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New D–A– π –A organic sensitizers for efficient dye-sensitized solar cells†

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Four novel metal-free D–A– π –A organic sensitizers (ND01–ND04) based on *N*-annulated perylene (NP) derivatives as efficient electron donors for dye-sensitized solar cells (DSSCs) are designed. Among them, ND02 featuring bulky 4-methoxyphenyl as the additional electron-donating substituents on the NP unit shows a power conversion efficiency as high as 8.30%.

Since the seminal paper published by Grätzel and co-workers in 1991,¹ dye-sensitized solar cells (DSSCs) have gained considerable attention in academic and industrial communities as alternatives to conventional silicon-based solar cells, owing to their low cost and easy fabrication process combined with high power conversion efficiencies (PCEs).² As one of the crucial components in DSSCs, the sensitizer exerts a significant influence on PCEs as well as the stability of the cells. Thus, tremendous efforts have been devoted to the development of new and highly efficient sensitizers through extending the absorption spectra and improving the charge mobility and light stability. To date, ruthenium polypyridine complexes-based DSSCs have showed a PCE of about 12%,³ while zinc porphyrin-based DSSCs maintained the record-breaking PCE of 13.0%.⁴ Particularly, pure metal-free organic sensitizers alternative to metal-complex counterparts have drawn increasing attention due to their low cost without noble metal, easy molecular tailoring, tunable spectral properties, and comparable PCEs.⁵ In general, most organic sensitizers have a donor– π –acceptor (D– π –A) configuration featuring intramolecular charge transfer (ICT) properties.⁶ Further tailoring molecular structures and optimizing energy levels to improve the photovoltaic

performance can be achieved *via* incorporating an additional electron-withdrawing unit such as diketopyrrolopyrrole (DPP),⁷ benzothiadiazole,⁸ and isoindigo⁹ between the donor and the π -bridge as an auxiliary acceptor, which is termed the D–A– π –A configuration.¹⁰

The donor groups have a substantial effect on the cell performance because they not only affect the absorption spectra but also adjust the energy levels of the sensitizers.¹¹ Even the subtle changes in the structure of the donors may lead to notable improvement in the performance of the sensitizers. Although several organic chromophores have been employed as donors in organic dyes, the efficient electron donors used in sensitizers with broad absorption spectra and high molar extinction coefficient are still scanty. Recently, Wu and our group independently reported several fused-conjugated compounds based on *N*-annulated perylene (NP),¹² the unique structural character and electro-rich nature of NP make them promising as electron donors for organic sensitizers.¹³

With this in mind, we have chosen NP as the electron donor to develop four new metal-free D–A– π –A organic sensitizers, namely ND01–ND04 (Fig. 1). In their structures, DPP was used as the auxiliary acceptor, thiophene as the π -linker, and cyanoacrylic acid as the acceptor moiety. While branched 2-ethylhexyl chains^{7a} were introduced into the amine site, both the NP and DPP moieties with the aim of improving the dye solubility and suppressing the

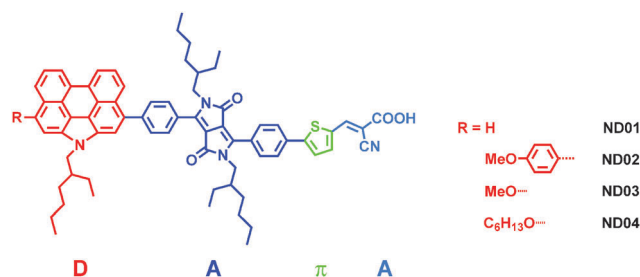


Fig. 1 Chemical structures of dyes ND01–ND04 with four parts: D (donor), A (auxiliary acceptor), π (π -linker); and A (acceptor moiety).

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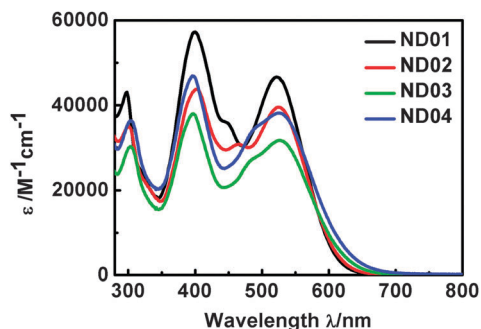


Fig. 2 Absorption spectra of **ND01–ND04** dyes in CHCl_3 .

dye aggregation. In addition, different substituents of varying electron-donating ability were attached on the *peri*-position of the NP unit for fine-tuning their photoelectronic properties and achieving excellent cell performances based on corresponding dyes. The facile synthesis of dyes **ND01–ND04** is described in detail in Scheme S1 (ESI[†]) in the supporting information.

The UV-vis absorption spectra of the four dyes in chloroform are shown in Fig. 2. All of these dyes exhibited similar and broad absorption spectra covering a wide range from 300 to 700 nm. The absorption spectra exhibited two major prominent fine absorption bands in the visible region, which can be ascribed to a localized aromatic π - π^* transition and ICT transition, respectively. As summarized in Table S1 (ESI[†]), the absorption maxima at low energy transition of **ND01–ND04** appeared at 522, 526, 527, 527 nm, respectively. Therefore, **ND02–ND04** dyes were slightly red-shifted by 4–5 nm relative to **ND01**, which can be interpreted that the additional electron-donating substituents (alkoxyl or 4-methoxyphenyl) incorporating into the *peri*-position of NP can further enhance the donor ability of NP and broaden the absorption spectrum. After anchoring on TiO_2 , all dyes showed similar absorption spectra with a few nanometer-shift hypsochromically to those of spectra measured in solution (Fig. S1, ESI[†]), which might be ascribed to the deprotonation of the carboxylic acid.¹⁴ The almost identical fine absorption peaks were observed with and without the co-adsorbent chenodeoxycholic acid (CDCA) on the TiO_2 film, which suggest that the aggregation is inhibited effectively due to the presence of the branched 2-ethylhexyl chains on the NP and DPP imide-positions (Fig. S2, ESI[†]).

The energy levels of **ND01–ND04** were investigated by cyclic voltammetry (Fig. S3, Table S1, ESI[†]). The LUMO levels of four dyes determined to be -1.27 , -1.39 , -1.36 and -1.30 V vs. NHE, respectively, which were more negative than the conduction band edge of TiO_2 (-0.5 V vs. NHE), indicating that the electron injection process from the excited dye molecule to the conduction band of TiO_2 is energetically favorable. In contrast to **ND01**, the LUMO levels of **ND02–ND04** with alkoxyl or 4-methoxyphenyl groups were more negative as expected. The HOMO levels of those four dyes were more positive than that of the iodide/triiodide (I^-/I_3^-) couple redox (0.4 V vs. NHE), ensuring an efficient regeneration of the oxidized dyes.

DSSCs were fabricated according to the literature procedure.¹⁵ The incident photo-to-current conversion efficiency (IPCE) spectra

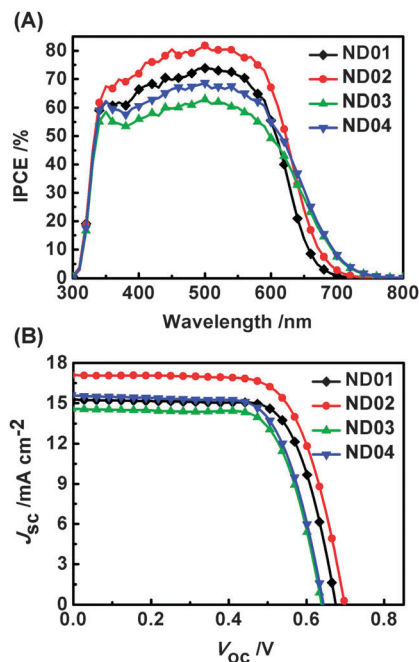


Fig. 3 IPCE spectra (A) and I - V curves (B) of DSSCs sensitized by **ND01–ND04** with liquid electrolyte.

of the DSSCs based on **ND01–ND04** are shown in Fig. 3(A). Compared to the absorption spectra of sensitized films, the IPCE spectra of **ND01–ND04** were broadened obviously, and maintained a high plateau in the wide range of 340–620 nm. It is worth noting that the IPCE of **ND02** exceeded 70% from 385 to 600 nm with a maximum value of 82%, indicating a high short-circuit photocurrent density (J_{sc}). However, the IPCE of **ND03** was lower than those of **ND01**, **ND02** and **ND04**, which might be due to the relatively lower molecular extinction coefficient of **ND03** (Table S1, ESI[†]), thus resulting in a relatively lower J_{sc} .

The photovoltaic performance was measured under the irradiation of AM 1.5 G (100 mW cm^{-2}) simulated solar light and the results are shown in Fig. 3(B) and Table 1. The **ND02**-sensitized solar cell produced the best results among the four dyes, with a J_{sc} of 17.14 mA cm^{-2} , an open-circuit voltage (V_{oc}) of 698 mV, a fill factor (FF) of 0.694 and a PCE as high as 8.30% whereas **ND01**, **ND03**, and **ND04** showed relatively lower PCEs of 7.46%, 6.69% and 7.01%, respectively. The high PCE of the **ND02**-sensitized solar cell is mainly ascribed to its relatively higher J_{sc} and V_{oc} compared to other dyes. The former is due to the higher IPCE values, and the latter can be explained by the fact that the bulky 4-methoxyphenyl group as an additional

Table 1 Photovoltaic performance of DSSCs based on four dyes, **ND01–ND04**, with a liquid electrolyte

Dye	J_{sc} [mA cm^{-2}]	V_{oc} [mV]	FF	PCE ^a [%]
ND01	15.29	675	0.723	7.46
ND02	17.14	698	0.694	8.30
ND03	14.60	639	0.717	6.69
ND04	15.59	643	0.699	7.01

^a Tested under irradiation of AM 1.5 G simulated solar light (100 mW cm^{-2}).

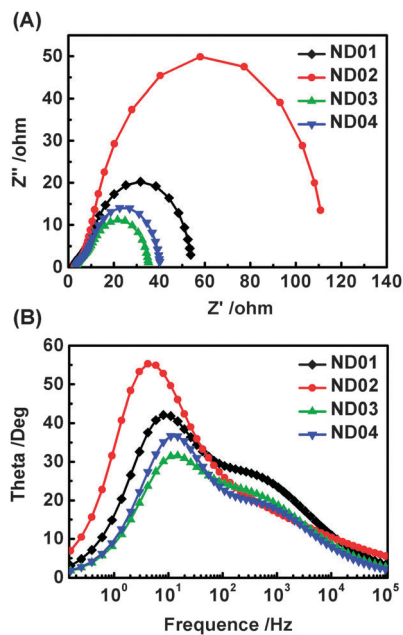


Fig. 4 EIS spectra of DSSCs tested at -0.6 V forward bias in the dark: (A) Nyquist and (B) Bode phase plots.

electron-donating substituent attaching on the NP donor unit is helpful to reduce the access of I_3^- ions to the TiO_2 surface, thus increasing the electron lifetime and V_{OC} .¹⁶ In addition, the J_{SC} and PCE values of the four dyes are basically consistent with their IPCE values.

Electrochemical impedance spectroscopy (EIS) was performed to elucidate the difference in the V_{OC} for the devices sensitized by these dyes. Two semicircles were observed in the Nyquist plots (Fig. 4(A)). The larger semicircle represents the charge-transfer resistance (R_{ct}) at the TiO_2 /dye/electrolyte interface. The radius of the larger semicircle and the corresponding R_{ct} values increased in the order **ND03** < **ND04** < **ND01** < **ND02**, which is well consistent with the increase of V_{OC} in the DSSCs based on **ND01–ND04**. In addition, the electron lifetime calculated from the Bode phase plots (Fig. 4(B)) also increased in the order **ND03** (10.7 ms) < **ND04** (14.3 ms) < **ND01** (19.6 ms) < **ND02** (37.9 ms), which further supported the order of V_{OC} in these devices. The largest R_{ct} and the longest electron lifetime for **ND02**-based DSSCs indicated that the bulky 4-methoxyphenyl group is beneficial to retard charge recombination and enhance V_{OC} as discussed above, which led to higher PCEs.

In summary, four new metal-free D–A– π –A organic sensitizers (**ND01–ND04**) based on NP derivatives as efficient electron donors were designed and synthesized for highly efficient DSSCs. The subtle chemical modification on the donor part with additional electron-donating substituents leads to great variations in device performances. The bulky 4-methoxyphenyl group attached on the donor unit can reduce charge recombination and enhance V_{OC} to some extent. As a result, the DSSCs based on **ND02** achieved a remarkable overall power conversion efficiency of up to 8.30% with a J_{SC} of 17.14 $mA\ cm^{-2}$, a V_{OC} of 698 mV and a FF of 0.694. Further work to improve the device

performance by developing new D–A– π –A dyes using NP derivatives as electron donors is underway in our laboratories.

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