



Design of high-performance dye-sensitized solar cells by variation of the dihedral angles of dyes



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ABSTRACT

Two new metal-free organic sensitizers (i.e., IAH and IDH) based on a D- π -A configuration were designed to elucidate the effect of the alkyl chain location at the thiophene π -bridge on their photovoltaic performance. IAH, in which the alkyl chain is closer to the acceptor moiety, is more planar than IDH, in which the alkyl chain is closer to the donor moiety. Therefore, IAH induces more effective π -conjugation and electron injection from the dye excited state to the TiO₂ conduction band, leading to a higher short-circuit photocurrent (J_{sc}). In contrast, IDH more effectively inhibits electron transfer from the conduction band of TiO₂ to the dye excited state, resulting in a higher open-circuit photovoltage (V_{oc}). Under standard AM 1.5 simulated sunlight, the IAH-based cells exhibited an overall conversion efficiency of 6.90%; this value is higher than that of the IDH-sensitized cells, which reached 86% of the conversion efficiency of N719 cells.

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1. Introduction

Dye-sensitized solar cells (DSSCs) are intensively investigated because of their cost-effectiveness and ability for application in flexible devices.^{1,2} In 2005, DSSCs employing ruthenium complexes as sensitizers achieved a power conversion efficiency (η) greater than 12% under a standard global air mass of 1.5.³ Meanwhile, metal-free organic dyes, which usually feature an electron donor- π bridge-electron acceptor (D- π -A) configuration, are widely used because of their low material costs, easy synthetic routes, high molar extinction coefficients, and environmental friendliness, especially compared to ruthenium-based dyes.^{4–7} Over the past decade, many kinds of organic dyes with D- π -A configurations have been explored for DSSCs.^{8–13} It is well known that controlling the assembly morphology of sensitizers on the TiO₂ surface facilitates electron injection and suppresses charge recombination.^{14,15} The introduction of alkyl chains to dye skeletons based on thiophene or its derivatives has proven to be an effective method for improving DSSC performance because they prevent dye aggregation and reduce charge recombination between the TiO₂ semiconductor and electrolyte.^{16–20} However, depending on their location in the dye, alkyl chains may increase

the dihedral angle between the donor and π -bridge moieties; this could reduce the planarity of the molecular structure, impede efficient intramolecular charge transfer, and influence electron injection to the TiO₂ conduction band, which may reduce the short-circuit photocurrent (J_{sc}). Therefore, it is vital to determine the optimal position of the alkyl chains to improve device performance. This study examines the effect of the alkyl chain location in two indole-based D- π -A dyes (i.e., IDH and IAH; Fig. 1) with n-hexyl substitution at the π -bridge on DSSC performance. Compared to IDH, the J_{sc} of IAH increased significantly, from 12.77 to 16.16 mA cm⁻²; however, the open-circuit voltage (V_{oc}) decreased by 50 mV from 680 to 630 mV. The average efficiency of IAH-based DSSCs is 6.90% with an I⁻/I₃⁻-based electrolyte under AM 1.5 simulated sunlight; in contrast, the average efficiency of IDH-based DSSCs is only 6.27%. The structures of the dyes are shown in Fig. 1.

2. Results and discussion

2.1. Photophysical properties

The UV-vis absorption spectra of IAH and IDH in chloroform at room temperature are shown in Fig. 2a, and the corresponding data are summarized in Table 1. Compared to that of IDH, the spectrum of IAH shows a red-shifted absorption maximum peak (λ_{max}) and higher corresponding molar absorption coefficients (ϵ); this was attributed to the differences of the dihedral angles between the

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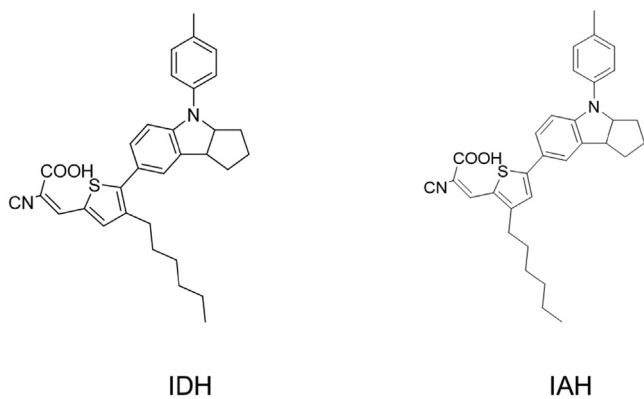


Fig. 1. Structures of IDH and IAH.

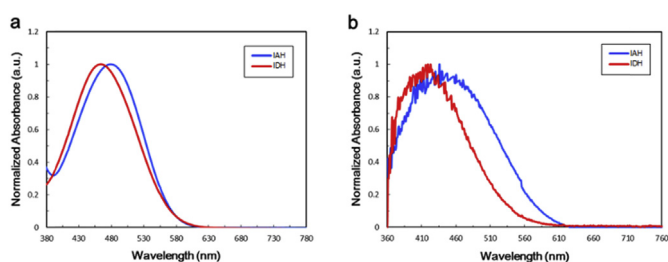


Fig. 2. Absorption spectra of IDH and IAH (a) in chloroform solution (5.0×10^{-5} M) and (b) on TiO_2 film (5 μm).

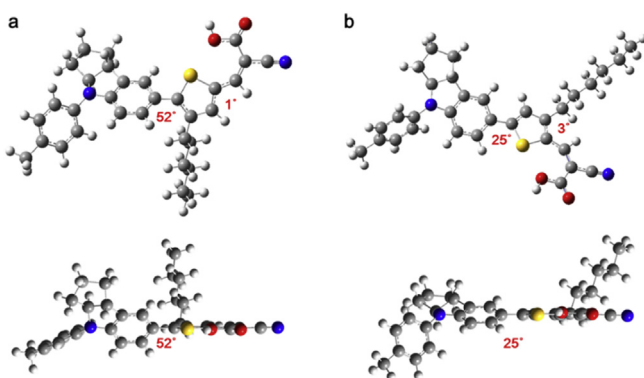


Fig. 3. Dihedral angles of IDH (a) and IAH (b).

donor and π -bridge moieties (see Fig. 3).

The steric hindrance between an electron donor part and π -bridge depends on the location of alkyl chains. The dihedral angle of IDH, where the alkyl chain is closer to the donor part, is 52° which is much bigger than that of IAH (25°). The more twisted molecular structure of IDH leads to a lower absorption maximum and molar absorption coefficients when compared to IAH.

Table 1
The absorption spectral data of two dyes.

	λ_{max} (nm) ^a	λ_{max} (nm) ^b	The degree of blue shift (nm)	ϵ , $\text{M}^{-1} \text{cm}^{-1}$	E_{0-0}
IAH	480	436	44	67,900	2.16
IDH	465	423	42	57,980	2.17

^a In chloroform solution (5.0×10^{-5} M).

^b On TiO_2 film (5 μm).

The absorption peaks of the two dyes adsorbed on TiO_2 exhibit similar blue-shifts (Fig. 2b) as those evident in the corresponding solution spectra. This phenomenon was ascribed to deprotonation of the carboxylic acid groups and intermolecular aggregation.²¹

2.2. Electrochemical properties

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of dyes play a crucial role in electron injection to the conduction band (E_{cb}) of TiO_2 and dye regeneration during device operation.²² The electrochemical properties of IAH and IDH were studied using CV in DCM solutions containing 0.1 M TBAPF₆ as the supporting electrolyte and calibrated with respect to ferrocene (Fig. 4). The LUMO levels of IDH and IAH were estimated to be -2.84 and -3.03 eV, respectively; these values are much higher than the energy level of the conduction band of TiO_2 (-4.26 eV), which ensures efficient charge injection from the dye excited state to the TiO_2 conduction band. The HOMO levels of IDH and IAH are -5.01 and -5.19 eV, respectively, and are lower than the energy level of the I^-/I_3^- redox couple in the electrolyte (-4.92 eV); thus, they are suitable to complete the circuit of the device and regenerate the dyes.

To further elucidate the photophysical properties of the two dyes, DFT calculations were performed at the B3LYP/6-31G level; the results are shown in Fig. 5. The HOMOs are delocalized throughout the entire π -conjugated system, while the LUMOs are localized on the cyanoacrylic acid and thiophene groups. From these results, we assume that intramolecular charge transfer between the donor and acceptor would be favorable, allowing efficient electron injection from the dye to the conduction band of the TiO_2 semiconductor.

2.3. Photovoltaic performance of the DSSCs

To ensure a valid comparison, all the dyes were used in the fabrication of DSSCs and tested under the same conditions. The J-V curves of the DSSCs are illustrated in Fig. 6. IAH with E1 (DMPII 0.6 M, LiI 0.1 M, I_2 0.03 M, TBP 0.5 M, and acetonitrile only) as the sensitizer produced a J_{sc} of 16.16 mA cm^{-2} , V_{oc} of 0.68 V, fill factor (FF) of 0.68, and performance up to 6.90%, which is comparable to that of N719 (8.02%). Under the same conditions, the IDH-based DSSC offered a J_{sc} of 12.77 mA cm^{-2} , V_{oc} of 0.72 V, FF of 0.72, and performance up to 6.27%. The conversion efficiency (η) of IAH was higher than that of IDH by $\sim 10\%$ because of the larger J_{sc} , even though the V_{oc} was smaller (see Table 2).

The broader range of light absorption for IAH compared to that of IDH (Fig. 2b) may contribute to the higher J_{sc} , as confirmed by the IPCE spectra (Fig. 7). The IPCE curve of the IAH dye revealed a broad response from 340 to 740 nm with a peak value of 66% at ~ 440 nm. Compared with IAH, IDH presented a slightly lower maximum IPCE value (64% at 440 nm), and the response band was much narrower. Therefore, the slightly lower J_{sc} of IDH was reasonable. In the case of N719, although it showed the broadest spectrum, the maximum values were relatively low, which led to a lower J_{sc} (15.12 mA cm^{-2}) than that of IAH (16.16 mA cm^{-2}).

There were no significant differences in the dye loading

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