Utilization of Carboxylated 1,3-Indandione as an Electron Acceptor in Dye-Sensitized Solar Cells

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The performance of dyes containing carboxylated 1,3-indandiones as electron acceptors was examined. The compounds that included a monocarboxylic group on the 1,3-indandione moiety showed good overall power conversion efficiencies (ca. 2.38%), the values of which were comparable to those of cyanoacrylate derivatives with the same donor–π-linker structure.

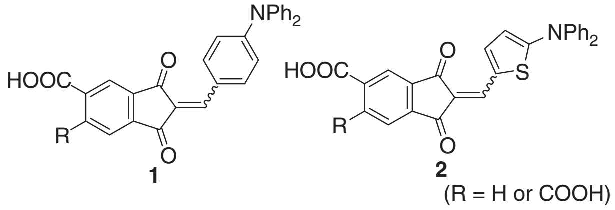
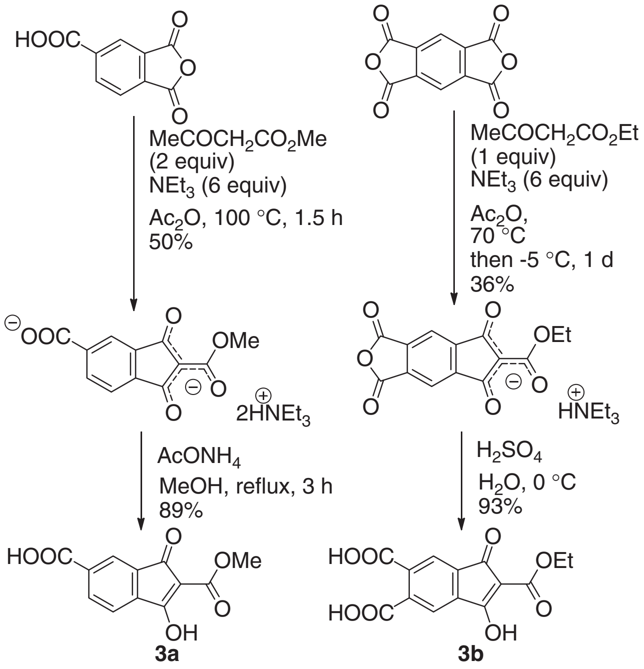


Chart 1.



Scheme 1. Synthesis of 1,3-indandione derivatives **3**.

Dye-sensitized solar cells (DSSCs) have attracted considerable attention since Grätzel's report[1] in 1991 on their easy production compared to conventional semiconductor-type solar cells. Sensitizers containing ruthenium, such as N3,[2] N719,[3] and black dye,[4] showed efficiencies of up to ca. 11% under AM 1.5 irradiation.[5] There is also increasing interest in metal-free organic sensitizers because of the expense and difficulty associated with the purification of ruthenium–metal complexes. Many organic sensitizers have been examined,[6] and most of the efficient organic dyes contain donor–π–acceptor (D–π–A) structures. Wang and co-workers achieved a high conversion efficiency (ca. 10%) using thienothiophene derivatives connected with a diphenylamino moiety as the donor and cyanoacrylic acid as the acceptor.[7] Various donating groups have been investigated, and aryl amine groups such as diphenylamine, (difluorenyl)phenylamine, and indole are among the best donors for DSSCs.[8] On the other hand, the variation on the acceptor side is rather limited; the cyanoacrylic acid group is one of the most useful acceptors. To achieve more efficient dyes, the developments of electron-accepting groups must be necessitated.

1,3-Indandione has a planar structure with a benzene ring connected to two carbonyl groups, and contains an active methylene moiety to facilitate the elongation of π-conjugation by condensation with aldehydes. In addition, because of its electron-withdrawing strength, 1,3-indandione is employed as an acceptor to produce nonlinear optical (NLO) chromophores.[9] However, to the best of our knowledge, there has been no report on the utilization of the 1,3-indandione structure as an organic sensitizer for DSSCs. Herein, we report a study on the photovoltaic ability of D–π–A-type chromophores **1** and **2** containing 1,3-indandiones (Chart 1). We selected the diphenylamino group as the donor part, and phenylene and thienylene as π-linkers because of the synthetic facility and the easy comparison with another dyes. Mono- and dicarboxylated derivatives of 1,3-indandione were examined because the number of carboxylic groups would affect both the electronic properties and the interaction with the TiO_2 surface. For instance, perylene dyes were used as sensitizers through the formation of two carboxylic groups by opening the carboxylic anhydride ring onto the TiO_2 surface.[10]

The synthesis of carboxylated 1,3-indandiones was reported by Rotbergs (for monocarboxylate derivative)[11] and Krief (for dicarboxylate derivative).[12] The monocarboxylated derivative **3a** could be prepared in 45% yield (two steps) according to the reported procedure (Scheme 1). Introduction of active methylene to pyromellitic dianhydride proceeded in 36% yield by warming the mixture to 70 °C to dissolve the pyromellitic dianhydride in the acetic anhydride prior to the addition of other reagents, whereas 18% yield was obtained by the mentioned procedure.[12] The protonation of the monocondensation product proceeded easily to give dicarboxylated derivative **3b** in 93% yield. In addition, **1** and **2** were synthesized

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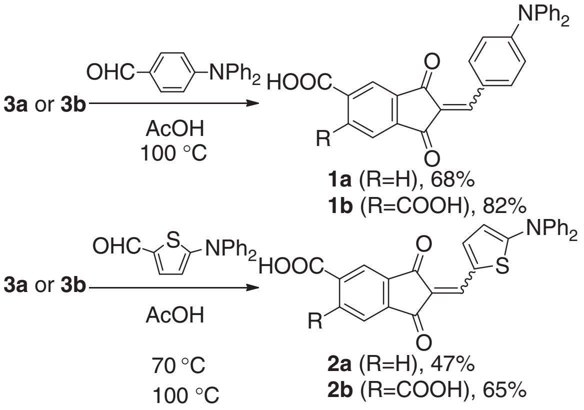
Table 1. Physical Properties and DSSC Performance Parameters of **1a**, **1b**, **2a**, and **2b**

Compound	λ_{max}/nm (ε_{max}/M^{-1} cm^{-1})$^{a)}$	E_{HOMO} /eV$^{b)}$	Edge of absorption/nm	E_{LUMO} /eV$^{c)}$	J_{SC} /mA cm$^{-2\,d)}$	V_{OC} /V$^{d)}$	$ff^{d)}$	η /%$^{d)}$
1a	492 (49400)	−5.73	546	−3.46	5.46	0.66	0.66	2.38
2a	525 (66500)	−5.78	566	−3.59	5.87	0.60	0.62	2.20
1b	503 (40400)	−5.70	564	−3.50	3.32	0.57	0.67	1.26
2b	547 (67500)	−5.62	596	−3.54	4.00	0.55	0.64	1.40
N719	—	—		—	12.68	0.77	0.54	5.29

a) Measured in THF (3.0×10^{-5} M). b) Measured with photoemission yield spectroscopy on RIKEN KEIKI AC-1. c) Estimated from E_{HOMO} and the edge of absorption (λ) by the equation of E_{LUMO} (eV) = E_{HOMO} (eV) + 1240/λ (nm). d) DSSC performances were measured under AM 1.5 irradiation.



Scheme 2. Formation of D–π–A chromophores **1** and **2**.

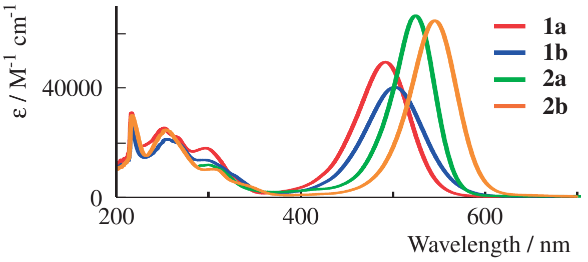


Figure 1. Absorption spectra of **1a**, **1b**, **2a**, and **2b** in THF (3.0×10^{-5} M).

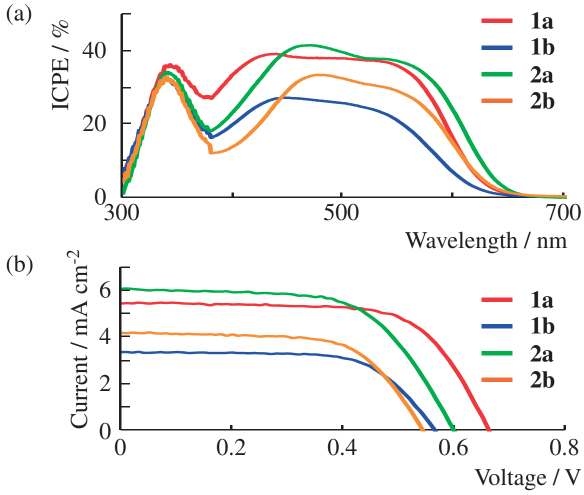


Figure 2. (a) *J*–*V* characteristics and (b) IPCE spectra of DSSCs based on **1a**, **1b**, **2a**, and **2b**.

in moderate to good yields by the condensation reaction of **3** with the corresponding aromatic aldehydes (Scheme 2).

The absorption spectra of **1** and **2** were measured in THF (Table 1 and Figure 1). The maximum absorption (λ_{max}) of the monocarboxylated compound with a phenylene linker (**1a**) was observed at 492 nm with a high molecular absorption coefficient (ε_{max}). Upon introduction of another carboxylic group at the benzene ring of the 1,3-indandione moiety (**1b**), λ_{max} was shifted by about 11 nm to a longer wavelength. This is because the additional carboxylate has electron-withdrawing character. A further bathochromic shift was achieved by changing the π-linker from phenylene to thienylene, which resulted in absorption peaks at 526 and 547 nm in **2a** and **2b**, respectively. Increases in ε_{max} were also observed. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy-level composition lies on the proper level for the TiO_2–I^-/I_3^- system (Table 1). The LUMO levels of all the compounds were sufficiently more positive than the conduction band (CB) energy level of TiO_2 (−4.16 eV),[13] implying that electron injection into the CB of TiO_2 is feasible. The HOMO levels were also able to accept electrons from the iodine/iodide redox system (−4.85 eV AVS (absolute vacuum scale))[14] after electron injection into the CB of TiO_2. The photocurrent density–voltage (*J*–*V*) curves and incident photon-to-current conversion efficiency (IPCE) spectra are shown in Figure 2, and the DSSC performance results are summarized in Table 1. We found that the 1,3-indandione structure with a carboxylate moiety worked as the electron-accepting part for the DSSCs. The maximum IPCE value of **1a** was 39% at 439 nm, and the wavelength range of the photocurrent active zone was from 390 to 650 nm. The cell with **1a** showed a short-circuit current density (J_{SC}) of 5.46 mA cm^{-2}, an open-circuit voltage (V_{OC}) of 0.66 V, and a fill factor (*ff*) of 0.66, leading to an overall power conversion efficiency (η) of 2.38% based on the device performance of $\eta = 5.29\%$ for N719. 3-[4-(Diphenylamino)phenyl]-2-cyanoacrylic acid, which comes from the conversion of the 1,3-indandione moiety of **1a** into cyanoacrylic acid, showed resembling properties on J_{SC} and V_{OC} (Table S1). But its *ff* gave a slightly smaller value than **1a**, which suggests that the efficient conversion can be achieved in **1a**. And an overall power conversion efficiency of 3-[4-(diphenylamino)phenyl]-2-cyanoacrylic acid is 1.2–2.79% (compared to 3.1–8.04% for N719).[15] Therefore, the 1,3-indandione acceptor has a comparable ability to that of cyanoacrylate for use in DSSCs. The wavelength range of the thienylene derivative **2a** was shifted to longer wavelengths than that of **1a**. This is rationalized by the bathochromic shift of $\lambda_{\rm max}$ observed between **1a** and **2a**. The $J_{\rm SC}$ value of **2a** increased to 5.87 mA cm^{-2}, whereas $V_{\rm OC}$ decreased by 0.60 V. As a result, η of **2a** (2.20%) was smaller than that of **1a**.

Low efficiencies were obtained for **1b** and **2b**. A decrease of IPCE was observed with decreasing conversion efficiency, even though the $\varepsilon_{\rm max}$ of **1b** and **2b** showed the same value on that of **1a** and **2a**, respectively. To find the reason for the inefficient performances, the effect of the addition of DCA (deoxycholic acid) was examined to suppress dye aggregation on TiO_2 surface by coadsorption.[16] However, the same performances in **1b** were observed either with or without DCA. Therefore, the aggregation of the dyes was not influenced. We carried out a study using density functional theory (DFT) calculations at the B3LYP/6-31+G* level (Figure S1). The geometry of the double bond in **1a** was not affected on the orbital shapes and energy levels of the HOMO and the LUMO. Both the HOMOs of **1a** and **1b** lie on the donating diphenylamino group and the phenylene linker, and the LUMOs spread to the carboxylic group attached to the 1,3-indandione moiety, which allows facile electron transfer from the excited dye to TiO_2. However, only one carboxylic moiety is involved in the LUMO of **1b**, although there are two carboxylic groups. The energy levels of LUMO+1 of **1b**, which lies in both carboxylic moieties, is higher than that of the LUMO. In the case of **1b**, both carboxylic groups can be applied as the anchor to connect to TiO_2, but, because of the problems of dianion formation and/or the proper distance on TiO_2 for connecting both anchors, **1b** may be connected to TiO_2 using only one carboxylic groups which is not selective whether the LUMO is possessed or not. Therefore, the only compound connected with carboxylate possessing the LUMO orbital will be utilized to transfer the electron to TiO_2 efficiently because of orbital correlation restrictions. It is the reason for the low efficiencies observed for **1b** and **2b**.

In summary, we synthesized dyes **1a**, **1b**, **2a**, and **2b** containing a 1,3-indandione structure with a carboxylic moiety as an acceptor for DSSCs. All the materials showed photovoltaic sensitizing abilities with $\eta \approx 2.38\%$. It is shown that the 1,3-indandione derivatives possess a comparable ability to the well-examined cyanoacrylic acid group. We examined the effect of the additional carboxylic group on 1,3-indandione, and found that a decrease in η was obtained in spite of the bathochromic shift of the absorption spectra compared to those of the monocarboxylated materials. Further investigations to improve the performance of DSSCs based on the 1,3-indandione structure are underway.

Supporting Information

Experimental procedure of **1**, **2**, fabrication and comparison of DSSCs, and results of DFT calculation. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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