Polycycles

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A Metal-Free N-Annulated Thienocyclopentaperylene Dye: Power Conversion Efficiency of 12% for Dye-Sensitized Solar Cells**

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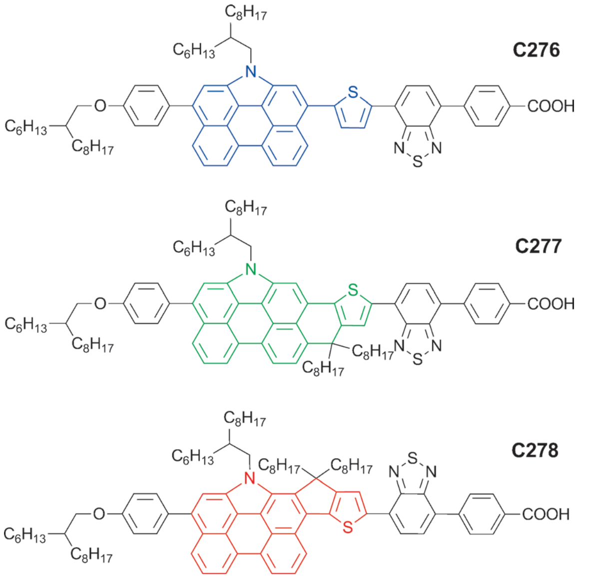
Abstract: *Reported are two highly efficient metal-free perylene dyes featuring N-annulated thienobenzoperylene (NTBP) and N-annulated thienocyclopentaperylene (NTCP), which are coplanar polycyclic aromatic hydrocarbons. Without the use of any coadsorbate, the metal-free organic dye derived from the NTCP segment was used for a dye-sensitized solar cell which attained a power conversion efficiency of 12% under an irradiance of 100 mW cm^{-2}, simulated air mass global (AM1.5G) sunlight.*

To address the global issue on ecofriendly and low-cost conversion of solar energy to clean electricity, unrelenting research efforts have been devoted to dye-sensitized solar cells (DSCs),[1] characteristic of an interconnected network of wide-band-gap semiconducting nanocrystals, from the aspects of materials synthesis, interface engineering, and device physics.[2] The performance parameters of a DSC are intrinsically modulated to significant extent by light absorption, interfacial energetics, and multichannel charge-transfer dynamics, all of which are intimately linked to a photosensitizing molecule chemically anchored on the surface of an oxide semiconductor. Some ruthenium polypyridine[3] and zinc porphyrin[4] complexes have been demonstrated so far as the best performing DSC dyes from the respective viewpoints of stability and efficiency. However, a ruthenium dye has the disadvantage of resource scarcity and heavy-metal toxicity. A push-pull zinc poryphyrin dye suffers from low synthetic yield and use of highly toxic raw materials such as thiophosgene ($CSCl_2$) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Thereby, metal-free organic donor–acceptor (D–A) dyes have also attracted interest owing centrally to abundant raw materials, bright colors, and flexible molecular designs.[5] In this regard, some organic small molecules derived from the coplanar perylene skeleton are endowed with a large molar absorption coefficient, high luminescence yield, and excellent photostability, thus triggering their widespread applications as fluorescent lipid probes, light-emitting materials, automotive paints, and pigments for synthetic fibers and engineering resins.[6] Also, perylene has been actively pursued as a polycyclic aromatic hydrocarbon (PAH) module of some metal-free organic dyes for DSCs,[7] the best of which has already displayed a power conversion efficiency of 10.4% at the air mass 1.5 global (AM1.5G) conditions.[8]

Herein, for the first time we construct two coplanar, electron-rich PAH blocks, N-annulated 6*H*-thieno[3′,2′:5,4]-benzo[*cd*]perylene (NTBP) and its isomer N-annulated 13*H*-thieno[2′,3′:3,4]cyclopenta[*b*]perylene (NTCP) as illustrated in Scheme 1. In our design of the metal-free D–A dyes **C277** and **C278** (Scheme 1), with the electron-acceptor 4-(benzo[*c*]-[1,2,5]thiadiazol-7-yl)benzoic acid (BTBA),[9] less soluble and rigid PAH segments NTBP and NTCP are end-capped with an alkoxyphenyl group and also side-functionalized with aliphatic chains to attenuate the strong intermolecular π–π stacking. The dye aggregation is widely believed to deteriorate carrier photogeneration owing to excited-state annihilation.[10] During a preliminary test, the judiciously tailored dye **C278**, derived from the PAH segment NTCP, was used to make a coadsorbate-free DSC exhibiting a power conversion efficiency (PCE) of 12% at AM1.5G conditions. Meanwhile, the fascinating traits of NTBP- and NTCP-based PAH units



Scheme 1. Chemical structures of the perylene dyes **C276**, **C277**, and **C278** with BTBA as an electron acceptor. NTBP and NTCP are displayed in green and red, respectively, and their unfused counterpart NPT is marked in blue.

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for DSC dyes will also be dissected by a joint theoretical and experimental study on energy levels, light absorption, and charge recombination, by referring to the 4-(thiophen-2-yl)-6*H*-phenanthro[1,10,9,8-*cdefg*]carbazole (NPT) based control **C276** (Scheme 1).

The synthetic routes for these D–A dyes are depicted in Scheme S1 in the Supporting Information. The previously reported 3-bromo-1-(2-hexyldecyl)-10-(4-((2-hexyldecyl)-oxy)phenyl)-1*H*-phenanthro[1,10,9,8-*cdefg*]-carbazole (**1**)[8] was cross-coupled with facile thiophen-2-ylboronic acid to afford 1-(2-hexyldecyl)-3-(4-((2-hexyldecyl)oxy)phenyl)-10-(thiophen-2-yl)-1*H*-phenanthro[1,10,9,8-*cdefg*]carbazole (**2**) in excellent yield by the palladium-catalyzed Suzuki–Miyaura reaction, by use of the very active phosphine ligand 2-(2′,6′-dimethoxybiphenyl)dicyclohexylphosphine (Sphos).[11] In contrast, **1** was used in a rapid halogen–lithium exchange with *n*-butyilithium and then transformed into its derived stannane, which was cross-coupled with the sterically hindered butyl 2-bromothiophene-3-carboxylate by a Stille reaction to give the intermediate butyl 2-(1-(2-hexyldecyl)-10-(4-((2-hexyldecyl)oxy)phenyl)-1*H*-phenanthro[1,10,9,8-*cdefg*]carbazol-3-yl)thiophene-3-carboxylate (**3**) in good yield, by use of a highly active catalyst developed by Little and Fu.[12] Subsequently, **3** underwent a carbonyl addition reaction with octylmagnesium bromide to form the tertiary alcohol 9-(2-(1-(2-hexyldecyl)-10-(4-((2-hexyldecyl)oxy)phenyl)-1*H*-phenanthro[1,10,9,8-*cdefg*]carbazol-3-yl)thiophen-3-yl)heptadecan-9-ol (**4**), which underwent intramolecular Friedel–Crafts cyclization in the presence of the solid acid catalyst Amberlyst 15 to concurrently afford 11-(2-hexyldecyl)-13-(4-((2-hexyldecyl)oxy)phenyl)-6,6-dioctyl-6,11-dihydrothieno[3′,2′:8,9]chryseno[10,11,12,1-*bcdefg*]carbazole (**5**) and 13-(2-hexyldecyl)-2-(4-((2-hexyldecyl)oxy)-phenyl)-12,12-dioctyl-12,13-dihydrophenanthro[1,10,9,8-*cdefg*]thieno[2′,3′:3,4]cyclopenta[1,2-a]carbazole (**6**) in an excellent yield of 90%. The ratio of **6** with respect to **5** is about 2. The electron-rich compounds **2**, **5**, and **6** were treated with a superbase, *tert*-butyllithium, and chlorotrimethylstannane in turn to generate the corresponding stannanes, which were cross-coupled with butyl 4-(7-bromobenzo[*c*]-[1,2,5]thiadiazol-4-yl)benzoate to yield esterified dyes. Finally, the hydrolysis of carboxylic esters were conducted with a strong base, KOH, as the catalyst and the products were acidified with a diluted hydrochloric acid aqueous solution to afford **C276**, **C277**, and **C278**. For synthetic details, see the Supporting Information.

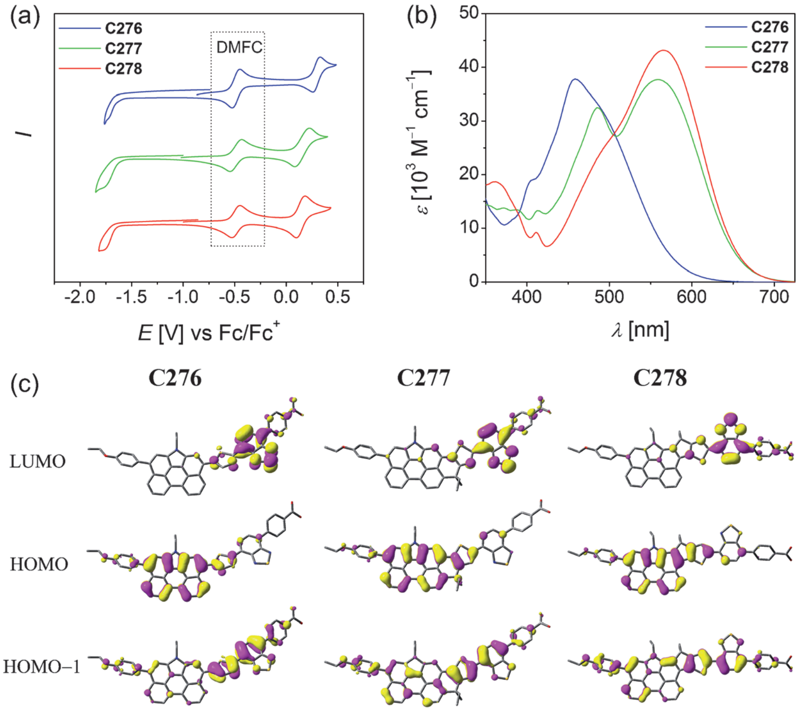

Figure 1. a) Cyclic voltammograms of **C276**, **C277**, and **C278** dissolved in THF with 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMITFSI) as a supporting electrolyte. Decamethylferrocene (DMFC) was added as internal reference and all potentials are further calibrated with respect to ferrocene (FC). b) Electronic absorption spectra of dyes dissolved in THF (10 μm). c) Cantor plots of molecular orbitals involved in the $S_0 \rightarrow S_1$ transitions. The large aliphatic substituents were replaced with ethyl to improve computational efficiency.

To unveil conjugated-backbone-dependent energy levels and energy gaps, we carried out electrochemical measurements, over a wide potential window, on the dyes dissolved in THF in a nitrogen-filled glovebox. In our nonaqueous electrochemical tests, the potential scan rate was kept low, that is, 5 mV s^{-1}, and an *iR* drop was compensated. We also used electrochemically reversible decamethylferrocene (DMFC) as the internal reference, which has a more suitable redox potential than ferrocene (FC) for metal-free DSC dyes. The formal redox potential difference between DMFC and FC in THF is 0.489 V. From the vertically shifted cyclic voltammograms (CVs) presented in Figure 1 a, we estimated the lowest unoccupied molecular orbital (LUMO) levels and the highest occupied molecular orbital (HOMO) levels by using the equation: $E = -4.88 - e\,E_{\text{onset}}$ where E_{onset} is the onset potential of reduction and oxidation of a ground-state dye. In good agreement with our previous comparisons on D–A dyes with fused and unfused aromatic units,[13] it was found that in comparison to **C276** with NPT, both **C277** with NTBP and **C278**, with NTCP, feature a 0.16 eV destabilized HOMO energy level. In addition, the LUMO energy level is stabilized by 0.02 eV for **C277** and is destabilized by 0.01 eV for **C278**. Overall, the LUMO/HOMO energy gaps are significantly reduced upon the utilization of NTBP and NTCP instead of NPT. It is thus reasonable to observe in Figure 1 b that the maximum absorption wavelengths $(\lambda_{\text{max}}^{\text{EA}})$ of **C277** and **C278** are red-shifted about 100 nm in contrast to that of **C276**. The relative alignments of the LUMO, HOMO, and $\lambda_{\text{max}}^{\text{EA}}$ can be nicely reproduced by theoretical calculations as listed in Table S1. In general, the $S_0 \rightarrow S_1$ vertical electronic transitions to LUMO for all these dyes mainly stem from HOMO and HOMO-1, and is characteristic of intramolecular charge transfer as perceived from contour plots of molecular orbitals in Figure 1 c.

To diagnose the possible influence of dye alteration on electron injection yield (ϕ_E), the time-correlated single-photon counting (TCSPC) technique was used to examine the quenching of photoluminescence (PL) from dye-grafted mesoporous titania films, with the corresponding dye-grafted alumina films as controls.[14] In our experiments, all films were immersed in a tris(2,2′-bipyridine)cobalt electrolyte[15] for DSCs. The contents of the electrolyte can be found in the Supporting Information. Because there are no downhill offsets of the LUMO energy levels of these perylene dyes with respect to the conduction band edge of alumina, the PL decays (blue curves in Figure S1) reflect the radiative and radiationless deactivations of electronically excited states. However, it can be easily discerned that the substitution of alumina with titania evokes significant PL quenching (red curves in Figure S1), thus suggesting the occurrence of electron injection at the energy-offset titania/dye interface. By calculating the integral areas of the PL traces of the dye-coated alumina (green curves in Figure S1) and titania (magenta curves in Figure S1) films, we made a rough estimation of the ϕ_E values: 98 % for **C276**, 96 % for **C277**, and 98 % for **C278**. Our attenuated total reflection Fourier transform infrared (ATR-FTIR) measurements (see Figure S2) have shown that physical adsorption on the surface of titania is almost inappreciable for these perylene dyes. The slightly low ϕ_E value for **C277** could be related to the fact that it has the lowest LUMO energy level amongst these three dyes. A very efficient electron injection could be therefore expected for DSCs presented in the following part of this paper, despite the fact that a minor quantity of dye molecules do not inject electrons into titania because of dynamic competition between electron injection and other excited-state deactivation channels.

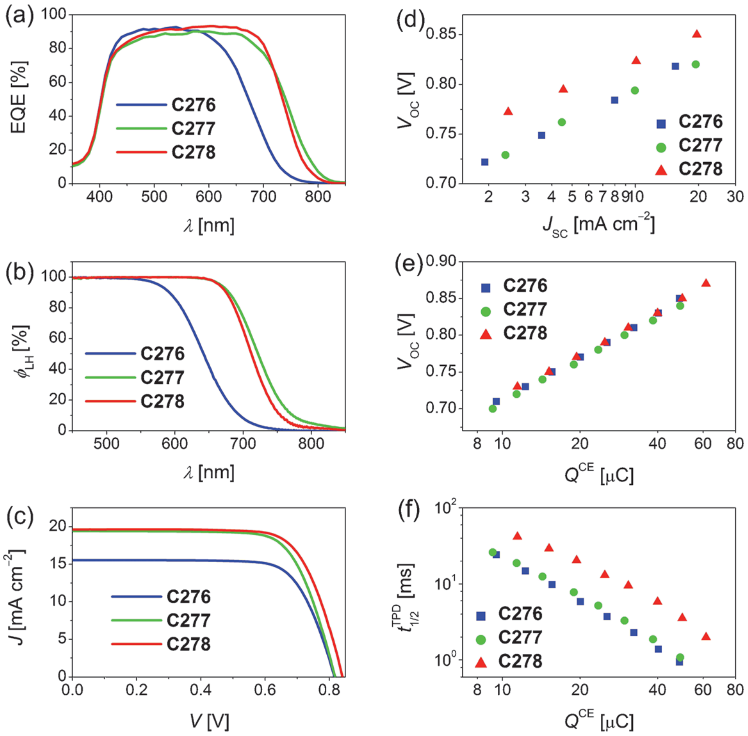

Figure 2. a) External quantum efficiency (EQE) plotted against wavelength (λ) for cells made with dye-grafted bilayer (4.0 + 5.0 μm thick) titania films in combination with a cobalt electrolyte. An antireflection film is laminated on top of a DSC during measurements. The aperture area of the employed metal mask is 0.160 cm^2. b) Light-harvesting yield (ϕ_{LH}) plotted against wavelength (λ) for the 6.0 μm-thick, dye-grafted mesoporous titania films immersed in a cobalt electrolyte. c) Current-voltage (J–V) characteristics of cells measured under an irradiance of 100 mW cm^{-2}, simulated AM1.5G sunlight. d) Plots of open-circuit photovoltage (V_{OC}) as a function of short-circuit photocurrent density (J_{SC}). e) Plots of charge stored in a dye-grafted titania film (Q^{CE})as a function of open-circuit photovoltage (V_{OC}). f) Comparison of electron half-lifetime $\left(t_{1/2}^{TPD}\right)$ against Q^{CE}.

Shown in Figure 2a are the photocurrent action spectra of DSCs made with a bilayer dye-grafted titania film and a Co-bpy electrolyte. The details for cell fabrication are described in the Supporting Information. The maximum external quantum efficiencies (EQEs) are about 92 % for cells with **C276** and **C278**. The significant red-shifted onset wavelengths of photocurrent response for **C277** and **C278** are in good accordance with the wavelength-dependent light-harvesting yield (ϕ_{LH}) as presented in Figure 2b. The current density-voltage (J–V) characteristics (Figure 2c) were measured at an irradiance of 100 mW cm^{-2}, simulated AM1.5G sunlight, and the extracted cell parameters are tabulated in Table 1. The short-circuit photocurrent density (J_{SC}), open-circuit photovoltage (V_{OC}), and fill factor (FF) of a typical DSC with **C276** are 15.54 mA cm^{-2}, 818 mV, and 73.6 %, respectively, thus yielding a PCE of 9.4 %. In good accord with the integrals of EQEs over the standard AM1.5G emission spectrum, **C277** and **C278** both exhibit markedly enhanced J_{SC} values of 19.42 and 19.64 mA cm^{-2}, respectively, which contribute to their corresponding higher PCEs of 11.5 and 12.0 %. It can be noted from Table 1 that under the same conditions of cell fabrication and measurement, the efficiency achieved by the metal-free organic dyes **C277** and **C278**, without the use of any coadsorbate, are even higher than that of 10.6 % by the well-known zinc porphyrin dye **YD2-*o*-C8** (see Figure S3).[4b] Note that these perylene dyes show good photochemical stability (see Figure S5).

Table 1: Averaged photovoltaic parameters of 10 cells measured under an irradiance of 100 mW cm^{-2}, simulated AM1.5G sunlight.[a]

Dye	J_{SC}^{EQE} [mA cm^{-2}]	J_{SC} [mA cm^{-2}]	V_{OC} [mV]	FF [%]	PCE [%]
C276	15.71 ± 0.19	15.54 ± 0.20	818 ± 3	73.6 ± 0.3	9.4 ± 0.2
C277	19.28 ± 0.13	19.42 ± 0.11	820 ± 2	72.4 ± 0.2	11.5 ± 0.2
C278	19.55 ± 0.06	19.64 ± 0.05	843 ± 3	72.8 ± 0.3	12.0 ± 0.1
YD2-*o*-C8	16.74 ± 0.18	17.07 ± 0.12	860 ± 4	72.2 ± 0.3	10.6 ± 0.2

[a] J_{SC}^{EQE} is derived by wavelength integration of the product of the standard AM1.5G emission spectrum (ASTM G173-03) and the EQEs measured at short-circuit. We have noted that there is a linear dependence of photocurrent on irradiance (see Figure S4) and thereby evaluated the validity of measured photovoltaic parameters by comparing calculated J_{SC}^{EQE} values with experimental J_{SC} values.

The dye structure correlated V_{OC} dissimilarity was also compared at a certain J_{SC} by recording J–V curves under a series of irradiances attenuated with metal meshes and plotting V_{OC} as a function of J_{SC}. It is noted from Figure 2 d that at a given J_{SC}, the cell with **C278** displays an obviously higher V_{OC} than those with **C276** and **C277**. The charge extraction (CE)[16] and transient photovoltage decay (TPD)[17] measurements were further performed to scrutinize the interfacial energetic and dynamic origins of dye-dependent V_{OC} values.[18] As Figure 2 e shows, at a certain photovoltage an almost invariable charge stored in the mesoporous titania film (Q^{CE}) can be extracted from all cells, thus implying that the change of dye molecules may not alter the conduction-band edge and electron-trap states of titania. However, it is interesting to perceive that with respect to **C277**, a DSC with **C278** is typical of prolonged half-lifetime $\left(t_{1/2}^{TPD}\right)$ for electrons stored in titania, which is in good accord with the V_{OC} variation. An improved dye load amount of $1.6\times10^{-8}\,\mathrm{mol\,cm^{-2}\,\mu m^{-1}}$ for **C278**, with respect to that of $1.5\times10^{-8}\,\mathrm{mol\,cm^{-2}\,\mu m^{-1}}$ for **C277**, could positively contribute to an attenuated recombination of electrons in titania with cobalt(III) ions in the electrolyte. However, the dye load amount of $1.8\times10^{-8}\,\mathrm{mol\,cm^{-2}\,\mu m^{-1}}$ in the cell with **C276** is even higher, therefore we ascribe the fast charge recombination to the lack of blocking effect from two additional octyl chains.

To summarize, we have designed two coplanar polycyclic aromatic hydrocarbons of N-annulated thienobenzoperylene and thienocyclopentaperylene. These electron-rich blocks have been integrated into donor–acceptor organic dyes for efficient solar-to-electricity conversion. To the best of our knowledge, this is the first time that a metal-free organic dye has reached such a high power conversion efficiency of 12 % for dye-sensitized solar cells without any coadsorbate, thus paving a new way for highly powerful DSC dyes. Our work should encourage further molecular engineering of perylene dyes and stimulate active design of other innovative organic materials for applications in new generation solar cells.

Keywords: cyclic voltammetry · dyes/pigments · energy conversion · polycycles · solar cells

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