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## Novel Near-Infrared Carboxylated 1,3-Indandione Sensitizers for Highly Efficient Flexible Dye-Sensitized Solar Cells

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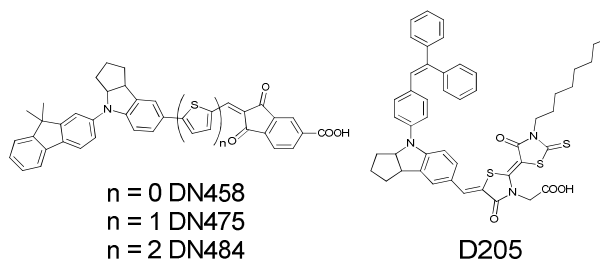
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**Three novel metal-free organic dyes (DN458, DN475 and DN484) were designed for use in plastic-substrate dye-sensitized solar cells (PDSCs). The photoelectric conversion region of DN475 was successfully expanded into the near-infrared region. As a result, an energy conversion efficiency of 5.76% was achieved.**

Dye-sensitized solar cells (DSCs) have been extensively studied for use as next-generation solar cells because they can be produced using inexpensive materials and processes.<sup>1</sup> A conversion efficiency exceeding 12% has recently been reported for a DSC on a glass substrate.<sup>2</sup> However, as a substrate, plastic films have several benefits over glass; for example, plastic film is lightweight, flexible and crack-resistant, making it easy to handle.<sup>3</sup> But the conversion efficiency of plastic-substrate dye-sensitized solar cells (PDSCs) is lower than that of DSCs on glass substrates. Because TiO<sub>2</sub> photoelectrodes cannot be prepared by high-temperature sintering (≈150°C) in PDSCs, the following limitations arise: (1) no multilayer-structured TiO<sub>2</sub> photoelectrode can be produced, which is optically disadvantageous, and (2) TiO<sub>2</sub> photoelectrodes should be thin films because TiO<sub>2</sub> particles in TiO<sub>2</sub> photoelectrodes exhibit low conductivity. To improve conversion efficiency, various methods have been studied for producing TiO<sub>2</sub> photoelectrodes. For example, a conversion efficiency exceeding 6% has been attained using a Ru dye with a high absorption coefficient (N719, etc.) and a thin-film TiO<sub>2</sub> photoelectrode.<sup>4</sup> Furthermore, we have prepared TiO<sub>2</sub> photoelectrodes using the flat press method with a Ru dye (black dye) and an organic dye (N15) with a co-sensitized PDSC to achieve a high conversion efficiency of 8.3%.<sup>5</sup>

Although current PDSCs that use organic dyes have lower

performance compared to PDSCs that use Ru-based dyes,<sup>3b</sup> metal-free organic dyes pose fewer environmental hazards and entail no resource constraints. In addition, organic dyes exhibit a wide absorption range with high optical absorption coefficients; thus, they are promising for use as dyes in PDSCs. For example, T. Miyasaka et al. have reported a conversion efficiency of 5.2% for a PDSC using D205.<sup>6</sup> To improve the performance of PDSCs that use organic dyes, it is essential to use both the visible and the near-infrared (NIR) regions of light.<sup>7</sup> In this study, we seek a new direction in molecular design towards creating efficient donor- $\pi$ -acceptor (D- $\pi$ -A) dye sensitizers with carboxylated 1,3-indandione groups. In particular, we have designed and synthesized a series of new indoline dye sensitizers that possess different numbers of thiophene units that serve as a  $\pi$ -conjugation bridge between an indoline skeleton, as the electron donor, and a carboxylated 1,3-indandione group,<sup>8</sup> as the acceptor. By introducing different numbers of thiophene units, we established a relation between the wavelength extended into the NIR region and electron lifetime. As a result, we achieved an energy conversion efficiency of 5.76%. This conversion efficiency is the highest among those reported so far for PDSCs that use metal-free organic photosensitizing dyes.



**Scheme 1** Chemical structures of D- $\pi$ -A dye sensitizers **DN458**, **DN475**, **DN484** and **D205**.

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Table 1. Optical and electrochemical properties of **DN458**, **DN475**, **DN484** and **D205**.

Dye	$\lambda_{\max}$ ( $\epsilon$ ) <sup>a</sup>	$F_{\max}$ <sup>a</sup>	$E_{0-0}$ <sup>b</sup>	$E_{\text{HOMO}}$ <sup>c</sup>	$E_{\text{LUMO}}$
DN458	327 (8 700)	638	2.12	0.83	-1.29
	540 (50 000)				
DN475	372 (20 800)	713	1.86	0.72	-1.14
	610 (42 000)				
DN484	389 (24 600)	663	1.93	0.78	-1.15
	605 (37 000)				
D205	395 (34 400)	637	2.08	0.92	-1.16
	552 (76 500)				

<sup>a</sup> Measured on  $1.0 \times 10^{-5}$  mol dm<sup>-3</sup> of substrate in chloroform at 25°C. <sup>b</sup>  $E_{0-0}$  was estimated from the intersection wavelength of absorption and luminescence spectra. <sup>c</sup> All potentials are given vs. SCE. Oxidation potentials of **DN458**, **DN475**, **DN484** and **D205** were measured in DMF containing 0.1 M LiClO<sub>4</sub>.

The absorption spectra of **DN458**, **DN475**, **DN484** and **D205**<sup>9</sup> (Scheme 1) in chloroform are shown in Fig. 1, and their spectral data are summarized in Table 1. The dyes **DN475** and **DN484** in chloroform showed a strong absorption band in the vicinity of 610 nm, which was assigned to intramolecular charge-transfer (ICT) excitation from the electron-donor moiety (indoline group) to the electron-acceptor moiety (carboxylated 1,3-indandione). The absorption maxima ( $\lambda_{\text{absmax}}$ ) for the ICT band of **DN475** and **DN484** occurred at a longer wavelength by ca. 70 nm than that of **DN458** and **D205**. The molar extinction coefficient ( $\epsilon$ ) for the ICT band of **DN475** and **DN484** were ca. 42,000 and 37,000 M<sup>-1</sup> cm<sup>-1</sup>, which were lower than those of **DN458** and **D205** (ca. 50,000 and 76,500 M<sup>-1</sup> cm<sup>-1</sup>). Moreover, **DN475** and **DN484** appeared to be blue in colour because of their weak absorption at 400–500 nm. The expansion of the conjugated system of the indoline group by introducing thiophene units between the donor and acceptor groups caused a redshift and broadening of the ICT band.

The absorption spectra of the dyes adsorbed on a TiO<sub>2</sub> film are shown in Fig. 2. The wavelengths of the absorption peaks for **DN458**, **DN475**, **DN484** and **D205** are blue-shifted by 65 nm, 105 nm, 100 nm and 18 nm, respectively, compared with those in chloroform.

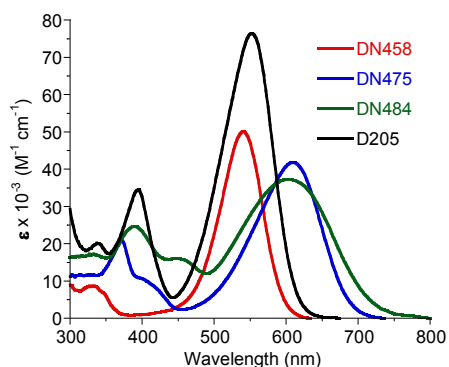


Fig. 1 Molar absorptivity spectra of **DN458**, **DN475**, **DN484** and **D205** in chloroform.

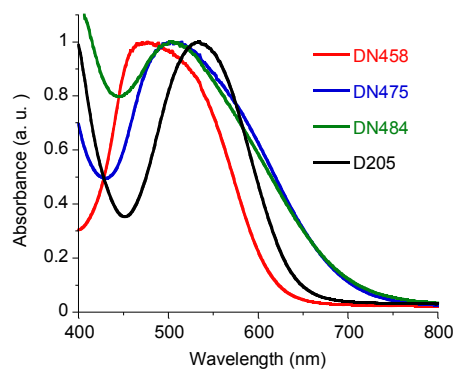
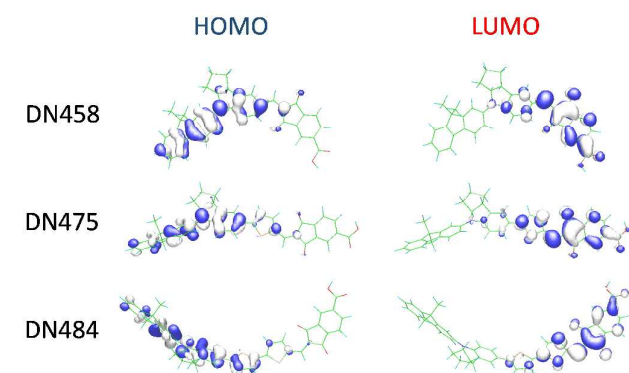


Fig. 2 Normalized absorption spectra of **DN458**, **DN475**, **DN484** and **D205** adsorbed on the TiO<sub>2</sub> film (film thickness: 4  $\mu\text{m}$ ).

Electrochemical measurements were conducted to determine the energy levels of HOMOs of **DN458**, **DN475**, **DN484** and **D205**. Quasi-reversible oxidation waves corresponding to oxidation were observed at 0.83, 0.72, 0.78 and 0.92 V vs. SCE in DMF solutions of **DN458**, **DN475**, **DN484** and **D205**, respectively (Table 1). The energy levels of HOMOs for **DN458**, **DN475**, **DN484** and **D205** were 0.72–0.92 V vs. SCE, thus indicating that all these dyes have similar energy levels of HOMO that are more positive than the I<sub>3</sub><sup>-</sup>/I<sup>-</sup> redox potential ( $\approx 0.2$  V vs. SCE). This certifies an efficient regeneration of the oxidized dyes by electron transfer from the I<sub>3</sub><sup>-</sup>/I<sup>-</sup> redox couple in the electrolyte. The lowest transition energies ( $E_{0-0}$ ) of **DN458**, **DN475**, **DN484** and **D205** were 2.12, 1.86, 1.93 and 2.08 eV, respectively, as calculated from the intersection wavelength of the absorption and luminescence spectra (Fig. S1). Accordingly, the LUMO energy levels of **DN458**, **DN475**, **DN484** and **D205** were -1.29, -1.14, -1.15 and -1.16 (vs. SCE), respectively (Table 1). The LUMO energy level of **DN458** was more negative than that of **D205**, while those of **DN475** and **DN484** were nearly at the same level. This suggests that electron injection from the photoexcited **DN458**, **DN475** and **DN484** into the conduction band of TiO<sub>2</sub> is thermodynamically possible. These results indicate that the energy levels of HOMOs and LUMOs of **DN458**, **DN475** and **DN484** are suitable for both effective electron injection from the excited states of dyes into the conduction band of TiO<sub>2</sub> and effective reduction of the resulting oxidized forms of dyes by I<sup>-</sup> in the electrolyte solution.

Frontier molecular orbitals of **DN458**, **DN475** and **DN484** are shown in Fig. 3 and Fig. S2. HOMOs (HOMO and HOMO-1) of **DN458**, **DN475** and **DN484** were localized mainly at indoline groups.

LUMOs (LUMO and LUMO-1) of **DN458**, **DN475** and **DN484** were



**Fig. 3** Frontier molecular orbitals (HOMO and LUMO) of **DN458**, **DN475** and **DN484** calculated by DFT/B3LYP/6-31+G\*.

mainly at the carboxylated 1,3-indandione groups and were stabilized largely by the presence of carboxyl groups. These results suggest that electron transfer from the indoline group to the carboxylated 1,3-indandione group, which led to electron injection into the conduction band of TiO<sub>2</sub>, is thermodynamically favourable. Solar cell performances of PDSCs using **DN458**, **DN475**, **DN484** and **D205** are summarized in Table 2 and Fig. S3. The PDSC with **DN475** showed a 5.76% conversion efficiency, which is higher than that obtained for PDSCs with **DN458** and **DN484**. This higher conversion efficiency of **DN475** is attributed to the much higher short-circuit current ( $J_{sc}$ ). The incident photon-to-current conversion efficiency (IPCE) obtained for **DN475** was extended into the NIR region (ca. 900 nm) at a longer wavelength than that of **DN458** (Fig. 4). Although a value for IPCE of PDSC with **DN484** was observed in the NIR region, the value was lower than that for **DN475**. In addition, the conversion efficiency of **DN475** was higher than that of **D205**, which demonstrates that the strategy of expanding the absorption region of a dye to longer wavelengths can lead to a higher performance of PDSCs.

The highest values of the IPCE for the dyes of **DN458**, **DN475** and **D205** decrease in the following order: **DN458**>**D205**>**DN475**. If the  $\Delta G$  between the LUMO of the dye and the conduction band of TiO<sub>2</sub> is small, recombination increases and the value of IPCE decreases when TBP is added to electrolyte.<sup>10</sup> In other words, for TBP-containing electrolytes, **DN458** behaves differently from the other dyes because there is a large  $\Delta G$  between the dye LUMO and TiO<sub>2</sub> conduction band and, consequently, the value of IPCE does not decrease. In contrast,  $\Delta G$  is small for both **D205** and **DN475**, and this means that these dyes are significantly affected by the presence of TBP; hence, recombination increases and, in turn, the IPCE decreases.

To gain further insight into the lower conversion efficiency and the IPCE value of PDSC with **DN484**, electron lifetimes in the TiO<sub>2</sub> photoelectrodes of PDSCs with **DN458**, **DN475**, **DN484** and **D205** were investigated using open-circuit voltage decay (OCVD) measurements. The electron lifetimes in the TiO<sub>2</sub> photoelectrodes of the PDSC with **DN484** were found to be much shorter than those of **DN458**, **DN475** and **D205** at the matched  $V_{oc}$  value (Fig. 5). These results indicate that backward electron transfer reactions were promoted in **DN484** compared with those in **DN458**, **DN475** and **D205**. Although the energy

level of the LUMO for **DN484** was more negative than that for **DN475**, the shorter electron lifetime is considered to be the major reason for the lower  $V_{oc}$  value for **DN484**. The lower  $J_{sc}$  value for **DN484** can also be reasonably explained by this shorter electron lifetime.

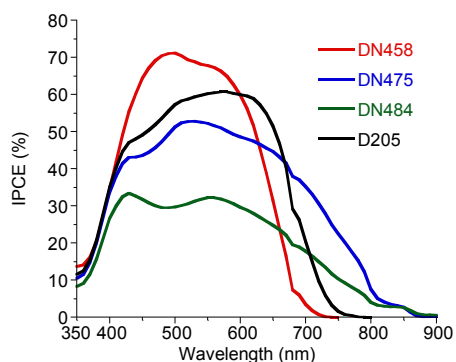
For application in PDSCs, we have synthesized three novel metal-free organic sensitizers; each contains a carboxylated 1,3-indandione group and an indoline group linked by thiophene groups serving as  $\pi$ -conjugated bridges. To increase conversion efficiency, our strategy here is to extend the absorption region to longer wavelengths. The PDSC with **DN475** showed a 5.76% conversion efficiency, which is higher than that with the **D205** benchmark (5.44%). To the best of our knowledge, this is the highest efficiency obtained to date for PDSCs based on metal-free organic sensitizers. The advantage of these organic sensitizers is that they can be modified in several ways to obtain still higher efficiencies and superior light-harvesting properties in the NIR region. We are currently investigating the optimization of the donor component and cell fabrication. In addition, the PDSC using **DN475** appears to be blue in colour. High-level efficiencies and design properties are required for practical application of PDSCs, and the findings from this study should contribute towards realizing those applications. On the other hand, the TiO<sub>2</sub> photoelectrodes used for PDSC has a lower conductivity than that used for the glass substrate. For example, if TiO<sub>2</sub> layers grown in a one-dimensional manner, and used for glass substrate, are employed, performance of PDSCs can be improved.<sup>11</sup>

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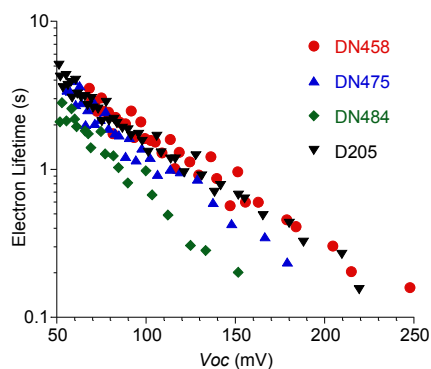
**Table 2.** Solar-cell performance of PDSCs with **DN458**, **DN475**, **DN484** and **D205**<sup>a</sup>.

Dye	$J_{sc}$ [mA cm <sup>-2</sup> ]	$V_{oc}$ [V]	FF [-]	$\eta$ [%]
DN458	12.56	0.695	0.598	5.18
DN475	13.57	0.684	0.625	5.76
DN484	5.89	0.459	0.524	1.45
D205	11.57	0.694	0.679	5.44

<sup>a</sup> The electrolyte was an acetonitrile solution containing 0.05 M I<sub>2</sub>, 0.1 M LiI, 0.6 M EMImI and 0.005 M TBP. The TiO<sub>2</sub> film thickness and active area were 6  $\mu$ m and 0.25 cm<sup>2</sup>, respectively. Irradiation was performed using a solar simulator (AM 1.5, 100 mW cm<sup>-2</sup>).



**Fig. 4** IPCE spectra of PDSCs based on **DN458**, **DN475**, **DN484** and **D205**.



**Fig. 5** Electron lifetimes as a function of  $V_{oc}$  of the PDSCs with **DN458**, **DN475**, **DN484** and **D205**.

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