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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 improvement in the stability and efficiency, especially ruthenium sensitizer-based DSCs which have show a 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, we could obtain novel sensitizers with wide absorption spectra, appropriate energy levels and improved carrier transport 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 a 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-workers introduced the NP unit into 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]

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 the NP donor as an additional electron donor and the 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 a π spacer that may cause a certain difference in electrons injected into the TiO_2 film. Meanwhile, the introduction of a branched alkyl chain into the 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 Fig. 1 and their synthetic routes are shown in Scheme 1. The steric unit of triphenylamine derivatives and the conjugated linker of a different number of thiophene units were introduced to the donor NP segment *via* a Suzuki reaction. The acceptor of 2-cyanoacetic acid was obtained *via* a 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**.

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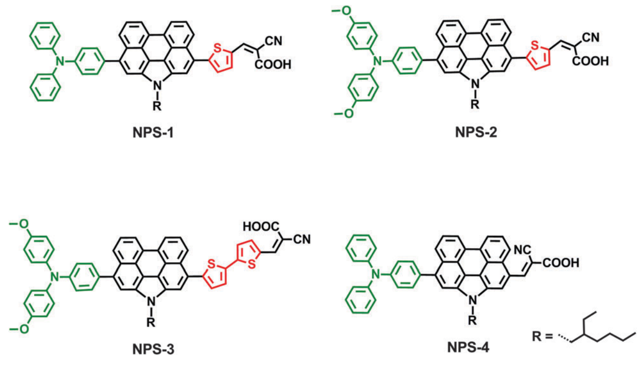
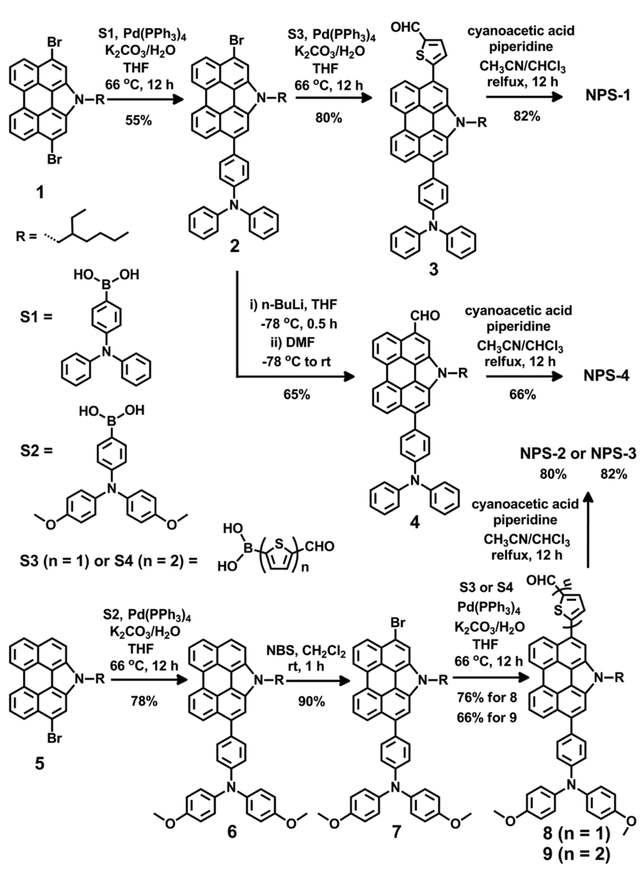


Fig. 1 Molecular structures of the dyes **NPS-1–NPS-4**.



Scheme 1 Synthetic routes of the dyes **NPS-1–NPS-4**.

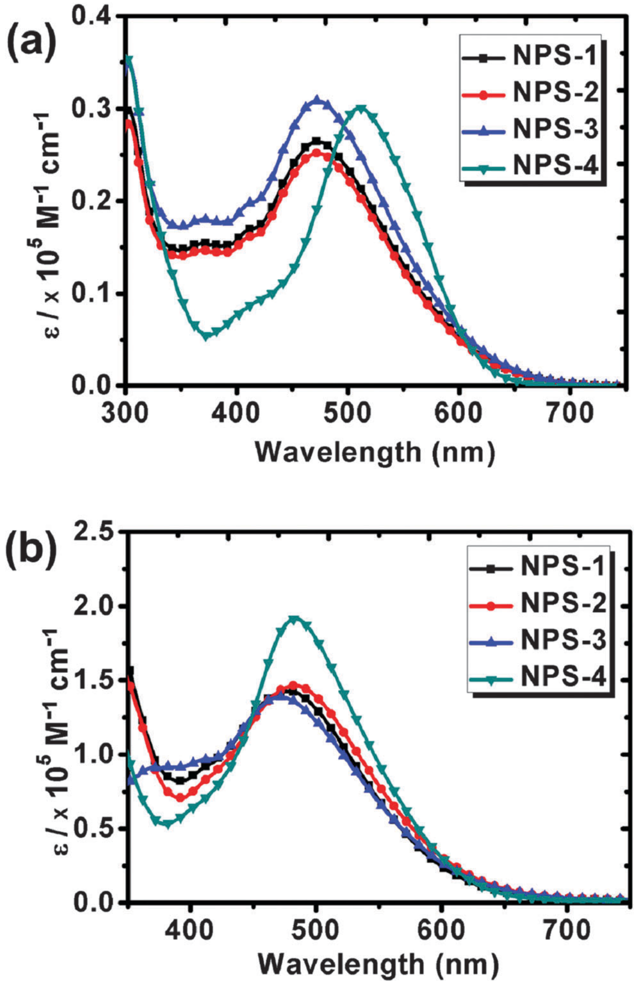


Fig. 2 UV-Vis absorption spectra of the dyes **NPS-1–NPS-4**: (a) in CH_2Cl_2 (1×10^{-5} M) and (b) on single layer TiO_2 transparent films.

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}	$E_{0\text{-}0}{}^{c}$/ 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 the film adsorbed on TiO_2. [c] $E_{0\text{-}0}$ 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 − $E_{0\text{-}0}$.

UV-vis absorption spectra of four organic dyes in CH_2Cl_2 solution and on TiO_2 transparent film are shown in Fig. 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 good electronic delocalization throughout the whole molecular system.[12,13] Remarkably, the maximum absorption peak of the dyes **NPS-1** and **NPS-2** is somewhat bathochromically 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 dye **NPS-4** is hypsochromically 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 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 into 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 explain that the NP unit directly attached to cyanoacetic acid brings forth strengthened intramolecular charge transfer interactions. It should be noted that the molar extinction coefficient of **NPS-4** on a 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 under the same conditions. Comparing the absorption onset of these dyes, there is no significant bathochromic-shift of absorption thresholds despite the introduction of two methoxy groups and a thiophene-conjugated bridge. The band gap energies ($E_{0\text{-}0}$) 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 Fig. S1 (ESI†) 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 into triphenylamine improves the electron-donating ability of the dye. Meanwhile, the oxidation potential of **NPS-3** is almost similar 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 $E_{\text{HOMO}} - E_{0\text{-}0}$, were −1.29, −1.43, −1.44 and −1.26 V, *vs.* NHE, respectively. Consequently, we found that 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 insight into the molecular structure and electron distribution, density functional theory (DFT) calculations were performed at the B3LYP/6-31G* level. The electron distributions of the HOMOs and LUMOs of dyes **NPS-1–NPS-4** are shown in Fig. S2 (ESI†). 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 the acceptor and efficient electron injection from the dye to the conduction band of TiO_2.

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 ESI†).[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 Fig. 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 is attributed to the reduced charge combination at the TiO_2/dye/electrolyte interface by tailoring two methoxy groups. However, the IPCE of **NPS-4** is higher relative to those of **NPS-1–NPS-3** which maybe due to the relatively high molar extinction coefficient in films. Under standard global AM 1.5 solar conditions (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 the NP unit directly attached to cyanoacetic acid is beneficial for electron 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 electron 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^-/I_3^- and the oxidized state dye, thus improving the V_{oc}.[18]

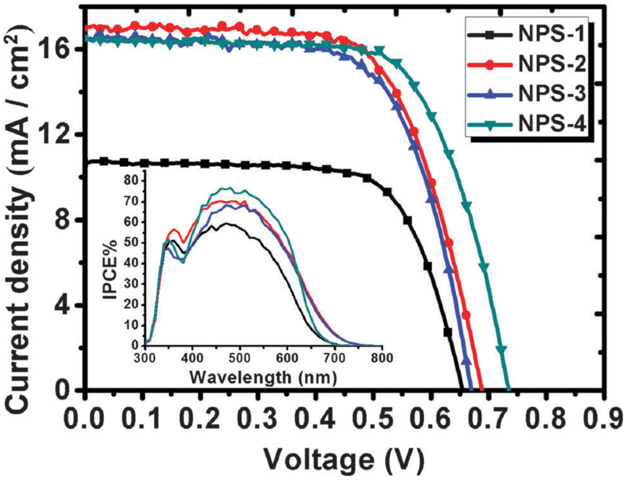


Fig. 3 Photocurrent density–voltage (*J–V*) curves and the IPCE spectra (inset) of DSCs based on the dyes **NPS-1–NPS-4**.

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

Fig. 4 illustrates the 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 of **NPS-4** > **NPS-2** > **NPS-3** > **NPS-1**. The influence of dyes on V_{oc} has been mostly attributed to the 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.

To summarize, a series of novel metal-free organic sensitizers based on *N*-annulated perylene derivatives, in which triphenylamine

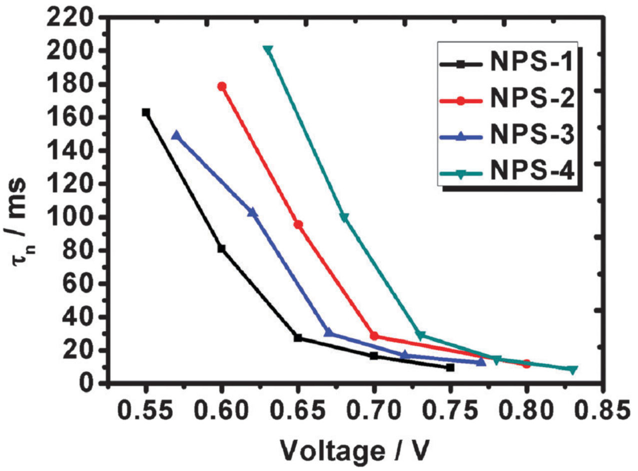


Fig. 4 Electron lifetime determined by photovoltage decay measurements of devices with the dyes **NPS-1–NPS-4**.

derivatives were introduced as additional electron donors 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 into triphenylamine could efficiently reduce charge recombination. Meanwhile, the NP unit directly attached to the acceptor unit of cyanoacetic acid without the thiophene π-spacer is beneficial for electron injection into the TiO_2 film. The DSCs fabricated with these organic dyes displayed remarkable overall conversion efficiency in the 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.

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