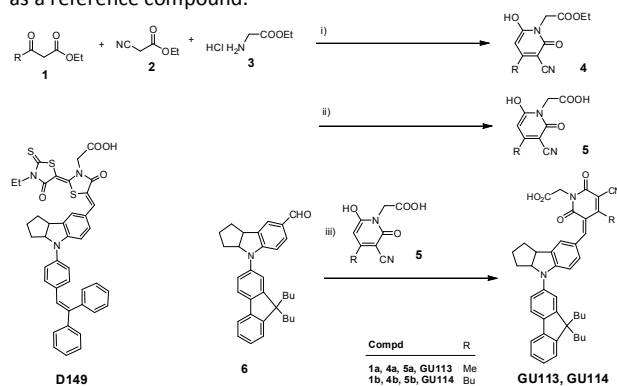
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**To make a molecular design of efficient indoline dyes, the fluorescence lifetime should be longer than ca. 0.8 ns in chloroform in addition to their suitable HOMO and LUMO levels and bathochromic UV-vis absorption band.**

Indoline dyes are one of the most efficient organic sensitizers in dye-sensitized solar cells (DSSCs). **D149** was reported to exhibit highly conversion efficiency of 6.1% on titanium oxide.<sup>[1]</sup> Since then, much effort has been made to obtain more efficient indoline dyes by changing the anchor moieties such as cyanoacrylic acid,<sup>[2,3]</sup> single,<sup>[4,5]</sup> double,<sup>[6-9]</sup> and triple rhodanines.<sup>[10]</sup> The double rhodanine dyes **D205**,<sup>[6]</sup> **DN319**,<sup>[7]</sup> and **DN315**<sup>[8]</sup> have been reported to exhibit higher efficiency than **D149**. As the acceptor anchor moieties affect the energy levels of indoline dyes, it is important to check the HOMO and LUMO levels. The relationship between the HOMO level and maximum incident photon-to-current efficiency (IPCE) of indoline dyes has been reported.<sup>[11]</sup> As the HOMO level of double rhodanine indoline dyes is close to I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox level, the stabilization of the HOMO level, the positive shift of the oxidation potential ( $E_{ox}$ ), is required. To prepare new indoline dyes, we made a molecular design of pyridone acetic acid derivatives. These novel indoline dyes, **GU113** and **GU114**, were predicted to show stabilized HOMO level and similar HOMO-LUMO gap to **D149** by the DFT calculations. Unfortunately, these dyes did not act as sensitizers due to less electron injection ability from the excited state to the conduction band of zinc oxide. To obtain efficient indoline dyes, an additional parameter of electron injection, beside the DFT calculations, is proposed in this report.

Novel indoline dyes **GU113** and **GU114** were synthesized as shown in Scheme 1. Ethyl alkanoylacetates **1**, ethyl

cyanoacetate (**2**), and glycine ethyl ester hydrochloride (**3**) were allowed to react in the presence of piperidine to give ethyl pyridone acetates **4**, whose ester group was hydrolyzed to afford pyridone acetic acids **5**. These compounds were allowed to react with an aldehyde **6** to provide **GU113** and **GU114**. **D149** was also prepared as a reference compound.



**Scheme 1.** Reagents and conditions: i) **3** (20.0 mmol), TEA (29.7 mmol), 5 min, EtOH (2 mL), then **1** (20.0 mmol), **2** (20.0 mmol), piperidine (6.1 mmol), reflux, 9 h, ii) **4** (1.8 mmol), AcOH-HCl (2:1, 3 mL), reflux, 3 h, iii) **5** (0.70 mmol), **6** (0.86 mmol), EtOH (10 mL), rt, 1 d.

The structure of **GU113** was optimized by the B3LYP/3-21G level. Figure 1 indicates that the double bond of **GU113** at the 7-position is Z form due to steric repulsion between the hydrogen atom at the 8-position on the indoline ring and the methyl group on the pyridone ring. The indoline chromophore is almost planar, the dihedral angle between the indoline and pyridone moiety  $\theta^1$  being 0.5°. Meanwhile, the fluorenyl moiety can act as steric hindrance to prevent intermolecular  $\pi/\pi$  interactions for the planar indoline chromophores, the dihedral angle  $\theta^2$  being 45.6°. The HOMO and LUMO levels of **GU113** were calculated to be -5.45 and -2.74 eV, respectively. Those of **D149** have been reported to be -5.07 and -2.37 eV, respectively.<sup>[9]</sup> Thus, the HOMO and LUMO levels of **GU113** are more stable than those of **D149**. The energy gap between HOMO and LUMO level of **GU113** (2.71 eV) is similar to Table 1 Properties of indoline dyes

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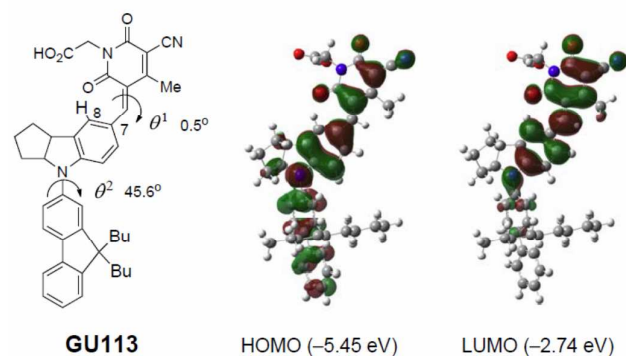
+ Electronic Supplementary Information (ESI) available: [synthesis of **GU113** and **GU114**]. See DOI: 10.1039/x0xx00000x

Dyes	$\lambda_{\max}(\varepsilon)^a$ nm	$F_{\max}^a$ nm	$\Phi_f^a$	$\tau_f^a$ ns	$k_f^b$ $10^9 \text{ s}^{-1}$	$k_{nr}^c$ $10^9 \text{ s}^{-1}$	$E_{ox}^d$ V	$E_{ox} - E_{0-0}^e$ V	HOMO <sup>f</sup> eV	LUMO <sup>f</sup> eV	$f_g^g$
<b>GU113</b>	577 (70,500)	679	_h	_h	_h	_h	+0.47	-1.52	-5.45	-2.74	1.29
<b>GU114</b>	577 (76,400)	679	_h	_h	_h	_h	+0.48	-1.50	_i	_i	_i
<b>D149</b>	394 (39,400), 550 (77,700)	642	0.10	0.90	0.11	1.00	+0.37	-1.72	-5.07	-2.37	1.25
<b>D205</b>	394 (34,000), 551 (68,000)	642	0.10	0.95	0.11	0.95	+0.35	-1.73	-5.06	-2.36	1.26
<b>DN319</b>	398 (36,700), 564 (69,500)	656	0.18	1.17	0.15	0.68	+0.37	-1.66	-5.18	-2.53	1.23
<b>DN351</b>	395 (29,300), 565 (71,000)	654	0.20	1.51	0.13	0.53	+0.36	-1.65	-5.22	-2.52	1.19

<sup>a</sup>Measured on  $1.0 \times 10^{-5} \text{ mol dm}^{-3}$  of substrate in chloroform at 25°C. <sup>b</sup>Calculated by  $\Phi_f/\tau_f$ . <sup>c</sup>Calculated by  $(1-\Phi_f)/\tau_f$ . <sup>d</sup>vs Fc/Fc<sup>+</sup> in DMF.

<sup>e</sup>Calculated on the basis of  $E_{ox}$  and  $\lambda_{int}$ . <sup>f</sup>Calculated by the B3LYP/6-31G(d,p)/B3LYP/3-21G level. <sup>g</sup>Oscillator strength. <sup>h</sup>Not measured due to low  $\Phi_f$ . <sup>i</sup>Not calculated.

that of **D149** (2.70 eV). The isodensity surface plots of **GU113** indicate the intramolecular charge-transfer chromophoric system from the indoline to pyridone moiety. These results suggested that **GU113** could act as a sensitizer for zinc oxide.

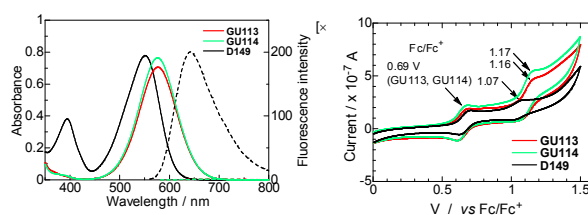


**Fig. 1.** DFT calculations of **GU113** (B3LYP/6-31G(d,p)//B3LYP/3-21G).

The UV-vis absorption and fluorescence spectra and the cyclic voltammogram of **GU113**, **GU114**, and **D149** are indicated in Figure 2. The results are also listed in Table 1. The absorption maxima ( $\lambda_{\max}$ ) of **GU113** and **GU114** were observed at 577 nm, being more bathochromic than **D149** (550 nm). The molar absorption coefficients ( $\varepsilon$ ) of **GU113**, **GU114**, and **D149** were observed to be 70,500, 76,400, and 77,700  $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ , respectively. Thus, no remarkable differences in the  $\varepsilon$  values were observed among them. However, the fluorescence intensity of **GU113** and **GU114** was too small. Therefore, the fluorescence quantum yield ( $\Phi_f$ ) and fluorescence lifetime ( $\tau_f$ ) could not be measured.

The cyclic voltammogram was measured vs. Ag quasi reference electrode (QRE) in DMF in the presence of ferrocene. The oxidation of **GU113** and **GU114** were observed at +1.16 (Fc/Fc<sup>+</sup>: +0.69 V) and +1.17 V (Fc/Fc<sup>+</sup>: +0.69 V), respectively. Therefore, the  $E_{ox}$  of **GU113** and **GU114** were calculated to be +0.47 and +0.48 V vs Fc/Fc<sup>+</sup>, respectively. The oxidation of **D149** was observed at +1.07 V (Fc/Fc<sup>+</sup>: +0.71 V), being the  $E_{ox}$  value +0.36 V vs Fc/Fc<sup>+</sup>. Thus, the  $E_{ox}$  levels of **GU113** and **GU114** were more positive

than that of **D149**, being in consistent with the DFT calculations that the HOMO level of **GU113** (-5.45 eV) is more stable than that of **D149** (-5.07 eV). As no reduction peak was observed for the indoline dyes, the  $E_{ox}-E_{0-0}$  value was calculated as described in our previous paper.<sup>[8]</sup> The UV-vis absorption spectra for the calculations are shown in Figure S1. The  $E_{ox}-E_{0-0}$  levels of **GU113**, **GU114**, and **D149** were calculated to be -1.52, -1.50, and -1.72 V vs. Fc/Fc<sup>+</sup>, respectively. The  $E_{ox}-E_{0-0}$  level of **GU113** and **GU114** is slightly more positive than that of **D149**. The conduction band of zinc oxide and  $\Gamma/13^-$  redox levels were assumed to be -0.95 and -0.05 V vs Fc/Fc<sup>+</sup>, respectively. Therefore, from the viewpoint of thermodynamics, **GU113** and **GU114** could act as sensitizers.

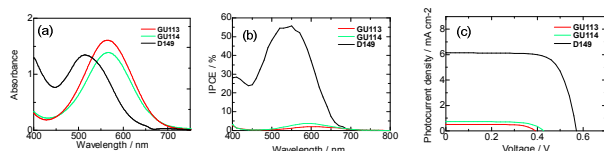


**Fig. 2.** UV-vis absorption and fluorescence spectra and cyclic voltammogram of **GU113**, **GU114**, and **D149**. (a) UV-vis absorption and fluorescence spectra measured at  $1.0 \times 10^{-5} \text{ mol dm}^{-3}$ . Solid and dotted lines represent UV-vis absorption and fluorescence spectra, respectively. (b) cyclic voltammogram in the presence of ferrocene. Measured in DMF vs AgQRE at scan rate  $100 \text{ mV s}^{-1}$ .

The electrodes were formed by the screen printing of zinc oxide (diameter: 6 mm,  $0.28 \text{ cm}^2$ ) films on F-doped tin-oxide-coated (FTO) glass plates (4 mm thick) with zinc oxide pastes prepared from nanoparticle zinc oxide. The thickness of zinc oxide layer was 12  $\mu\text{m}$ . 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 (**GU113**, **GU114**: 90 min, **D149**: 2 min). Platinum (6  $\mu\text{m}$  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, which is 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. An action spectrum was obtained under monochromatic light with a constant photon number ( $0.5 \times 10^{16}$  photon  $\text{cm}^{-2} \text{s}^{-1}$ ). I-V characteristics were measured under illumination with AM 1.5 simulated sun light ( $100 \text{ mW cm}^{-2}$ ) through a shading mast (5.0 mm x 4.0 mm) by using a Bunko-Keiki CEP-2000 system.

The UV-vis absorption spectra on zinc oxide, IPCE spectra, and I-V curve of **GU113**, **GU114**, and **D149** are shown in Figure 3 and Table 2. Figure 3a depicts the UV-vis absorption spectra of **GU113**, **GU114**, and **D149** on zinc oxide. They showed similar absorbance at  $\lambda_{\text{max}}$ , suggesting that similar amounts of **GU113**, **GU114**, and **D149** were adsorbed on zinc oxide. Actually, similar number of dyes were adsorbed on zinc oxide being in the range of 0.207 to 0.259 molecule per  $\text{nm}^2$ . Figure 3b indicates that the maximum IPCE values of **GU113** and **GU114** are 2.0 and 3.7%, respectively, whereas that of **D149** is 56.0%. Figure 3c depicts that the short-circuit photocurrent density ( $J_{\text{sc}}$ ) of **GU113** and **GU114** is very low. Consequently, the conversion efficiency ( $\eta$ ) of **GU113** and **GU114** was significantly low compared with that of **D149**.



**Fig. 3.** Photoelectrochemical properties of **GU113**, **GU114**, and **D149**. (a) UV-vis absorption band on zinc oxide, (b) IPCE spectra, and (c) I-V curve.

**Table 2** Photoelectrochemical properties of **GU113**, **GU114**, and **D149**

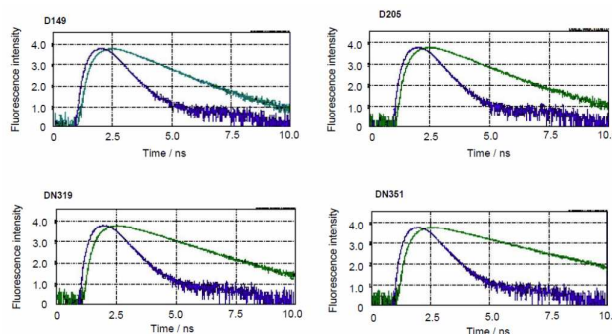
Dyes	$\lambda_{\text{max}}^a$ nm	Number of adsorbed dye number $\text{nm}^{-2}$	max IPCE <sup>b</sup> %	max APCE <sup>b</sup> %	$J_{\text{sc}}^b$ $\text{mA cm}^{-2}$	$V_{\text{oc}}^b$ V	$ff^b$	$\eta^b$ %
<b>GU113</b>	568	0.215	2.0	3.9	0.50	0.39	0.73	0.14
<b>GU114</b>	568	0.259	3.7	4.0	0.73	0.43	0.68	0.21
<b>D149</b>	545	0.207	56.0	61.9	6.14	0.57	0.73	2.57

<sup>a</sup>On zinc oxide film. <sup>b</sup>under AM 1.5 irradiation ( $100 \text{ mW cm}^{-2}$ ).

As **GU113** and **GU114** have suitable energy levels and sufficient light absorbing ability, their low IPCE values could be attributed to less electron injection from the excited state of dye molecule to the conduction band of zinc oxide. The rate of electron injection from excited sensitizers to the conduction band of titanium oxide has been reported to be 0.1 ns-order.<sup>[12]</sup> In the case of **D149**, the rate has been reported to be 0.33 ns<sup>[13]</sup> and 0.14 ns<sup>[14]</sup> on titanium oxide. Therefore, the  $\tau_f$  of adsorbed sensitizers should be sufficiently long to inject electrons. It is clear that the  $\Phi_f$  of **GU113** and **GU114** was very low indicating that the lifetime in the excited state is too short, whereas that of **D149** was observed to be 0.1. We consider that though it is best to measure the excited lifetime of the adsorbed sensitizers on semiconductors, more convenient parameter for the electron injection should be proposed. The  $\tau_f$  of **D149** has been reported in the range of 0.178 to 0.800 ns<sup>[15]</sup> and 0.190 to 0.720 ns<sup>[16]</sup> depending on the solvent. In chloroform, the  $\tau_f$  of **D149** has been reported to be 0.800 ns<sup>[15]</sup> and 0.720 ns<sup>[16]</sup>. In our work, the  $\tau_f$  of **D149** was observed to be 0.90 ns in chloroform as shown in

Figure 4 and Table 3. Thus, no remarkable differences of  $\tau_f$  were observed in chloroform. Therefore, chloroform was selected as a solvent to measure the fluorescence lifetime.

**D205** ( $\eta = 4.92\%$ ), **DN319** ( $\eta = 5.15\%$ ), and **DN351** ( $\eta = 5.34\%$ ) have been reported to exhibit excellent performance on zinc oxide.<sup>[8]</sup> These dyes are fluorescent in chloroform showing the  $\Phi_f$  value larger than 0.10 as shown in Table 1. The  $\tau_f$  of **D205**, **DN319**, and **DN351** were measured to be 0.95, 1.17, and 1.51 ns in chloroform, respectively, as shown in Figure 4 and Table 3. It is concluded that, to prepare more efficient indoline dyes than **D149**, the suitable HOMO and LUMO levels, bathochromic absorption band, intramolecular push-pull chromophoric system, and prevention of H-aggregate formation which are predicted by the calculations, are required. In addition, to inject electrons from the excited state to the conduction band of semiconductor, the  $\tau_f$  value of indoline dyes should be longer than ca. 0.8 ns in chloroform.



**Fig. 4.** Fluorescence decay curve of **D149**, **D205**, **DN319**, and **DN351** in chloroform at  $1.0 \times 10^{-5} \text{ mol dm}^{-3}$ .

**Table 3** Fluorescence lifetime of indoline dyes<sup>a</sup>

Dyes <sup>a</sup>	$\lambda_{\text{ex}}^b$ nm	$F_{\text{max}}^c$ nm	$\text{CH}_2^2$	$\tau_f^d$ ns
<b>D149</b>	470	640	1.06	0.90
<b>D205</b>	470	641	1.08	0.95
<b>DN319</b>	470	662	1.05	1.17
<b>DN351</b>	470	654	1.14	1.51

<sup>a</sup>Measured on  $1.0 \times 10^{-5} \text{ mol dm}^{-3}$  of substrate in chloroform. <sup>b</sup>Excitation wavelength. <sup>c</sup>Fluorescence maximum. <sup>d</sup>Fluorescence lifetime.

## Conclusions

DFT calculations are efficient methods to make a molecular design of sensitizers for dye-sensitized solar cell. Because the calculations can predict the HOMO and LUMO levels, UV-vis absorption maximum, molar absorption coefficient, and chromophoric system. However, to obtain highly efficient sensitizers, it is also important to consider their lifetime in the singlet state which is not predicted by the calculations. Efficient indoline dyes are required to have fluorescence lifetime longer than ca. 0.8 ns in chloroform.

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