



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

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ABSTRACT

Substituted 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.

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1. Introduction

Highly efficient organic sensitizers for dye-sensitized 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

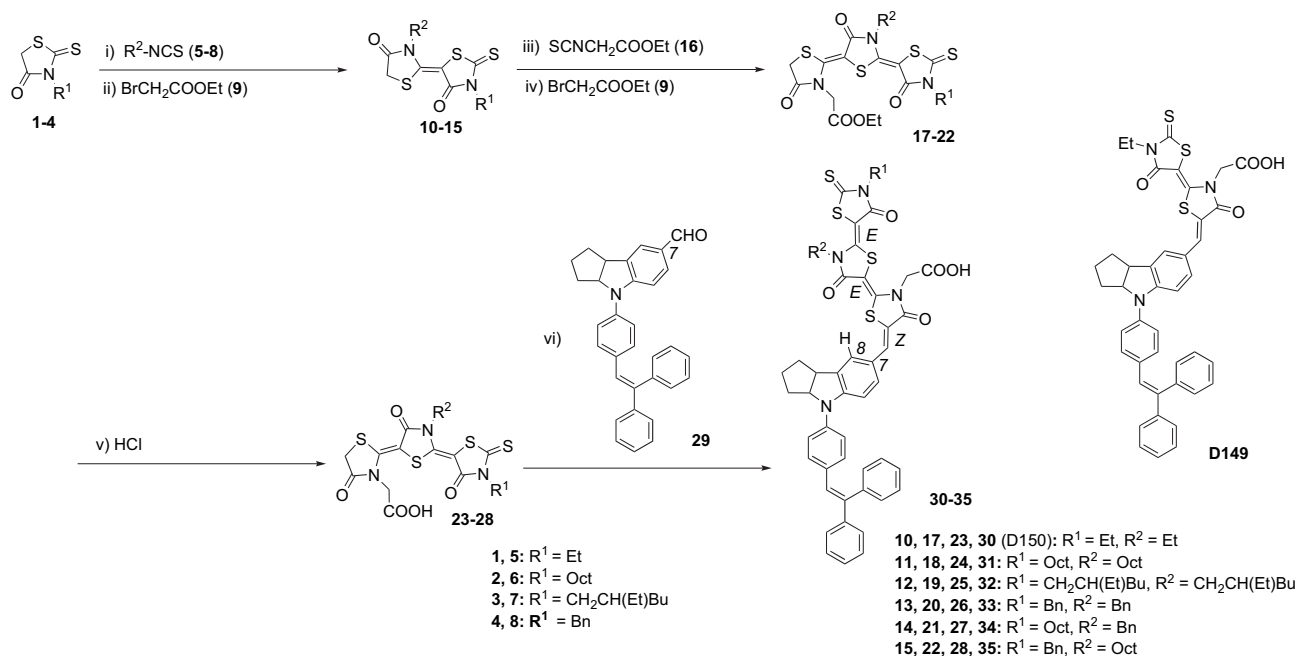
show high conversion efficiency. In a series of our study on survey of sensitizers, we report herein the use of substituted triple rhodanine indoline dyes in a zinc oxide dye-sensitized solar cell.

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), AcNH₄ (4.9 equiv), reflux, 4 h.

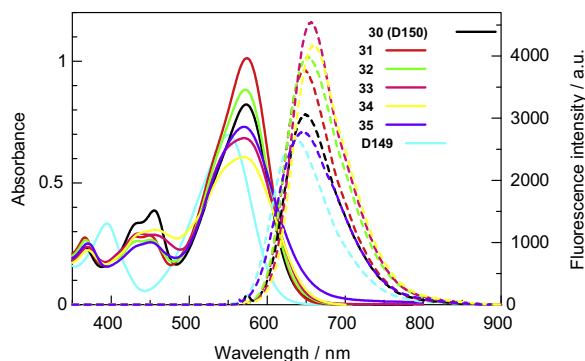


Figure 1. UV–vis absorption and fluorescence spectra of **30–35** and D149. Measured on 1×10^{-5} mol dm⁻³ of substrate in chloroform at 25 °C. Solid and dotted lines represent UV–vis absorption and fluorescence spectra, respectively.

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

Table 1
Properties of indoline dyes

Compd	λ_{max} (ε) ^a /nm	F_{max} /nm ^a	RFI ^b	E_{ox}/V^c	$E_{\text{ox}} - E_{0-0}/\text{V}^d$	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

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

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