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N-Annulated perylene–based metal-free organic sensitizers for dye-sensitized solar cells

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A series of novel metal-free organic sensitizers based on N-annulated perylene derivatives have been designed and synthesized, and exhibit broad absorption spectra in the visible region. The dye-sensitized solar cells exhibit overall conversion efficiencies ranging from 4.90% to 8.28% under AM 1.5 solar conditions.

Dye-sensitized solar cells (DSCs) have attracted significant attention due to their clean and pollution-free nature, low-cost fabrication and high power conversion efficiency.[1] Since the first demonstration in 1991,[2] DSCs have gained great improvements in the stability and efficiency, especially ruthenium sensitizer-based DSCs having shown very impressive solar-to-electricity power conversion efficiency (PCE) of over 11%.[3] However, owing to the high cost and a resource restriction of the noble metal ruthenium, more efforts have been devoted to the development of metal-free organic sensitizers in recent years for the wide availability of the raw materials.[4] Generally, donor-π-acceptor (D-π-A) configuration is the typical structure of organic sensitizers because of the efficient intramolecular charge transfer properties. Through changing the three elements of donor moiety, π-linker and acceptor moiety, it could obtain novel sensitizers with wide absorption spectra, appropriate energy levels and improved carrier transporting ability.[5] Among the common organic donor moieties of indoline, triarylamine, coumarin, and carbazole,[6] triphenylamine is one of the most popular donor units due to its powerful electron-donating ability and steric structure.[7]

We are particularly interested in the design and synthesis of heteroatom-annulated rylene dyes.[8] In the past few years, we have demonstrated the efficient synthesis of N-annulated perylene (NP) on gram scale and longer N-annulated perylene derivatives (bis-N-annulated quaterrylene and tri-N-annulated hexarylene), which have received considerable interest due to their excellent optical and physical properties such as high molar extinction coefficient, high fluorescence quantum and tunable energy band gap.[9] Meanwhile they have strong electron-donating character owing to the introduction of nitrogen atoms to the bay region, and have been proved to be excellent candidates as donor segments of organic dyes. For example, Wu and co-worker introduced the NP unit to the porphyrin-based dyes and the power conversion efficiencies of the

DSCs exceeded 10% under simulated AM 1.5 global sunlight.[10] Quite recently, Wang reported a new metal-free NP-based D-A dye C261 showing a PCE as high as 8.8%.[11]
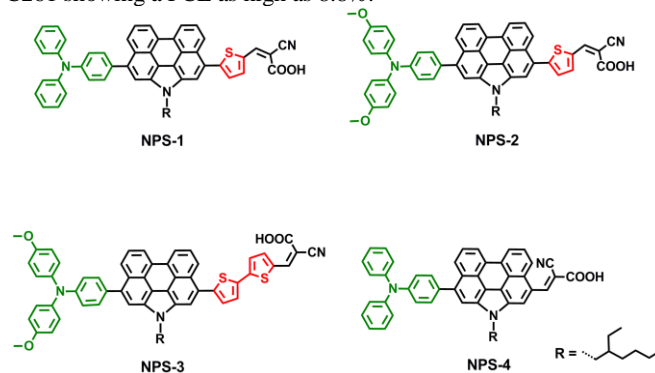

Fig. 1 Molecular structures of the dyes **NPS-1~NPS-4**.

In order to further explore the relationship between the structure and properties of organic sensitizers, herein, we designed and synthesized a series of pure organic dyes based on NP, in which triphenylamine derivatives were introduced into NP donor as an additional electron donor and steric unit to prevent the molecular π-π aggregation, and 2-cyanoacetic acid as an electron acceptor. A different number of thiophene units were chosen to serve as π spacer that may cause certain difference in electrons injected on the TiO$_2$ film. Meanwhile, the introduction of branched alkyl chain to NP unit would improve the solubility and decrease the dye aggregation in the solid film. The structures of the dyes **NPS-1~NPS-4** are shown in Figure 1 and their synthetic routes are shown in Scheme 1. The steric unit of triphenylamine derivatives and the conjugated linker of different number of thiophene units were introduced to the donor NP segment via Suzuki reaction. The acceptor of 2-cyanoacetic acid was obtained via Knoevenagel condensation reaction of the aldehydes with cyanoacetic acid in the presence of piperidine. It should be noted that in order to avoid the bromination of triphenylamine, 2Br-NP **1** instead of 1Br-NP **5** was chosen as the starting material for the synthesis of **NPS-1** and **NPS-4**.
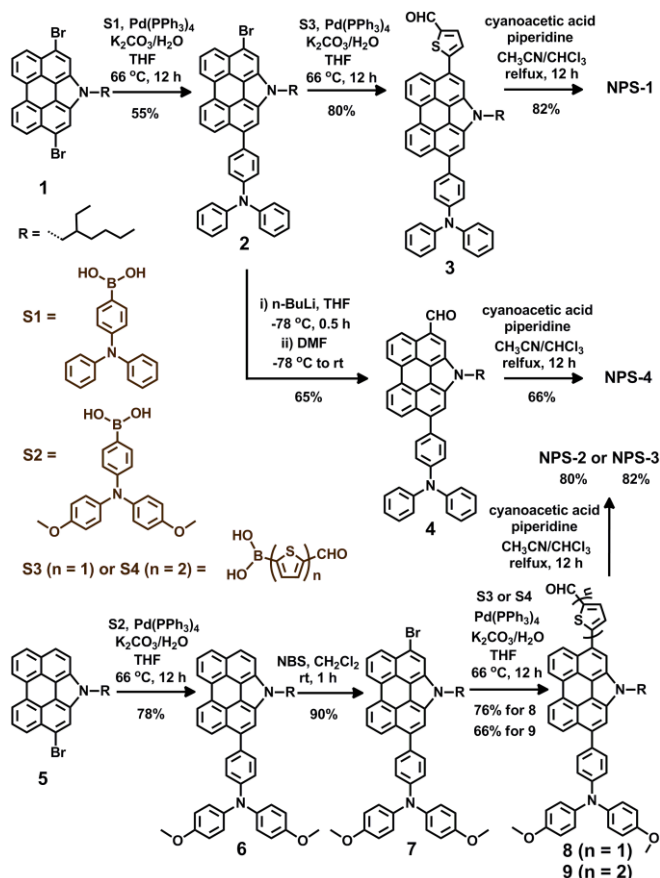
Scheme 1 Synthetic routes of the dyes **NPS-1~NPS-4**.

UV-vis absorption spectra of the four organic dyes in CH_2Cl_2 solution and on TiO_2 transparent film are shown in Figure 2 and the corresponding data are summarized in Table 1. All of these dyes exhibit broad and strong absorption bands in the range of 350-700 nm both in solution and on film, which suggests a good electronic delocalization throughout the whole molecular system.[12,13] Remarkably, the maximum absorption peak of the dyes **NPS-1** and **NPS-2** are somewhat bathochromic-shifted by 6 and 10 nm from 472 nm in CH_2Cl_2 solution to 478 and 482 nm on TiO_2 film caused by J-aggregates. By contrast, the maximum absorption peak of the dyes **NPS-4** is hypsochromic-shifted by 28 from 512 nm in CH_2Cl_2 solution to 484 on TiO_2 film, which could be attributed to either the formation of H-aggregates[14] or deprotonation of the carboxylic acid.[15] There is no obvious change between in solution and on solid film for **NPS-3**, and the maximum absorption peaks are both at 472 nm. Therefore, the incorporation of methoxy groups to triphenylamine has no effect on the absorption spectra. The dye **NPS-4** was red-shifted by 40 nm relative to **NPS-1~NPS-3** in solution, which can be explained that NP unit directly attached to the cyanoacetic acid brings forth a strengthened intramolecular charge transfer interactions. It should be noted that the molar extinction coefficient of **NPS-4** on TiO_2 film becomes much higher than others probably due to that the amount of dye **NPS-4** loading on TiO_2 is higher than other dyes at the same conditions. Comparing the absorption onset of these dyes, there is not a significant bathochromic-shift of absorption thresholds despite the introduction of two methoxy groups and thiophene-conjugated bridge. The band gap energies (E_{0-0}) of the dyes **NPS-1~NPS-4** were 2.00, 1.99, 1.98 and 2.02 eV, respectively, which were calculated from their absorption thresholds of dyes in CH_2Cl_2 solution.

The electrochemical properties of the dyes were investigated by cyclic voltammetry (CV) in CH_2Cl_2 solutions. The CV curves are shown in Figure S1 and the relevant data are summarized in Table 1. The HOMOs of **NPS-1~NPS-4** corresponding to their first oxidation potentials are 0.71, 0.56, 0.54 and 0.76 V *vs.* NHE, respectively. It is clear that the dye **NPS-2** is oxidized at low potentials than **NPS-1** because the introduction of methoxy groups to triphenylamine improves the electron-donating ability of the dye. Meanwhile, the oxidation potential of **NPS-3** is almost the same to **NPS-2** implying that the longer thiophene linkers have no obvious influence on the redox properties of dyes. The estimated excited state potentials corresponding to the LUMO levels, calculated from $E_{HOMO} - E_{0-0}$, were -1.29, -1.43, -1.44 and -1.26 V, *vs.* NHE, respectively. Consequently, we found the LUMO levels of **NPS-1~NPS-4** were more negative than the conduction band (CB) of the TiO_2 electrode (−0.5 V vs. NHE), indicating that electron injection from the LUMO orbital into the CB of TiO_2 is energetically permitted.[16]

To gain an insight into the molecular structure and electron distribution, density functional theory (DFT) calculations were performed at the B3LYP/6-31G*. The electron distributions of the HOMOs and LUMOs of dyes **NPS-1~NPS-4** are shown in Figure S2. The calculation indicates that the HOMOs of four dyes are delocalized over the π-conjugated system of planar NP and triphenylamine. The LUMOs of **NPS-1~NPS-3** are delocalized over the cyanoacetic acid and thiophene spacer, whereas the LUMO of **NPS-4** is delocalized over the cyanoacetic acid and NP. Accordingly, these observations can facilitate charge migration from the donor to acceptor and efficient electron injection from the dye to the conduction band of TiO_2.
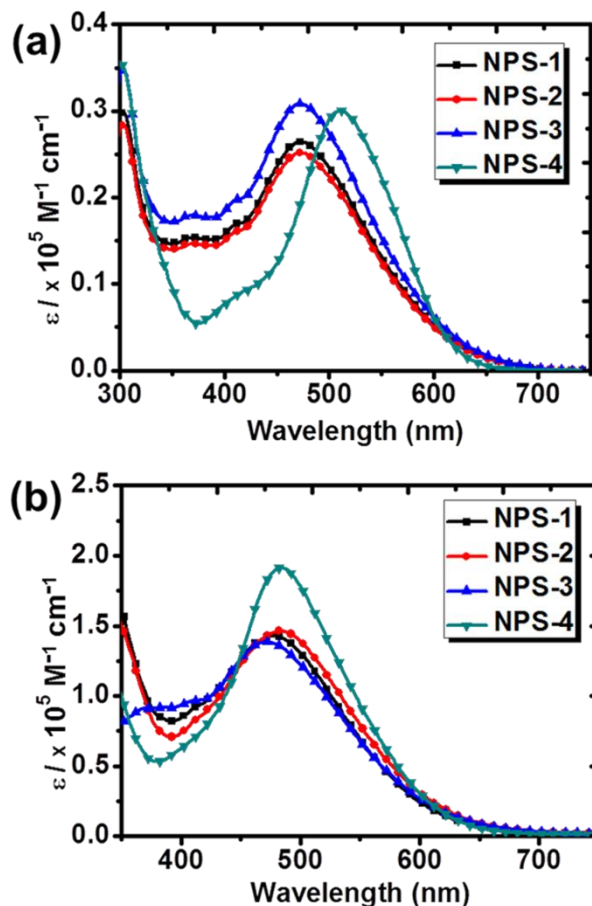
Fig. 2 UV-Vis absorption spectra of the dyes **NPS-1~NPS-4**: (a) in CH_2Cl_2 (1×10^{-5} M) and (b) on single layer TiO_2 transparent films.

Table 1 Optical and electrochemical properties of the dyes

Dyes	$\lambda_{max}{}^{a}$ /nm	$\lambda_{max}{}^{b}$ /nm	ε^{a} /10^4 M^{-1} cm^{-1}	$E_{0-0}{}^{c}$/eV	HOMO ^{d}/V (vs NHE)	LUMO ^{e}/V (vs NHE)
NPS-1	472	478	2.64	2.00	0.71	-1.29
NPS-2	472	482	2.52	1.99	0.56	-1.43
NPS-3	472	472	3.08	1.98	0.54	-1.44
NPS-4	512	484	3.01	2.02	0.76	-1.26

^{a} Measured in CH_2Cl_2 solution (1×10^{-5} M). ^{b} Absorption maxima of film adsorbed on TiO_2. $^c E_{0-0}$ values were estimated from the onset absorption wavelength in CH_2Cl_2 solution. ^{d} The formal oxidation potentials (*vs* NHE) in CH_2Cl_2 were internally calibrated with ferrocene (0.4 V *vs*. NHE) and taken as the HOMO. ^{e} The LUMO was calculated from HOMO $- E_{0-0}$.
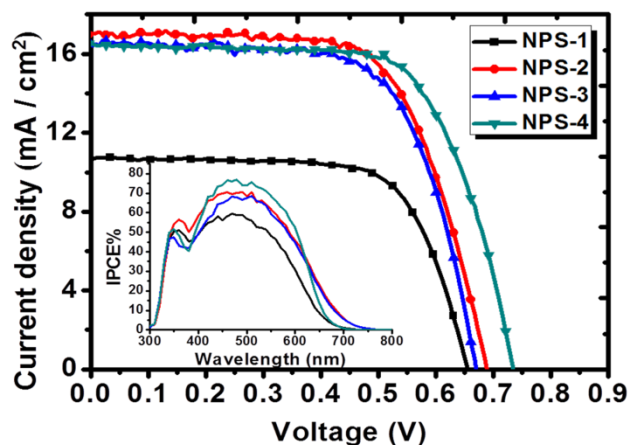

Fig. 3 Photocurrent density-voltage (*J-V*) curves and the IPCE spectra (inset) of DSCs based on the dyes **NPS-1~NPS-4**.

Table 2 Photovoltaic performances of DSCs based on the dyes **NPS-1~NPS-4**

Dyes	V_{oc}/V	J_{sc}/mA cm^{-2}	FF	η %
NPS-1	0.655	10.75	0.700	4.90
NPS-2	0.687	17.05	0.661	7.74
NPS-3	0.669	16.60	0.666	7.40
NPS-4	0.734	16.50	0.684	8.28

The DSC devices were fabricated to test the photovoltaic performance of **NPS**s according to the literature procedure (The method for the cell fabrication is described in the SI).[17] The action spectrum of incident photo-to-current conversion efficiency (IPCE) and the photocurrent density-voltage (*J-V*) curves for the DSCs based on the dyes are illustrated in Figure 3 and the detailed performance parameters are displayed in Table 2. The IPCE for DSCs based on **NPS-2~NPS-4** exceeds 70% over the spectral region ranging from 400 to 580 nm, and reaches a wide maximum of approximately 71%, 70% and 76% in the 430~550 nm range, respectively. The IPCE value of **NPS-2** was higher than that of **NPS-1** which attributed to the reduced charger combination at the TiO_2/dye/electrolyte interface by tailoring two methoxy groups. However, the IPCE of **NPS-4** are higher relative to those of **NPS-1~NPS-3** which maybe be due to the relatively higher molar extinction coefficient in films. Under standard global AM 1.5 solar condition (100 mW cm^{-2}), the dye **NPS-3** bearing dithiophene π-spacer shows lower η values compared to the **NPS-2** containing thiophene π-spacer. Under the same conditions, the **NPS-4** sensitized cell having no thiophene π-spacer gave a short-circuit photocurrent density (J_{sc}) of 16.50 mA cm^{-2}, an open-circuit photovoltage (V_{oc}) of

0.734 V, and a fill factor (*ff*) of 0.684, corresponding to an overall conversion efficiency (η) of 8.28%. These results imply that NP unit directly attached to the cyanoacetic acid is beneficial to electrons injection into the conduction band (E_{cb}) of TiO_2 film. Compared to **NPS-1**, **NPS-2** has a larger J_{sc}, which originates from the broader IPCE spectra. On the other hand, the V_{oc} of DSCs is relevant to the electronic density of E_{cb} of TiO_2. The introduction of methoxy substituents into the structure of **NPS-2** could reduce the charge recombination between excited electrons in the E_{cb} and holes located on the redox $I_3{}^-$ and the oxidized state dye, thus improving the V_{oc}.[18]

Figure 4 illustrates electron lifetime (τ_n) at different bias potentials for the four sensitizers, and the τ_n values show a significant gap among the sensitizers, resulting in the decreasing order **NPS-4** > **NPS-2** > **NPS-3** > **NPS-1**. The influence of dyes on V_{oc} has mostly been attributed to electron lifetime, which is related to factors such as molecular size, and dye adsorption behavior.[19] In our results, the trend of the τ_n values is well consistent with that of the V_{oc} values.
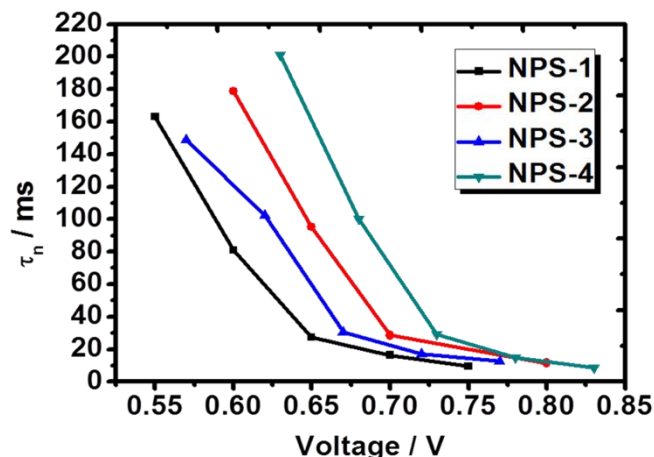
Fig. 4 Electron lifetime determined with photovoltage decay measurements of devices with the dyes **NPS-1~NPS-4**.

To summarize, a series of novel metal-free organic sensitizers based on N-annulated perylene derivatives, in which triphenylamine derivatives were introduced as additional electron donor and steric structures, different number of thiophenes as conjugated linkers, and 2-cyanoacetic acid as an electron acceptor, have been designed and synthesized. The methoxy groups introduced to triphenylamine could efficiently reduce charge recombination. Meanwhile, the NP unit directly attached to the acceptor unit of cyanoacetic acid without thiophene π-spacer is beneficial to electrons injection into the TiO_2 film. The DSCs fabricated with these organic dyes displayed remarkable overall conversion efficiency in a range of 4.90% – 8.28% with the best performance of solar cells based on **NPS-4** (η = 8.28%, J_{sc} = 16.50 mA cm^{-2}, V_{oc} = 0.734 V, and *ff* = 0.684). We believe that the photovoltaic performance will be greatly improved with further

structure modifications and DSC device optimizations which are ongoing in our laboratory.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedures, characterization, MS spectra, and copies of ^{1}H and ^{13}C NMR spectra for all new compounds. See DOI: 10.1039/c000000x/

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