

Double Donor-Thiophene Dendron-Perylene Monoimide: Efficient Light-Harvesting Metal-Free Chromophore for Solid-State Dye-Sensitized Solar Cells

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Dye-sensitized solar cells (DSCs) based on a stable large-band nanostructured semiconductor, such as titanium dioxide, are low cost and easily processable alternatives to conventional silicon wafers, and as such have lately drawn much attention.^[1] In particular, the solid-state DSCs show great potential owing to their increased stability compared to liquid DSCs. The reason for this stability is the exchange of the liquid electrolyte, which often bears the problem of leakage and electrode corrosion, for a solid hole-conducting material, mainly 2,2',7,7'-tetrakis(*N,N*-para-dimethoxyphenyl-amino)-9,9'-spirobifluorene (spiro-MeOTAD).^[2] However, compared to the parent liquid DSCs, solid-state DSCs have shown much lower efficiencies. Whilst ruthenium-based sensitizers, and now a first porphyrin sensitizer,^[3] have shown efficiencies up to approximately 11 % in liquid cells, solid-state DSCs only reach values of up to 6%.^[4] Most of the more efficient sensitizers are ruthenium-based, which have drawbacks such as cost, sustainability, and limited ease of band-gap manipulation. One very stable and metal-free alternative are sensitizers based on perylene monoimides, which are known for their excellent chemical, photochemi-

cal, and thermal stability as well as high absorptivity and acceptor ability. Another outstanding class of chromophores are thiophenes, in particular oligothiophenes, for their highly variable optical properties according to their architecture, extraordinary charge transport properties, and extinction.^[2,5] Both perylenes and thiophenes have found wide application in optoelectronic devices.

Herein, we present a donor-acceptor perylene monoimide with a branched terthiophene spacer group^[6,7] and a triphenylamine donor moiety^[8] (**1a**, Scheme 1) as well as a naphthalene analogue (**1b**, Scheme 1). As reported by Thomas et al. and Fischer et al., the combination of a triphenylamine donor and a branched oligothiophene spacer in combination with a 2-cyanoacrylate acceptor gave good efficiencies of up to 6.15 %^[6] and 6.8 %^[7] in liquid DSCs and up to 2.6 %^[7] in a solid-state DSC. Furthermore, three moieties—triphenylamine, oligothiophene, and perylene monoimide—have recently caused a stir in a p-DSC (NiO), showing a sevenfold increase in energy conversion efficiencies compared to preceding sensitizers.^[9] However, we have designed our sensitizers for n-DSCs (TiO₂), in which the perylene sensitizer **1a** in particular shows an outstanding efficiency of 3.8 % under 1.5 AM illumination (1 sun). To the best of our knowledge, this is an unprecedented performance for a perylene sensitizer, the best perylene sensitizer for solid-state DSCs so far being ID176 with an efficiency of 3.2 %.^[10]

Both compounds were prepared by the initial introduction of the terthiophene spacer group by Suzuki coupling with the brominated perylene (or naphthalene) imide, successive Suzuki coupling with the triphenylamine donor, and finally saponification and imidization with glycine to yield the final product (Scheme 1).

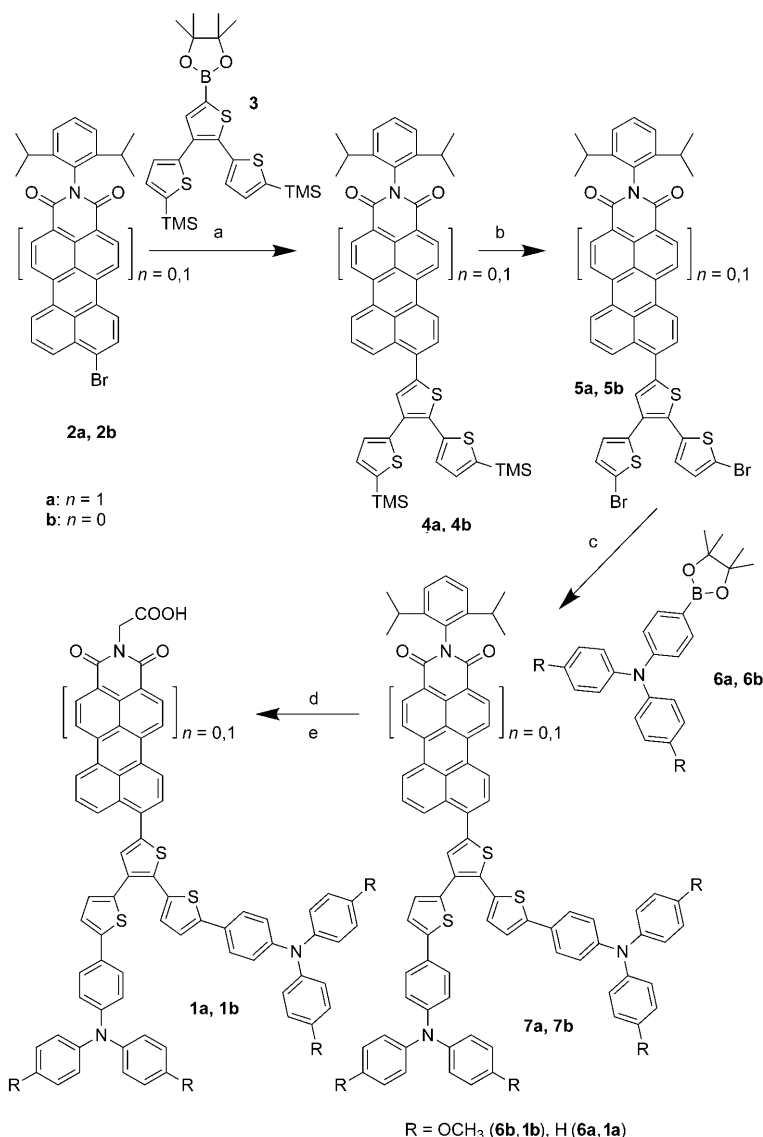
As described above, both sensitizers consist of an acceptor unit with a carboxylic acid anchor in the imide structure, a branched terthiophene (α - α connection and α - β connection of the thiophene units) and a triphenylamine donor. In

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Scheme 1. Synthesis of the donor-acceptor-perylene monoimides with thiophene dendron spacer groups (**1a** and **1b**): a) K_2CO_3 , $[\text{Pd}(\text{PPh}_3)_4]$, toluene, water, ethanol, 80°C , overnight (yields: **4a** 77 %, **4b** 92 %); b) NBS, THF, $0^\circ\text{C} \rightarrow \text{RT}$, 24 h (yields: **5a** 82 %, **5b** 84 %); c) K_2CO_3 , $[\text{Pd}(\text{PPh}_3)_4]$, toluene, water, ethanol, 80°C , overnight (yields: **7a** 43 %, **7b** 19 %); d) 2-methyl-2-butanol, KOH, reflux, overnight (yields: 90 % for $n=1$, 92 % for $n=0$); e) glycine, imidazole, 140°C , overnight (yields: **1a** 89 %, **1b** 91 %). TMS=trimethylsilyl, NBS=N-bromosuccinimide, THF=tetrahydrofuran.

order to achieve a stronger push-pull effect in the naphthalene sensitizer, the outer benzene rings of the triphenylamine donor bear *para*-methoxy groups.

A strong push-pull effect is desirable for broad absorption, and this fundamental concept has been employed in many donor-acceptor sensitizers. A strong vectorial excitation from the donor to the acceptor supports efficient charge separation. The insertion of a π -spacer leads to stronger orbital partitioning (OP), thus impeding the recombination of electrons in TiO_2 with holes located on the dye molecules.^[11] In fact, quantum-mechanical calculations show that for compounds **1a** and **1b** the LUMO is mainly located on the naphthalene and perylene cores, respectively. The

HOMO, on the other hand, can be found mainly on the donor moiety, which is fully conjugated through the thiophene groups. Both the HOMO and LUMO also extend to the terthiophene spacer connecting the donor and acceptor. Hence, considerable decoupling can be observed, whilst still allowing communication between the donor and acceptor.

The branched terthiophene moiety was chosen as a spacer because thiophenes exhibit excellent charge-transport properties and enhance absorptivity.^[2,5] As our group has shown before, variation of the architecture of a terthiophene moiety can significantly alter the absorption properties.^[12] Using a branched terthiophene instead of a single thiophene or linear oligothiophene followed our intentions of adding more than two thiophene groups, but still keeping the distance between donor and acceptor for efficient intramolecular charge-transfer reasonably short, and being able to introduce a second donor moiety. As one thiophene is α - β connected, the triphenylamine donor connected to this thiophene loses some of its strength due to weak conjugation, but still can generate electron transfer towards the perylene (or naphthalene) core and will not only affect the HOMO level but also shift the first reduction potential to a more-negative potential.

This elevation of the LUMO level energy enhances the electron injection from the dye to the conduction band of the TiO_2 . Moreover, this second spacer-donor branch increases the bulkiness of the molecule and presumably prevents aggregation, and hence unwanted recombination between the dye molecules.^[13] Furthermore, bulkiness can function as a barrier between the TiO_2 and the hole-transporting layer.^[14] Obviously, this effect is always a trade-off between the aforementioned positive effects and the undesired consequence of lower dye concentrations on the TiO_2 , thereby leading to less light harvesting.^[15]

Concerning the absorption characteristics, **1a** appears dark purple, and **1b** as brownish-orange to the human eye.

The absorption spectra of both dyes are displayed in Figure 1. **1a** shows a very broad absorption over the whole visible region with two strong absorption bands, one band

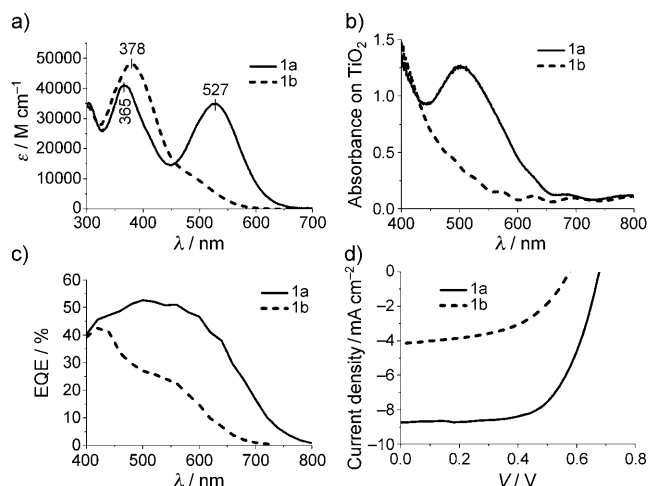


Figure 1. a) Absorption spectra (in CH_2Cl_2) of **1a** and **1b**; b) Absorbance on TiO_2 of **1a** and **1b**; c) IPCE of **1a** and **1b**; d) I–V curve of **1a** and **1b**.

around $\lambda=365$ nm and a strong band resulting from the $\pi-\pi^*$ transition of the PMI at $\lambda=527$ nm. On the other hand, **1b** shows one strong main band in the visible region with an absorption maximum of $\lambda_{\text{max}}=378$ nm. Moreover, a weak charge transfer band is observed around $\lambda=500$ – 600 nm.

Both dyes were incorporated into s-DSCs following the same procedure (see the Experimental Section). The absorptivity on TiO_2 as well as the IPCEs show a clear superiority of the perylene sensitizer in the visible region that is relevant for the cell performance. Whereas **1b** reaches a top IPCE value of 42% at 420 nm and then drops steadily with longer wavelength, **1a** has IPCE values of around 50% (top IPCE of 52% at 470 nm) from 460 to 580 nm and values of over 40% from 400–630 nm. Moreover, the IPCE curve of **1a** extends out to 800 nm, roughly 100 nm more bathochromic than the curve of **1b** (Table 1). Integration of the IPCE spectra results in current densities of 8.6 mA cm^{-2} for **1a** and 3.7 mA cm^{-2} for **1b**, in good agreement with the I/V measurements.

Table 1. Optical and electrochemical properties of **1a** and **1b**.

	λ_{max} [nm]/ ϵ [$\text{cm}^{-1} \text{ M}^{-1}$]	LUMO ^[a] / HOMO ^[a] / bandgap [eV]	I_{sc} [mA cm^{-2}]	V_{oc} [mV]	FF [%]	η [%] (1 sun)
1a	365/41.033 527/34.881	–3.5/ –5.0/ 1.5	–8.7	680	63	3.8
1b	378/47.967	–3.1/ –4.9/ 1.8	–4.2	580	51	1.2

[a] determined by cyclic voltammetry.

As for the application in DSCs, not only the absorption of the dyes but also their energy levels play an important role in determining their efficiency. The energy levels of the HOMO and LUMO, that is, the ionization potential and the electron affinity, were calculated using density functional theory (see the Supporting Information) and afterwards determined by cyclic voltammetry. Theoretical predictions for **1a** gave an energy level of -5.0 eV for the HOMO and -3.6 for the LUMO, whilst cyclic voltammetry measurements in dry dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte gave -5.0 eV and -3.5 eV, respectively. For **1b**, the calculated HOMO and LUMO energy levels were -4.7 eV and -3.0 eV, respectively. Again, there is a good coherence with the values determined by cyclic voltammetry: -4.9 eV (HOMO), -3.1 eV (LUMO). This result corresponds to 0.6 V (HOMO) and -0.9 V (LUMO) for **1a** and 0.5 V (HOMO) and -1.3 V (LUMO) for **1b** vs. NHE (normal hydrogen electrode). Comparing the reduction potentials of **1a** and ID176 in solution, the LUMO of **1a** is considerably higher than for ID176 (LUMO: -0.68 V vs. NHE; see the Supporting Information). As the energy of the conduction band of titaniumdioxide is approximately at -0.5 V versus NHE, the driving force of electron injection is roughly 0.4 eV for the perylene derivative **1a** and 0.8 eV for the naphthalene derivative **1b**. Thus, the driving force lies well above the desired minimum driving force of 0.2 eV for efficient electron injection.^[16] The ionization potential of the hole-transporting material spiro-MeOTAD -4.77 eV in vacuum^[17] is above the HOMO values of both dyes, thus allowing efficient dye regeneration.

From the electrochemical properties, the naphthalene sensitizer **1b**, with its higher LUMO, has the potential for much better electron injection. However, this sensitizer does not have an efficiency as high as the perylene sensitizer **1a**. One reason for this observation could be the lower driving force for the dye regeneration. Another cause could surely be found in the additional light harvesting of **1a**. Even though the absorptivity for **1b** in the region of 320–460 nm is higher, **1a** harvests and converts more sunlight through its additional absorption band in the visible region which—bearing in mind the solar spectrum—is of greater importance for photovoltaics than the UV region. This effect, which could already be assumed from the absorption spectra in dichloromethane or on TiO_2 , is affirmed by the EQE spectrum and reflected in the I_{sc} . Furthermore, the V_{oc} of **1a** and the fill factor (63% for **1a** compared to 51% for **1b**) are higher resulting in a three times higher efficiency for **1a**.

In summary, we have reported the synthesis, optical, electronic, and photovoltaic properties of a perylene-monoimide sensitizer with a terthiophene dendron spacer and a triphenylamine donor that shows an outstanding efficiency of 3.8% in a solid state DSC under 1.5 AM light illumination; to date, this is the highest reported efficiency for perylene-monoimide sensitizers as well as for similar sensitizer systems using a cyanoacrylate acceptor.^[7] For comparison, we prepared its naphthalene analogue, which gave a much

lower efficiency of 1.2%. Careful balance of the orbital energies and color tuning, in order to achieve a broad spectrum with high absorptivity as well as a sound degree of orbital partitioning and a considerate steric architecture of the molecule, have been key factors for the excellent photovoltaic performance of **1a**.

Experimental Section

Synthesis procedures and product characterization (^1H NMR, ^{13}C NMR, IR, UV/Vis absorption, high resolution mass spectroscopy) can be found in the Supporting Information.

Preparation of Solid-State Dye-Sensitized Solar-Cell Layers

First, a TiO_2 blocking layer was prepared on a fluorine-doped tin oxide (FTO)-covered glass substrate using spray pyrolysis.^[18] Next, a TiO_2 paste (Dyesol), diluted with terpineol, was applied by screen printing, resulting in a film thickness of 1.8 μm . All films were then sintered for 1 h at 450°C, followed by treatment in a 40 mm aqueous solution of TiCl_4 at 65°C for 30 min, followed by another sintering step. The electrodes were then dyed in 0.5 mm dye solution in CH_2Cl_2 . The dye-coated TiO_2 electrodes with both dyes contain an organic coadditive (BASF-A1). Spiro-MeOTAD was applied by spin-coating from a solution in chlorobenzene also containing 20 mm $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$. Fabrication of the device was completed by evaporation of 200 nm of silver as the counter electrode. The active area of the solid-state DSCs was defined by the size of these contacts (0.13 cm^2), and the cells were masked by an aperture of the same area for measurements. Current–voltage characteristics (1000 W m^{-2} , AM 1.5G) and the incident photon to current conversion efficiency (IPCE) spectra were measured for all cells.

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