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3-Aryl-4-hydroxycyclobut-3-ene-1,2-diones as sensitizers for TiO_2 solar cell

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Abstract

A series of 3-aryl-4-hydroxycyclobut-3-ene-1,2-diones were synthesized and examined as sensitizers for a TiO_2 solar cell. The compounds showed strong affinity for TiO_2 and the fluorescence intensity and self-assembly of the 3-aryl-4-hydroxycyclobut-3-ene-1,2-diones on the TiO_2 surface were important factors in enhancing the solar-light-to-electricity conversion efficiency. The highest efficiency of 0.96% was observed for 3-[4-(didodecylamino)phenyl]-4-hydroxycyclobut-3-ene-1,2-dione.

Keywords: Dye-sensitized solar cell; TiO_2, Semisquaric acids; Cyclic voltammetry; Solar-light-to-electricity conversion efficiency; Incident photon-to-current efficiency

1. Introduction

Since the discovery of the highly efficient ruthenium complex-sensitized solar cell, much attention has been paid to the survey of organic dye sensitizers [1–3]. Recently, coumarin [4], merocyanine [5], squarylium [6] and styryl [7] dyes have been proposed as sensitizers for solar cells. Semisquaric acids, which are the intermediates for the synthesis of squarilium dyes, have been also reported to act as sensitizers for a TiO_2 solar cell [8]. Semisquaric acids are classified into two groups: 3-arylidene- and 3-aryl-4-hydroxycyclobut-3-ene-1,2-diones. Though many derivatives and analogues of the former group have been proposed as sensitizers, only one example of the latter one, 3-[1-methyl-3-pyrrolyl]-4-hydroxycyclobut-3-ene-1,2-dione, has been reported to show 75% of incident photon-to-current efficiency (IPCE) at 450 nm. We report herein the systematic survey of 3-aryl-4-hydroxycyclobut-3-ene-1,2-diones as sensitizers for a TiO_2 solar cell.

2. Results and discussion

2.1. Synthesis of 3-aryl-4-hydroxycyclobut-3-ene-1,2-diones 3

The 3-aryl-4-hydroxycyclobut-3-ene-1,2-diones 3 were synthesized as shown in Scheme 1. Electron-

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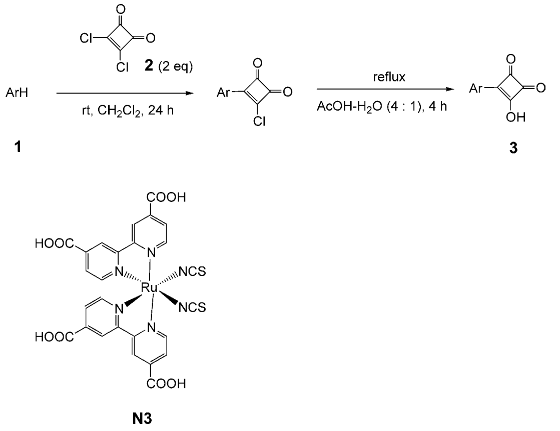


Scheme 1.

rich aromatic substrates **1** were reacted with 3,4-dichlorocyclobut-3-ene-1,2-dione (**2**) followed by hydrolysis to provide **3**. The yields of **3** were low due to the formation of a lot of by-products.

2.2. *Properties of 3-aryl-4-hydroxycyclobut-3-ene-1,2-diones 3*

The UV–vis absorption and fluorescence data are given in Table 1. No remarkable difference in the UV–vis absorption and fluorescence spectra was observed among the compounds. Spectra of **3d** are shown in Fig. 1 as an example. The absorption (λ_{max}, line A) and emission maxima (λ_{em}, line B) of **3d** in ethanol were observed at 386 and 466 nm, respectively.

The cyclic voltamgram of **3d** is shown in Fig. 2; the oxidation potential (E_{ox}) was observed at 0.49 V vs Ag/Ag$^+$. The E_{ox} corresponds to the energy level of HOMO and was calculated to be 0.46 V vs SCE. No electrochemical reduction potential (E_{red}) corresponding to the energy level of LUMO was observed in the range of 0 to −1.5 V. However, the E_{red} of **3d** could be calculated on the basis of its λ_{max}, being −2.76 V vs SCE. The details of measurement and calculations of E_{ox} and E_{red} are shown in the experimental section. The E_{ox} of **3h** and **3i** were also measured and calculated in the same way, being 0.46 and 0.48 V vs SCE, respectively. The E_{red} of **3h** and **3i** were also calculated to be −2.79 and −2.62 V vs SCE, respectively.

A schemetic energy diagram of TiO_2, **3d** and electrolyte (I_3^-/I^-) is shown in Fig. 3. The E_{red} of **3d** was sufficiently negative to inject electrons into the conduction band of TiO_2. The E_{ox} of **3d** was positive enough to accept electrons from the electrolyte. The other 3-aryl-4-hydroxycyclobut-3-ene-1,2-diones **3** as well as **3d** can also act as sensitizers for TiO_2 from a thermodynamic viewpoint.

2.3. *Photoelectrochemical properties of TiO$_2$ solar cell*

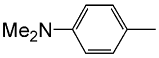
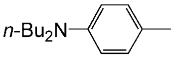
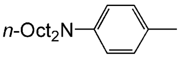
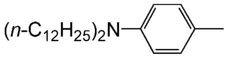
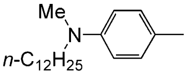
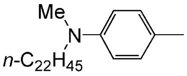
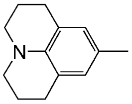
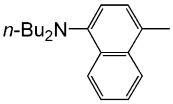
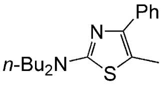
Typical UV–vis absorption and action spectra are shown in Fig. 1. The UV–vis absorption spectrum of **3d** in TiO_2 film was measured by dispersing **3d**-containing TiO_2 in barium sulfate to give line C, showing a bathochromic shift with spread of half-width compared with that in ethanol. The photocurrent action spectrum (line D) follows the line C, indicating photosensitization of TiO_2 by **3d**. The IPCE of **3d** was observed to be 43.0% at 410 nm.

It was impossible to measure the amount of **3** in the TiO_2 film, because, even when the TiO_2 film was treated with aqueous 10% potassium hydroxide solution and an aqueous 10% potassium hydroxide–ethanol (1:1) mixed solvent at room temperature for 30 min followed by extraction with DMSO, compounds **3** were not extracted. Styryl dyes containing a sulfo group have been reported to be completely desorbed by soaking in methanol [9]. Thus, the semisquaric acids **3** could chemically react with the hydroxyl group on the TiO_2 surface.

The *I–V* curve of **3d** is shown in Fig. 4. The highest short circuit photocurrent density (I_{sc}) and open circuit photovoltage (V_{oc}) were observed for **3d**, with values of 2.88 mA cm^{-2} and 0.59 V, respectively. The fill factor (ff) was calculated to be 58% and the solar-light-to-electricity conversion efficiency (η) was calculated to be 0.96% [3]. The *I–V* curve of the other derivatives were also obtained to calculate the ff and η values in the same way.

The results of cell performance are shown in Table 1. Values of IPCE, ff and η of **3** were observed in the range of 8.2–43.0, 49–62, and 0.06–0.96%, respectively. These values of N3 dye

Table 1
Properties and TiO_2 solar cell performance of semisquaric acids **3**

Compd	Ar	λ_{max}[a] (ε) (nm)	λ_{em}[b] (nm)	RFI[b]	λ_{max}[c] (nm)	IPCE (%)	I_{sc} (mA cm^{-2})	Voc (V)	ff (%)	η (%)
3a		377 (38,000)	467	0.07	400 (560)	16.3	0.55	0.50	49	0.13
3b		386 (40,000)	466	1.00	410 (560)	18.5	0.87	0.53	52	0.24
3c		385 (38,000)	466	0.23	410 (570)	35.5	1.65	0.54	62	0.55
3d		386 (39,000)	466	1.35	410 (570)	43.0	2.88	0.59	58	0.96
3e		383 (41,000)	463	0.21	410 (560)	36.5	1.99	0.54	59	0.64
3f		386 (41,000)[d]	489[d]	0.04[d]	–[e]	–[e]	–[e]	–[e]	–[e]	–[e]
3g		400 (36,000)	470	0.55	420 (600)	14.2	1.03	0.47	52	0.25
2h		379 (35,000)	509	0.88	440 (600)	8.2	0.30	0.40	51	0.06
3i		397 (33,000)	506	1.76	450 (610)	31.0	1.57	0.52	61	0.50
N3	–	315 (50,000), 395 (13,000), 535 (13,000)	–[f]	–[f]	525 (740)	58.4	7.60	0.70	60	3.19

[a] Measured in ethanol.

[b] Measured in ethanol on 3.0×10^{-5} mol dm^{-3} of substrate in ethanol at 25 °C.

[c] λ_{max} on TiO_2. The value in parentheses represents threshold on TiO_2.

[d] Measured in DMSO.

[e] The film was not prepared due to low solubility of **3f** into ethanol.

[f] Not measured.

by this method were observed to be 58.4, 60, and 3.19%, respectively.

The effect of a dialkylamino group on η was in the following order: didodecylamino derivative **3d** (0.96) > *N*-dodecyl-*N*-methyl derivative **3e** (0.64) > dioctylamino derivative **3c** (0.55) > juloridino derivative **3g** (0.25), dibutylamino derivative **3b** (0.24) > dimethylamino derivative **3a** (0.13). Thus, the longer the alkyl chain length, the higher was the conversion efficiency,

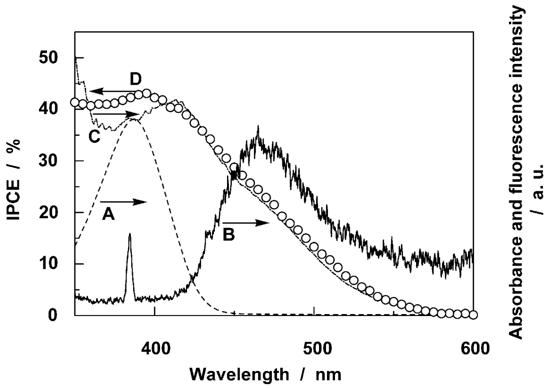


Fig. 1. UV–vis absorption, emission and action spectra of **3d**. A (dotted line): UV–vis absorption spectrum in ethanol, B (solid line): emission spectrum in ethanol, C (chain line): UV–vis absorption spectrum on TiO_2, D (open circle): action spec-

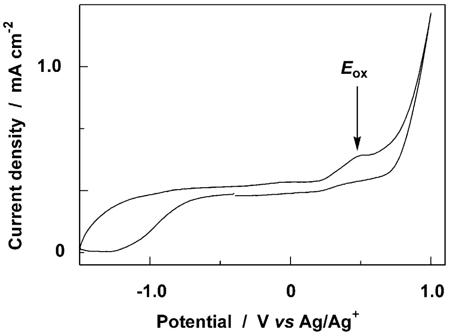


Fig. 2. Cyclic voltamgram of **3d**. Measured for **3d** at a glassy-carbon electrode vs Ag/Ag^+ in DMSO containing tetrabutylammonium perchlorate (0.1 mol dm^{-3}) at the scan rate of 100 mV s^{-1}.

suggesting that intermolecular interactions between alkyl groups is important to enhance efficiency.

The kinds of aromatic residue also affected the η value. The efficiency was in the order of aromatic moiety: thiazolyl **3i** (0.50) > phenylene **3b** (0.24) > naphthylene **3h** (0.06). This order was consistent with that of RFI of the compounds, being **3i** (1.76) > **3b** (1.00) > **3h** (0.88). Since the amount of 3 on the TiO_2 surface was large enough to inject electrons into TiO_2, intense fluorescence was required to enhance the efficiency of solar cell. Consequently, the di(dodecylamino) derivative **3d**, having the longest alkyl chain length and medium fluorescence intensity among 3, showed highest efficiency of the 3-aryl-4-hydroxycyclobut-3-ene-1,2-diones 3.

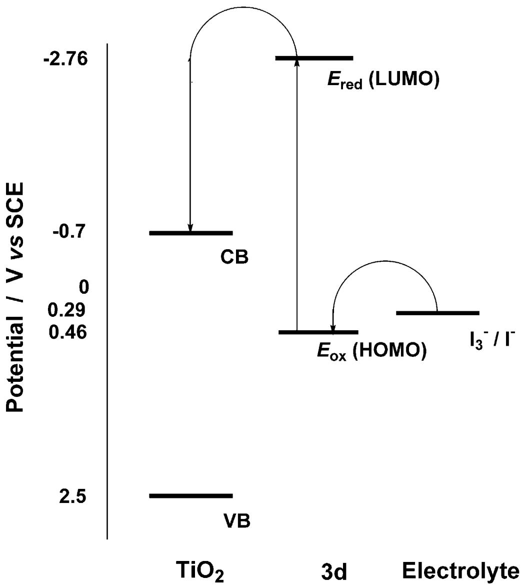


Fig. 3. Schemetic energy diagram of TiO_2, **3d** and electrolyte (I_3^-/I^-).

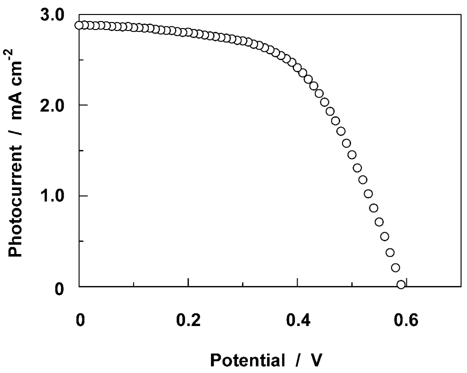
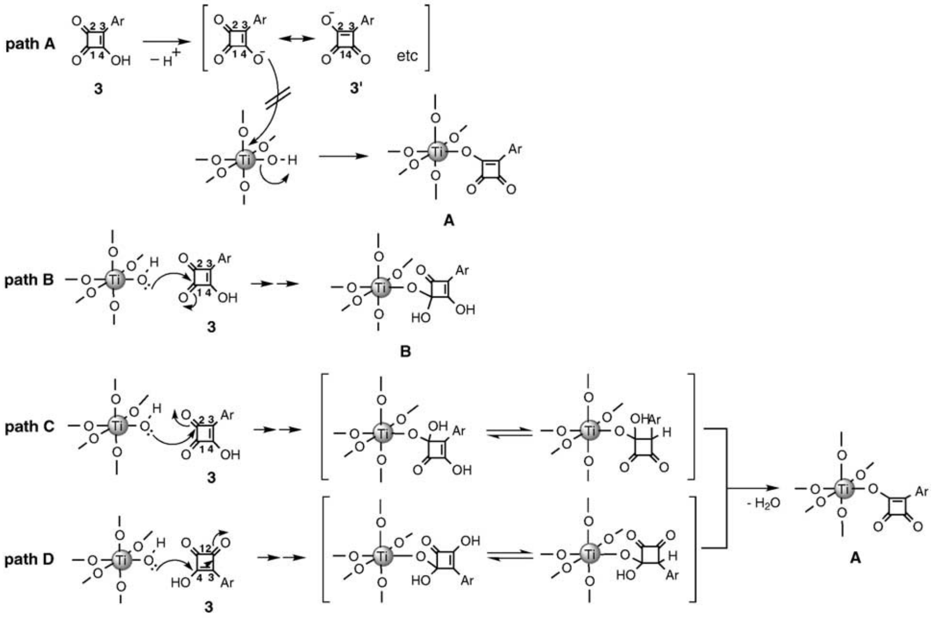


Fig. 4. *I–V* curve of **3d**.

Plausible reaction mechanisms of TiO_2 with 3 are shown in Scheme 2. The TiO_2 surface is surrounded by hydroxyl groups. Four mechanisms are taken into consideration for the reaction of TiO_2 with 3: path A; nucleophilic attack of 3 and/or its anion for Ti atom, path B; nucleophilic attack of the hydroxyl group on TiO_2 for the carbonyl carbon at the 1-position of 3, path C; nucleophilic attack of the hydroxyl group on TiO_2 for the carbonyl carbon at the 2-position of 3 followed by dehydration



Scheme 2.

(1,2-addition), and path D; a Michael-type 1,4-addition of the hydroxyl group on TiO_2 for the carbonyl-carbon at the 4-position followed by dehydration. The hydroxyl group of compounds **3** is acidic. Because the anion **3′** is stabilized due to conjugation with the carbonyl group at the 2-position and aromatic residue, this anion can attack the Ti atom. The anion **3′** has bulky carbonyl and aromatic groups adjacent to the anionic center and a Ti atom is also surrounded by four bulky oxygen atoms. These make the *syn*-substitution reaction to form product **A** very unlikely. Nucleophilic attack of the hydroxyl group of TiO_2 on **3** (paths B, C and D) seems likely to occur. As the product **B** from path **B** seems unstable, the paths C and/or D can preferentially proceed to give product **A**.

Schemetic representation of the products on the TiO_2 surface is shown in Fig. 5. 3-Aryl-4-hydroxycyclobut-3-ene-1,2-diones can aggregate due to strong intermolecular interactions at the polar carbonyl moieties. Furthermore, π–π interactions between the aryl moieties as well as hydrophobic interactions between the long alkyl chains can assist the self-assembly of **3d** on the TiO_2 surface to enhance conversion efficiency.

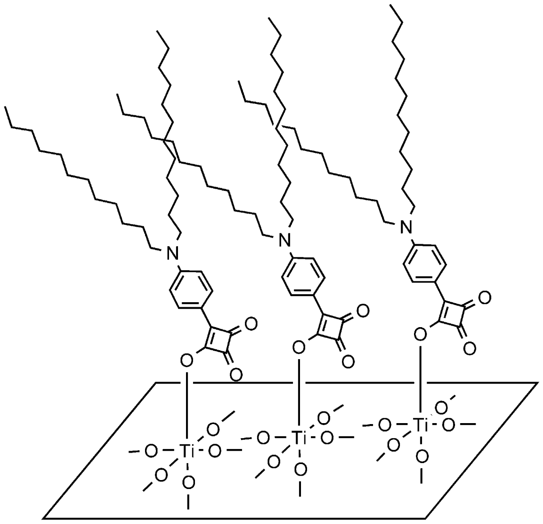


Fig. 5. Schemetic representation of the products on TiO_2 surface.

3. Conclusions

The systematic survey of 3-aryl-4-hydroxycyclobut-3-ene-1,2-diones as sensitizers for a TiO_2 solar cell was examined. The λ_{max} of these compounds in TiO_2 film was observed to be around 400–450 nm. The conversion efficiency increased as the intermolecular interactions operating between the hydrophobic alkyl chains increased to assist the self-assembly of 3-aryl-4-hydroxycyclobut-3-ene-1,2-diones on the TiO_2 surface. The efficiency also increased with increasing fluorescence intensity. The highest efficiency, 0.96%, was observed for 3-[4-(didodecylamino)-phenyl]-4-hydroxycy-3-clobutene-1,2-dione.

4. Experimental

4.1. Instruments

Melting points were measured with a Yanagimoto MP-52 micro-melting-point apparatus. UV–vis absorption and fluorescence spectra were recorded on Hitachi U-3500 and F-4500 spectrometers, respectively. NMR spectra were taken on a Varian Inova 400 spectrometer. Mass spectra were measured with a Shimadzu QP-1000 spectrometer. Cyclic voltammetry was performed with a Hokuto-denko Potentiogalvanostat HSV-100.

4.2. Materials

N,N-dimethylaniline (**1a**), juloridine (**1g**), alkyl iodides, and *N*-methylaniline were purchased from Tokyo Kasei Co., Ltd. TiO_2 (P25) was purchased from Nippon Aerosil Co., Ltd. *N,N*-Dialkylanilines **1b–d** and 1-(dibutylamino)naphthalene (**1h**) were prepared by the *N*-alkylation of arylamines. Unsymmetrical *N,N*-dialkylanilines **1e** and **1f** were synthesized by the *N*-alkylation of *N*-methylaniline [10]. 3,4-Dichlorocyclobut-3-ene-1,2-dione (**2**) [11] and 2-dibutylamino-4-phenylthiazole (**1i**) [12] were prepared as described in the literature.

4.3. Synthesis of 3-aryl-4-hydroxycyclobut-3-ene-1,2-diones 3

To a dichloromethane solution (20 ml) of *N,N*-dialkylarylamines **1** (5 mmol) was added 3,4-dichlorocyclobut-3-ene-1,2-dione **2** (1.5 g, 10 mmol) and the mixture was stirred at ambient temperature for 24 h. After concentration of the mixture, the product was isolated by column chromatography (SiO_2, CH_2Cl_2). The isolated product was then refluxed in an acetic acid–water (4:1) mixed solution (10 ml) for 4 h. After cooling, the resulting precipitate was filtered and washed with an ether-hexane mixed solution. The physical and spectral data are shown below.

4.3.1. 3-[4-(Dimethylamino)phenyl]-4-hydroxycyclobut-3-ene-1,2-dione (3a)

Yield 12%; mp >300 °C (dec); ^1H NMR (DMSO-d_6) δ 3.03 (s, 6H), 6.88 (d, $J = 8.6$ Hz, 2H), 7.87 (d, $J = 8.6$ Hz, 2H); EI-MS (70 eV) m/z (rel intensity) 217 (M^+; 67), 161 (100), 160 (66).

4.3.2. 3-[4-(Dibutylamino)phenyl]-4-hydroxycyclobut-3-ene-1,2-dione (3b)

Yield 30%; mp 244–245 °C (dec); ^1H NMR (DMSO-d_6) δ 0.91 (t, $J = 7.3$ Hz, 6H), 1.32 (sextet, $J = 7.3$ Hz, 4H), 1.49 (br s, 4H), 3.78 (br s, 4H), 6.83 (br s, 2H), 7.86 (br s, 2H); EI-MS (70 eV) m/z (rel intensity) 301 (M^+; 41), 259 (68), 258 (100), 216 (38), 203 (71), 202 (85), 160 (73), 146 (38).

4.3.3. 3-[4-(Dioctylamino)phenyl]-4-hydroxycyclobut-3-ene-1,2-dione (3c)

Yield 8%; mp 199–200 °C (dec); ^1H NMR (DMSO-d_6) δ 0.85 (t, $J = 5.8$ Hz, 6H), 1.25–1.27 (m, 20H), 1.51 (br, 4H), 3.35 (br s, 4H), 6.74 (br s, 2H), 7.82 (br s, 2H); EI-MS (70 eV) m/z (rel intensity) 413 (M^+; 40), 314 (100).

4.3.4. 3-[4-(Didodecylamino)phenyl]-4-hydroxycyclobut-3-ene-1,2-dione (3d)

Yield 30%; mp 174–175 °C (dec); ^1H NMR (DMSO-d_6) δ 0.84 (t, $J = 6.5$ Hz, 6H), 1.13-1.53 (m, 40H), 3.35 (br s, 4H), 6.84 (br s, 2H), 7.85 (d, $J = 8.6$ Hz, 2H); EI-MS (70 eV) m/z (rel intensity) 525 (M^+; 6), 487 (15), 371 (20), 370 (27), 333 (81), 332 (100), 178 (42).

4.3.5. 3-[4-(N-Dodecyl-N-methyl)anilino]-4-hydroxycyclobut-3-ene-1,2-dione (3e)

Yield 29%; mp 187–188 °C (dec); ^1H NMR (DMSO-d_6) δ 0.85 (t, $J = 7.0$ Hz, 3H), 1.23–1.27 (m, 18H), 1.50 (br s, 2H), 2.99 (s, 3H), 3.40 (t, $J = 7.0$ Hz, 2H), 6.86 (br s, 2H), 7.86 (d, $J = 8.7$ Hz, 2H); EI-MS (70 eV) m/z (rel intensity) 371 (M^+; 29), 315 (13), 216 (78), 160 (100), 159 (46).

*4.3.6. 3-[4-(N-Docosyl-N-methyl)anilino]-4-hydroxycyclobut-3-ene-1,2-dione (**3f**)*

Yield 25%; mp 195–196 °C (dec); ^{1}H NMR (DMSO-d_6) δ 0.85 (t, $J=6.8$ Hz, 3H), 1.22–1.27 (m, 38H), 1.50 (br s, 2H), 2.95 (s, 3H), 3.28–3.38 (m, 2H), 6.76 (d, $J=8.6$ Hz, 2H), 7.86 (d, $J=8.6$ Hz, 2H); EI-MS (70 eV) m/z (rel intensity) 525 (M$^+$; 3), 455 (26), 178 (100), 177 (40), 161 (57), 160 (79).

*4.3.7. 3-(2,3,6,7-Tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolium-9-yl)-4-hydroxycyclobut-3-ene-1,2-dione (**3g**)*

Yield 9%; mp 245–246 °C (dec); ^{1}H NMR (DMSO-d_6) δ 1.88 (br s, 4H), 2.70 (br s, 4H), 3.25 (br s, 4H), 7.44 (br s, 2H); EI-MS (70 eV) m/z (rel intensity) 351 (M$^+$; 35), 309 (83), 308 (100), 253 (70), 252 (84), 210 (17), 194 (19), 168 (24), 139 (35).

*4.3.8. 3-[4-(Dibutylamino)-1-naphthyl]-4-hydroxycyclobut-3-ene-1,2-dione (**3h**)*

Yield 7%; mp 220–220.5 °C (dec); ^{1}H NMR (DMSO-d_6) δ 0.79 (t, $J=7.1$ Hz, 6H), 1.23 (sextet, $J=7.1$ Hz, 4H), 1.39 (br, 4H), 3.42 (br, 4H), 7.56 (br, 3H), 8.25 (br, 1H), 8.44 (br, 1H), 9.19 (br, 1H); EI-MS (70 eV) m/z (rel intensity) 351 (M$^+$; 35), 309 (83), 308 (100), 253 (70), 252 (84), 210 (17), 194 (19), 168 (24), 139 (35).

*4.3.9. 3-[2-(Dibutylamino)-4-phenyl-5-thiazolyl]-4-hydroxycyclobut-3-ene-1,2-dione (**3i**)*

Yield 32%; mp 236–237 °C (dec); ^{1}H NMR (DMSO-d_6) δ 0.94 (t, $J=7.4$ Hz, 6H), 1.35 (sextet, $J=7.4$ Hz, 4H), 1.65 (quintet, $J=7.4$ Hz, 4H), 3.53 (t, $J=7.4$ Hz, 4H), 7.37–7.38 (m, 3H), 7.52–7.54 (m, 2H); EI-MS (70 eV) m/z (rel intensity) 384 (M$^+$; 60), 329 (33), 328 (42), 299 (35), 286 (40), 285 (48), 244 (49), 243 (63), 229 (100), 215 (33), 202 (41), 173 (37), 145 (50).

4.4. Electrochemical measurement of 3

To DMSO (100 ml) was added tetrabutylammonium perchlorate (3.42 g, 10 mmol). Compound **3** (0.01 mmol) was dissolved in 20 ml of this solution. Cyclic voltammetry was performed using a glassy-carbon electrode vs Ag/Ag$^+$ at a scan rate of 100 mV s^{-1}. The E_{ox} of ferrocene was used as a reference. The E_{ox} of ferrocene in DMSO was measured to be 0.19 V vs Ag/Ag$^+$, which should correspond to 0.16 V vs SCE in water. The E_{ox} of **3d** was measured to be 0.49 V vs Ag/Ag$^+$ in DMSO. This value corresponds to 0.43 V vs SCE.

The E_{red} of **3d** was calculated according to Eq. (1),

$$\Delta E = hc/\lambda \tag{1}$$

where ΔE, h, c, and λ represent the energy absorbed in an electronic transition (J), Planck's constant (6.63×10^{-34} J s), velocity of light (3×10^8 m s^{-1}) and wavelength in absorption maximum (nm), respectively. For example, in the case of **3d**, the $\lambda_{\max}$ was observed at 386 nm in ethanol. Then, the ΔE is calculated to be 5.15×10^{-19} J, which corresponds to be 3.22 eV. Since the E_{ox} of **3d** was measured to be 0.46 V vs SCE, the E_{red} is calculated to be −2.76 V vs SCE.

4.5. Preparation of TiO_2 solar cell

SnO_2 glass was sonicated in acetone for 15 min and then in 2-propanol for 15 min. The glass was stored in 2-propanol. The glass was again sonicated in 2-propanol, 0.5% aqueous detergent agent and finally distilled water before use. TiO_2 (8 g), water (1 ml) and concentrated nitric acid (0.9 ml) were mixed. The mixture was then triturated for about 3 h by adding 10 ml of water every 10 min. The total amount of water was 200 ml. To the mixture was carefully added Triton-X100 (ca. 0.2 ml) and the mixture was spread onto a SnO_2 glass and dried for 30 min. The film was heated at 450 °C for 30 min, cooled to 100 °C and then to ambient temperature.

The film was again heated at 450 °C for 30 min, cooled to 100 °C and then to ambient temperature before use. The film was put in a test tube and an ethanol solution (10 ml) of 3-aryl-4-hydroxycyclobut-3-ene-1,2-diones **3** (1×10^{-4} mol dm^{-3}) was poured into the test tube. All 3-aryl-4-hydroxycyclobut-3-ene-1,2-diones **3** except for **3f** were sufficiently soluble in ethanol to prepare the film. The dye-doped TiO_2 film was prepared by refluxing the ethanol solution for 1 h and then allowing to stand for 12 h at ambient temperature.

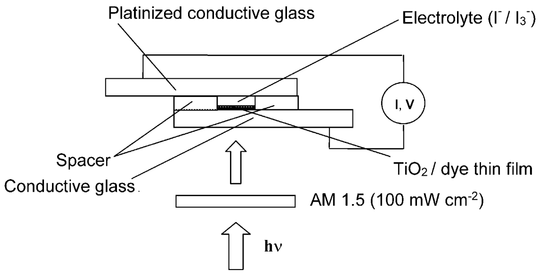


Fig. 6. TiO_2 solar cell.

4.6. Photoelectrochemical measurement of solar cell

A TiO_2 solar cell was prepared as shown in Fig. 6. A drop of 3-methoxypropionitrile solution containing lithium iodide (0.5 mol dm^{-3}), iodine (0.05 mol dm^{-3}), and of *t*-butylpyridine (0.5 mol dm^{-3}) was used as an electrolyte. All the photoelectrochemical measurements were performed on a Bunko-Keiki CEP-2000 system.

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