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Application of semisquaric acids as sensitizers for zinc oxide solar cell

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Abstract

A series of semisquaric acids were examined as sensitizers for the zinc oxide solar cell prepared by a one-step cathode deposition template method. Their cell performance was rather low due to high oxidation potential (E_{ox}) of semisquaric acids. However, the performance was improved by introducing long alkyl group on the nitrogen atom at the heteroaromatic moiety. A *N*-octadecylindolium derivative showed the best performance: the incident photon-to-current efficiency (IPCE) 38.0% at absorption maximum (λ_{max}) 423 nm, short circuit photocurrent density (I_{sc}) 1.116 mA cm^{-2}, open circuit photovoltage (V_{oc}) 0.421 V, fill factor (ff) 0.57, and solar-light-to-electricity conversion efficiency (η) 0.27%, respectively.

Keywords: Dye-sensitized solar cell; Semisquaric acids; Zinc oxide; Sensitizer; One-step cathode deposition template method

1. Introduction

Survey of sensitizers for dye-sensitized solar cell is of significance to prepare solar battery [1]. Coumarin [2], mereocyanine [3], polyene [4], indoline [5], styryl [6,7], and perylene dyes [8,9] have been reported to act as good sensitizers. Semisquaric acids have been also reported to act as sensitizers for titanium oxide solar cell [10]. Thus, titanium oxide has been usually used as the semiconductor for dye-sensitized solar cells. Recently, a one-step cathode deposition template method of zinc oxide thin film has been reported [11]. A good point of this method is to prepare porous zinc oxide film at low temperature (70 °C). We report herein the application of semisquaric acids as sensitizers for zinc oxide solar cell prepared by this method.

2. Experimental

2.1. Instruments

Melting points were measured with a Yanagimoto MP-52 micro-melting-point apparatus. NMR spectra were obtained by Varian Inova 400 and 500 spectrometers. EIMS spectra were recorded on a Shimadzu QP-1000 spectrometer. FABMS spectra were taken with a Jeol MStation 700 spectrometer using poly(ethylene-glycol) 600 as a matrix. UV–vis absorption and fluorescence spectra were taken on Hitachi U-3500 and

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F4500 spectrophotometers, respectively. Electrochemical measurements were carried out using a CH Instruments, Inc. electrochemical analyzer. Photoelectrochemical measurements were performed on a Bunko-Keiki CEP-2000 system.

2.2. Materials

2-Methyl-3*H*-indolenine (**1**), 2-methyl-4,5-benzo-3*H*-indolenine (**2**), 2-methylbenzothiazole (**3**), 2-methylquinoline (**4**), methyl iodide (**5a**), butyl iodide (**5b**), octadecyl iodide (**5c**), 3,4-dibutoxycyclobut-3-ene-1,2-dione (**10**) were purchased from Tokyo Kasei Co., Ltd.

*2.3. Synthesis of N-substituted heteroaromatic iodides **6–9***

To an acetonitrile solution (20 ml) of nitrogen-containing heteroaromatic compounds **1–4** (30 mmol) were added alkyl iodides **5** (100 mmol). The mixture was refluxed (**6**, **7**, and **9**: 48 h; **8**: 96 h). After the reaction was completed, the resulting precipitate was filtered and washed with ether. In the cases of **6b** and **7**, the reaction mixture was poured into ether (200 ml) to get the precipitate. The crude products were washed with ether. The physical and spectral data are shown below.

*2.3.1. 1,2,3,3-Tetramethyl-3H-indolium iodide (**6a**)*

Yield 95%; mp 230–233 °C; ^{1}H NMR (DMSO–d_6) δ = 1.53 (s, 6H), 2.77 (s, 3H), 3.97 (s, 3H), 7.60–7.65 (m, 2H), 7.81–7.84 (m, 1H), 7.89–7.93 (m, 1H); EIMS (70 eV) *m*/*z* (rel intensity) 173 (M^+–HI; 61), 158 (100).

*2.3.2. 1-Butyl-2,3,3-trimethyl-3H-indolium iodide (**6b**)*

Yield 89%; mp 136–138 °C; ^{1}H NMR (DMSO–d_6) δ = 0.95 (t, *J* = 7.6 Hz, 3H), 1.44 (sextet, *J* = 7.6 Hz, 2H), 1.55 (s, 6H), 1.82 (quintet, *J* = 7.6 Hz, 2H), 2.86 (s, 3H), 4.47 (t, *J* = 7.6 Hz, 2H), 7.61–7.66 (m, 2H), 7.84–7.88 (m, 1H), 7.97–8.01 (m, 1H); EIMS (70 eV) *m*/*z* (rel intensity) 215 (M^+–HI; 50), 173 (52), 159 (67), 158 (100), 144 (60), 143 (73), 115 (52).

*2.3.3. 1-Octadecyl-2,3,3-trimethyl-3H-indolium iodide (**6c**)*

Yield 94%; mp 104–106 °C; ^{1}H NMR (DMSO–d_6) δ = 0.85 (t, *J* = 7.5 Hz, 3H), 1.23–1.44 (m, 28H), 1.41 (quintet, *J* = 7.5 Hz, 2H), 1.54 (s, 6H), 1.83 (quintet, *J* = 7.4 Hz, 2H), 2.84 (s, 3H), 4.44 (t, *J* = 7.4 Hz, 2H), 7.61–7.65 (m, 2H), 7.83–7.86 (m, 1H), 7.96–7.99 (m, 1H); EIMS (70 eV) *m*/*z* (rel intensity) 411 (M^+–HI; 100), 173 (95).

2.3.4. 1-Butyl-2,3,3-trimethyl-4,5-benzo-3H-indolium iodide (7)

Yield 73%; mp 160–162 °C; ^{1}H NMR (DMSO–d_6) δ = 1.00 (t, *J* = 7.4 Hz, 3H), 1.51 (sextet, *J* = 7.4 Hz, 2H), 1.87 (s, 6H), 1.97 (quintet, *J* = 7.4 Hz, 2H), 3.19 (s, 3H), 4.79 (t, *J* = 7.4 Hz, 2H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 8.03–8.10 (m, 3H); EIMS (70 eV) *m*/*z* (rel intensity) 265 (M^+–HI; 56), 250 (100), 209 (43), 208 (74).

*2.3.5. 3-Butyl-2-methylbenzothiazolium iodide (**8**)*

Yield 81%; mp 188–191 °C; ^{1}H NMR (DMSO–d_6) δ = 0.94 (t, *J* = 7.6 Hz, 3H), 1.46 (sextet, *J* = 7.6 Hz, 2H), 1.83 (quintet, *J* = 7.6 Hz, 2H), 3.22 (s, 3H), 4.71 (t, *J* = 7.6 Hz, 2H), 7.81 (t, *J* = 8.2 Hz, 1H), 7.89 (t, *J* = 8.2 Hz, 1H), 8.34 (d, *J* = 8.2 Hz, 1H), 8.45 (d, *J* = 8.2 Hz, 1H); EIMS (70 eV) *m*/*z* (rel intensity) 205 (M^+–HI; 22), 149 (100), 148 (78), 128 (57), 127 (45).

*2.3.6. 1-Butyl-2-quinolinium iodide (**9**)*

Yield 49%; mp 138–140 °C; ^{1}H NMR (DMSO–d_6) δ = 1.00 (t, *J* = 7.8 Hz, 3H), 1.59 (sextet, *J* = 7.8 Hz, 2H), 1.88 (quintet, *J* = 7.8 Hz, 2H), 3.14 (s, 3H), 4.93 (t, *J* = 7.8 Hz, 2H), 8.00 (t, *J* = 7.9 Hz, 1H), 8.14 (d, *J* = 8.6 Hz, 1H), 8.24 (t, *J* = 7.9 Hz, 1H), 8.43 (d, *J* = 7.9 Hz, 1H), 8.61 (d, *J* = 7.9 Hz, 1H), 9.12 (d, *J* = 8.6 Hz, 1H); EIMS (70 eV) *m*/*z* (rel intensity) 199 (M^+–HI; 16), 170 (77), 143 (100), 115 (60).

*2.4. Synthesis of 3-butoxy-3,4-cyclobut-1,2-diones **11–14***

A butyl alcohol solution (12 ml) of *N*-alkyl heteroaromatic compounds **6–9** (8 mmol), 3,4-dibutoxycyclobut-3-ene-1,2-dione **10** (8 mmol), and triethylamine (1.6 ml) was heated at 60–70 °C for 1 h. After the reaction was completed, the mixture was cooled in refrigerator. The resulting precipitate was filtered, washed with ether, and purified by silicagel column chromatography (**11a**, **11b**, **12**, **13**, and **14**: $CHCl_3$/AcOEt = 10/1; **11c**: hexane/AcOEt = 3/1). The physical and spectral data are shown below.

*2.4.1. 3-Butoxy-4-(1,3,3-trimethyl-3H-indol-2-ylidenemethyl)-3-cyclobut-1,2-dione (**11a**)*

Yield 67%; mp 126–128 °C; ^{1}H NMR ($CDCl_3$) δ = 0.99 (t, *J* = 7.2 Hz, 3H), 1.50 (sextet, *J* = 7.2 Hz, 2H), 1.62 (s, 6H), 1.85 (quintet, *J* = 7.2 Hz, 2H), 3.36 (s, 3H), 4.84 (t, *J* = 7.2 Hz, 2H), 5.35 (s, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 7.25–7.28 (m, 2H); EIMS (70 eV) *m*/*z* (rel intensity) 325 (M^+; 72), 212 (100).

2.4.2. 3-Butoxy-4-(1-butyl-3,3-dimethyl-3H-indol-2-ylidenemethyl)-3-cyclobut-1,2-dione (**11b**)

Yield 38%; mp 128–129 °C; ^{1}H NMR ($CDCl_3$) $\delta = 0.98$ (t, $J = 7.4$ Hz, 3H), 0.99 (t, $J = 6.9$ Hz, 3H), 1.43 (sextet, $J = 7.4$ Hz, 2H), 1.50 (sextet, $J = 6.9$ Hz, 2H), 1.60 (s, 6H), 1.72 (quintet, $J = 7.4$ Hz, 2H), 1.85 (quintet, $J = 6.9$ Hz, 2H), 3.81 (t, $J = 7.4$ Hz, 2H), 4.84 (t, $J = 6.9$ Hz, 2H), 5.40 (s, 1H), 6.87 (d, $J = 8.0$ Hz, 1H), 7.06 (t, $J = 8.0$ Hz, 1H), 7.24–7.27 (m, 2H); EIMS (70 eV) m/z (rel intensity) 367 (M^+; 86), 254 (82), 226 (70), 212 (100).

2.4.3. 3-Butoxy-4-(1-octadecyl-3,3-dimethyl-3H-indol-2-ylidenemethyl)-3-cyclobut-1,2-dione (**11c**)

Yield 77%; mp 60–61 °C; ^{1}H NMR ($CDCl_3$) $\delta = 0.87$ (t, $J = 7.4$ Hz, 3H), 1.00 (t, $J = 7.3$ Hz, 3H), 1.24–1.40 (m, 30H), 1.50 (sextet, $J = 7.3$ Hz, 2H), 1.61 (s, 6H), 1.73 (quintet, $J = 7.4$ Hz, 2H), 1.86 (quintet, $J = 7.3$ Hz, 2H), 3.79 (t, $J = 7.4$ Hz, 2H), 4.85 (t, $J = 7.3$ Hz, 2H), 5.40 (s, 1H), 6.86 (d, $J = 7.4$ Hz, 1H), 7.06 (t, $J = 7.4$ Hz, 1H), 7.24–7.27 (m, 2H); EIMS (70 eV) m/z (rel intensity) 563 (M^+; 100), 450 (68), 212 (55).

2.4.4. 3-Butoxy-4-(1-butyl-2,3,3-trimethyl-4,5-benzo-3H-indol-2-ylidenemethyl)-3-cyclobut-1,2-dione (**12**)

Yield 67%; mp 169–170 °C; ^{1}H NMR ($CDCl_3$) $\delta = 1.01$ (t, $J = 7.5$ Hz, 3H), 1.03 (t, $J = 6.8$ Hz, 3H), 1.48 (sextet, $J = 7.5$ Hz, 2H), 1.54 (sextet, $J = 6.8$ Hz, 2H), 1.79 (quintet, $J = 7.5$ Hz, 2H), 1.90 (quintet, $J = 6.8$ Hz, 2H), 1.90 (s, 6H), 3.94 (t, $J = 7.5$ Hz, 2H), 4.89 (t, $J = 6.8$ Hz, 2H), 5.46 (s, 1H), 7.22 (d, $J = 8.1$ Hz, 1H), 7.38 (t, $J = 8.1$ Hz, 1H), 7.54 (t, $J = 8.1$ Hz, 1H), 7.84 (d, $J = 8.1$ Hz, 1H), 7.88 (d, $J = 8.1$ Hz, 1H), 8.10 (d, $J = 8.1$ Hz, 1H); EIMS (70 eV) m/z (rel intensity) 417 (M^+; 57), 262 (63), 247 (50), 218 (100).

2.4.5. 3-Butoxy-4-(3-butyl-3H-benzothiazol-2-ylidenemethyl)-3-cyclobut-1,2-dione (**13**)

Yield 61%; mp 139–140 °C; ^{1}H NMR ($CDCl_3$) $\delta = 1.00$ (t, $J = 7.7$ Hz, 3H), 1.01 (t, $J = 6.6$ Hz, 3H), 1.47 (sextet, $J = 7.7$ Hz, 2H), 1.51 (sextet, $J = 6.6$ Hz, 2H), 1.76 (quintet, $J = 7.7$ Hz, 2H), 1.85 (quintet, $J = 6.6$ Hz, 2H), 3.98 (t, $J = 7.7$ Hz, 2H), 4.78 (t, $J = 6.6$ Hz, 2H), 5.44 (s, 1H), 7.10 (t, $J = 8.2$ Hz, 1H), 7.16 (t, $J = 8.2$ Hz, 1H), 7.35 (d, $J = 8.2$ Hz, 1H), 7.46 (d, $J = 8.2$ Hz, 1H); EIMS (70 eV) m/z (rel intensity) 357 (M^+; 98), 244 (78), 202 (100), 160 (43).

2.4.6. 3-Butoxy-4-(1-butylqunolin-4-ylidenemethyl)-3-cyclobut-1,2-dione (**14**)

Yield 83%; mp 177–178 °C; ^{1}H NMR (DMSO–d_6) $\delta = 0.95$ (t, $J = 7.3$ Hz, 3H), 1.01 (t, $J = 7.1$ Hz, 3H), 1.44 (sextet, $J = 7.3$ Hz, 2H), 1.53 (sextet, $J = 7.1$ Hz, 2H), 1.70 (quintet, $J = 7.3$ Hz, 2H), 1.78 (quintet, $J = 7.1$ Hz, 2H), 3.34 (t, $J = 7.3$ Hz, 2H), 4.75 (t, $J = 7.1$ Hz, 2H), 5.26 (s, 1H), 7.32 (t, $J = 8.2$ Hz, 1H), 7.63 (t, $J = 8.2$ Hz, 1H), 7.67 (d, $J = 8.2$ Hz, 1H), 7.68 (d, $J = 8.2$ Hz, 1H), 7.71 (d, $J = 8.2$ Hz, 1H), 8.38 (d, $J = 8.2$ Hz, 1H); EIMS (70 eV) m/z (rel intensity) 351 (M^+; 31), 238 (58), 196 (94), 180 (100).

2.5. Synthesis of semisquaric acids **15–18**

To an ethanol solution (3 ml) of 3-butoxy-3,4-cyclobut-1,2-diones **11–14** (1 mmol) was added 40% aqueous sodium hydroxide (0.12 ml). The mixture was heated at 60–70 °C for 5 min. After the reaction was completed, the mixture was cooled and 2N hydrochloric acid (1.2 ml) was added. The product was purified by silicagel column chromatography (CH_2Cl_2/MeOH = 10/1). All products showed a single spot on the TLC plate. The physical and spectral data are shown below.

2.5.1. Semisquaric acid **15a**

Yield 56%; mp 175–179 °C; ^{1}H NMR (DMSO–d_6) $\delta = 1.56$ (s, 6H), 3.35 (s, 3H), 5.45 (s, 1H), 7.01 (t, $J = 7.5$ Hz, 1H), 7.11 (d, $J = 7.5$ Hz, 1H), 7.26 (t, $J = 7.5$ Hz, 1H), 7.39 (d, $J = 7.5$ Hz, 1H); FABMS m/z 270 (MH^+).

2.5.2. Semisquaric acid **15b**

Yield 61%; mp 102–103 °C; ^{1}H NMR (DMSO–d_6) $\delta = 0.93$ (t, $J = 7.4$ Hz, 3H), 1.37 (sextet, $J = 7.4$ Hz, 2H), 1.55 (s, 6H), 1.62 (quintet, $J = 7.4$ Hz, 2H), 3.85 (t, $J = 7.4$ Hz, 2H), 5.50 (s, 1H), 7.00 (t, $J = 7.6$ Hz, 1H), 7.08 (d, $J = 7.6$ Hz, 1H), 7.25 (t, $J = 7.6$ Hz, 1H), 7.38 (d, $J = 7.6$ Hz, 1H); FABMS m/z 312 (MH^+).

2.5.3. Semisquaric acid **15c**

Yield 52%; mp 82–85 °C; ^{1}H NMR (DMSO–d_6) $\delta = 0.85$ (t, $J = 6.8$ Hz, 3H), 1.21–1.31 (m, 30H), 1.55 (s, 6H), 1.63 (quintet, $J = 6.8$ Hz, 2H), 3.80 (t, $J = 6.8$ Hz, 2H), 5.48 (s, 1H), 6.95 (t, $J = 7.5$ Hz, 1H), 7.00 (d, $J = 7.5$ Hz, 1H), 7.21 (t, $J = 7.5$ Hz, 1H), 7.34 (d, $J = 7.5$ Hz, 1H); FABMS m/z 508 (MH^+).

2.5.4. Semisquaric acid **16**

Yield 50%; mp 126–127 °C; ^{1}H NMR (DMSO–d_6) $\delta = 0.94$ (t, $J = 7.4$ Hz, 3H), 1.40 (sextet, $J = 7.4$ Hz, 2H), 1.68 (quintet, $J = 7.4$ Hz, 2H), 1.83 (s, 6H), 3.96 (t, $J = 7.4$ Hz, 2H), 5.55 (s, 1H), 7.34 (t, $J = 8.1$ Hz, 1H), 7.49–7.54 (m, 2H), 7.90–7.93 (m, 2H), 8.12 (d, $J = 8.1$ Hz, 1H); FABMS m/z 362 (MH^+).

2.5.5. Semisquaric acid **17**

Yield 63%; mp 187–189 °C; ^{1}H NMR (DMSO–d_6) $\delta = 0.94$ (t, $J = 7.5$ Hz, 3H), 1.40 (sextet, $J = 7.5$ Hz, 2H), 1.62 (quintet, $J = 7.5$ Hz, 2H), 3.91 (t, $J = 7.5$ Hz, 2H), 5.47 (s, 1H), 6.98 (t, $J = 7.8$ Hz, 2H), 7.14

(d, $J = 7.8$ Hz, 1H), 7.23 (t, $J = 7.8$ Hz, 1H), 7.53 (d, $J = 7.8$ Hz, 1H); FABMS m/z 302 (MH^+).

2.5.6. Semisquaric acid **18**

Yield 88%; mp 165–167 °C; ^1H NMR (DMSO–d_6) $\delta = 1.01$ (t, $J = 7.4$ Hz, 3H), 1.52 (sextet, $J = 7.4$ Hz, 2H), 1.66 (quintet, $J = 7.4$ Hz, 2H), 3.17 (br, 2H), 5.29 (s, 1H), 7.12 (t, $J = 8.5$ Hz, 1H), 7.28 (d, $J = 8.5$ Hz, 1H), 7.37 (d, $J = 8.5$ Hz, 1H), 7.44–7.48 (m, 2H), 8.55 (d, $J = 8.5$ Hz, 1H); FABMS m/z 298 (MH^+).

3. Results and discussion

3.1. Synthesis

Semisquaric acids **15–18** were synthesized as shown in Scheme 1. Nitrogen-containing heteroaromatic compounds **1–4** reacted with alkyl iodides **5** to give the *N*-alkylated heteroaromatic iodides **6–9**. These compounds reacted with 1,2-dibutoxycyclobut-1-ene-3,4-dione (**10**) to give the butoxy derivatives **11–14** followed by hydrolysis to afford the semisquaric acids **15–18**.

3.2. UV–vis absorption and fluorescence spectra

Typical UV–vis absorption and fluorescence spectra of semisquaric acid are shown in Fig. 1. The λ_{max} and emission maxima (λ_{em}) of **15c** were observed at 423 and 459 nm, respectively. The molar absorption coefficient (ε) of **15c** was calculated to be 52400 $dm^3\,mol^{-1}\,cm^{-1}$.

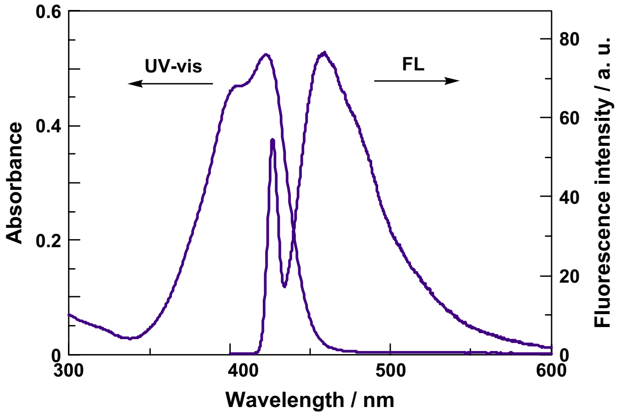
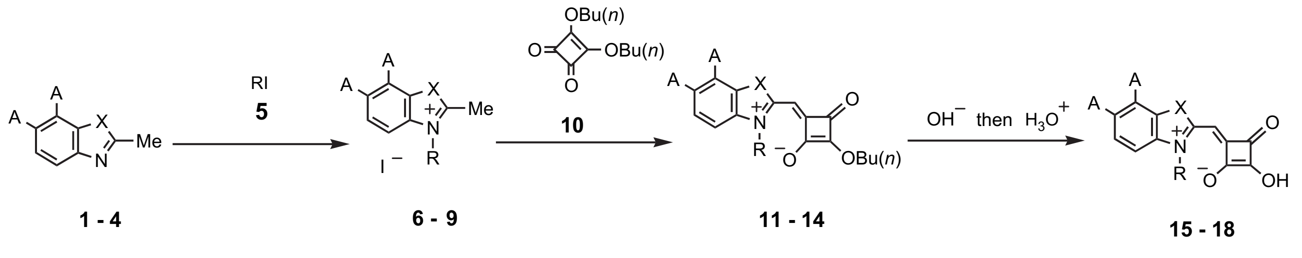


Fig. 1. UV–vis absorption and fluorescence spectra of **15c**. Measured in ethanol at the concentration of 1×10^{-5} mmol dm^{-3}.

The UV–vis absorption and fluorescence spectral data of semisquaric acid **15–18** are listed in Table 1. The λ_{max} was more bathochromic in the order of heteroaromatic moiety: 2-quinolinium (**18**, 465 nm) > benzothiazolium (**17**, 446) and benzoindolium (**16**, 442) > indolium (**15b**, 423). The ε values were observed in the range of 21400 to 52400 $dm^3\,mol^{-1}\,cm^{-1}$. No remarkable difference in λ_{max} and ε among the *N*-methyl-, -butyl, and -octadecyl indolium derivatives **15a**, **15b**, and **15c** was observed, being in the range of 419–423 nm and 44000–52400, respectively. No fluorescence was observed for **18**. The λ_{em} was more bathochromic in the order of heteroaromatic moiety: benzothiazolium (**17**, 478) and benzoindolium (**16**, 473) > indolium (**15b**, 458). The relative fluorescence intensity (RFI) increased as long the alkyl group was in **15**.



Compd	A	X
1	H	CMe_2
2	benzo	CMe_2
3	H	S
4	H	-CH=CH-

Compd	R
5a	Me
5b	*n*-Bu
5c	*n*-Octadecyl

Compd	A	X	R
6a, 11a, 15a	H	CMe_2	Me
6b, 11b, 15b	H	CMe_2	*n*-Bu
6c, 11c, 15c	H	CMe_2	*n*-Octadecyl
7, 12, 16	benzo	CMe_2	*n*-Bu
8, 13, 17	H	S	*n*-Bu
9, 14, 18	H	-CH=CH-	*n*-Bu

Scheme 1.

Table 1
Properties of semisquaric acids **15–18**

Compounds	λ_{max} (ε)^a/nm	λ^a_{em}/nm	RFI^a	E^b_{ox}/V	E_{red}/V^b	λ^c_{max}	Absorbance^c	IPCE^d/%	I^d_{sc}/mA cm^{-2}	V^d_{oc}/V	ff^d	η^d/%
15a	419 (44,100)	460	99	0.35	−2.61	419	2.0	22.0	0.728	0.386	0.57	0.16
15b	423 (44,000)	458	100	0.33	−2.60	423	2.5	19.9	0.703	0.397	0.56	0.15
15c	423 (52,400)	459	164	0.28	−1.65	423	1.9	38.0	1.116	0.421	0.57	0.27
16	442 (45,600)	473	378	0.40	−1.41	442	2.2	16.0	0.688	0.383	0.60	0.16
17	446 (40,500)	478	90	0.12	−2.66	446	2.0	5.6	0.355	0.323	0.55	0.06
18	465 (21,400)	–^{e}	–^{e}	0.16	−2.51	465	2.9	2.7	0.338	0.358	0.65	0.08

[a] Measured in ethanol.
[b] vs SCE in acetonitrile.
[c] On zinc oxide film.
[d] Action spectrum under monochromatic light with 0.2×10^{16} photon cm^{-2} sec^{-1} and I–V characteristics under white light with 100 mW cm^{-2}.
[e] No fluorescence.

3.3. Electrochemical properties

Since compounds **15–18** were less soluble in acetonitrile, the electrochemical measurement was carried out in DMSO. The oxidation potential (E_{ox}) of **15–18** was measured vs Ag in DMSO and was calibrated to E_{ox} vs SCE in acetonitrile on the basis of E_{ox} of ferrocene. The E_{red} of **15–18** was calculated on the basis of the E_{ox} and λ_{max} in DMSO. The E_{red} and E_{ox} of **15–18** are shown in Table 1. The E_{red} of **15–18** was negative enough to inject electrons into zinc oxide (−0.7 V vs SCE). The E_{ox} depended on the kinds of heteroaromatic moiety. The indolium **15** and benzoindolium derivatives **16** seem to act as sensitizers from thermodynamic viewpoint. However, the benzothiazolium and 2-quinolinium derivatives **17** and **18** showed rather positive E_{ox} against the energy level of electrolyte (I_3^-/I^-, 0.29 V).

3.4. Preparation of zinc oxide solar cell

A template zinc oxide thin film (thickness: ca. 3 μm) was prepared as described in Ref. [11]. After drying the template film at 150 °C for 1 h, the film was refluxed in the ethanol solution (5 mL) of semisquaric acids **15–18** (500 μmol dm^{-3}) for 3 h. These optimized conditions for preparing dye-doped zinc oxide film were obtained in advance by measuring the photoelectrochemical properties with three-electrode method. Then, the film was set in the solar cell as shown in Fig. 2. An acetonitrile–ethylenecarbonate (v/v = 1:4) mixed solution containing tetrabutylammonium iodide (0.5 mol dm^{-3}) and iodine (0.05 mol dm^{-3}) was used as an electrolyte.

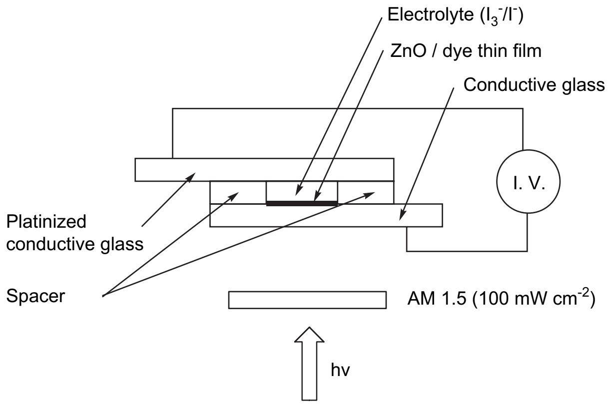


Fig. 2. Zinc oxide solar cell.

3.5. Photoelectrochemical properties of solar cell

Typical photocurrent density–action and UV–vis absorption spectra are shown in Fig. 3. The UV–vis absorption band of **15c** on zinc oxide was broad compared with that in ethanol suggesting the aggregation on the film. The photocurrent density–action spectrum traded the absorption band of **15c** on zinc oxide, indicating the photosensitization of zinc oxide by **15c**. The IPCE of **15c** was observed to be 38.0% at around 423 nm.

Typical photocurrent density–photovoltage (I–V) curve is shown in Fig. 4. The I_{sc} and V_{oc} of **15c** were observed at 1.116 mA cm^{-2} and 0.421 V, respectively. The ff and η were calculated to be 0.57 and 0.27%, respectively. The result of cell performance of the other semisquaric acids **15–18** are also shown in Table 1.

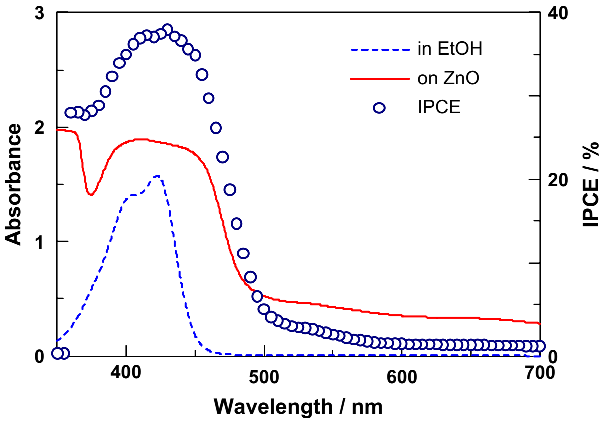


Fig. 3. Photocurrent density–action and UV–vis absorption spectra of **15c**.

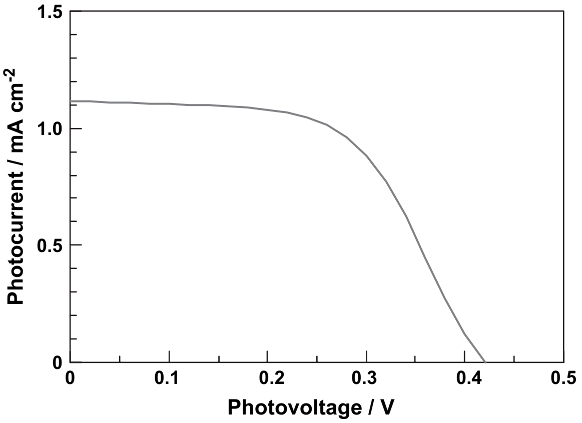


Fig. 4. Photocurrent density–photovoltage (I–V) curve of **15c**.

The amount of dyes on zinc oxide and energy levels of dyes can affect the IPCE values. From our experience, when the absorbance of dye-doped zinc oxide film is larger than 1.0, indicating more than 90% of photon is absorbed, the cell performance can be evaluated. The absorbance was observed in the range of 1.9–2.9, indicating that all the zinc oxide films can be evaluated. A plausible interaction between semiaquaric acids and semi conductors is discussed in our paper [12].

The IPCE value increased in the following order of N-butyl heteroaromatic derivatives: indolium (**15b**, 19.9%) > benzoindolium (**16**, 16.0) > benzothiazolium (**17**, 5.6) > qunolinium (**18**, 2.7). Thus, the compounds **17** and **18** showed less IPCE values. This result may be attributed to the rather high E_{ox} levels of **17** and **18**.

The IPCE value of dodecyl indolium derivative **15c** was highest among the methyl-, butyl-, and dodecylindolium derivatives **15a**, **15b**, and **15c**. This result is similar to our previous one that the introduction of long alkyl group into the heteroaromatic moiety in 3-aryl-4-hydroxycyclobut-3-ene-1,2-diones could improve the cell performance [12]. On the other hand, the introduction of long alkyl groups into 3-(2-carboxyethyl)-2-[4-(dialkylamino)styryl]benzothiazolium iodides did not improve the cell performance. Thus, the role of long alkyl group in the cell performance depends on the kind of dye molecule. No remarkable difference in E_{ox}, E_{red}, and amount of dye on zinc oxide film was observed among **15a**, **15b**, and **15c**. The orientation of dye molecule on zinc oxide surface, intense fluorescence, and/or higher solubility in ethanol, which can affect the circumstances of dye molecule on zinc oxide surface, might improve the cell performance.

4. Conclusion

A series of semisquaric acids was examined as sensitizers for zinc oxide solar cell prepared by the one-step cathode deposition template method. Their IPCE values were observed in the range of 2.7–19.9%, being rather low. However, the cell performance was improved by introducing long alkyl group into the molecule, the IPCE value being 38.0%.

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