

ChemComm

This article is part of the

Porphyrins & Phthalocyanines web themed issue

Guest editors: Jonathan Sessler, Penny Brothers and
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Cite this: *Chem. Commun.*, 2012, **48**, 4953–4955

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COMMUNICATION

Towards enhancing light harvesting—subphthalocyanines as electron acceptors†‡

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Received 16th February 2012, Accepted 30th March 2012

DOI: 10.1039/c2cc31167d

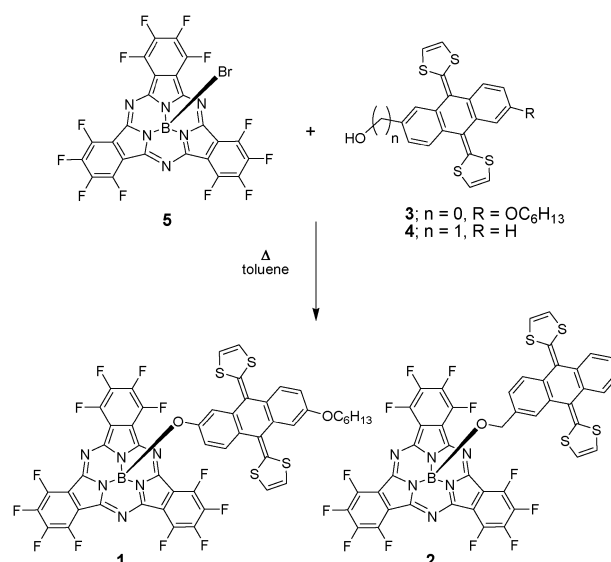
One carbon atom is too many. Two subphthalocyanine-extended TTF electron donor–acceptor conjugates were synthesized and characterized. Their photophysical properties prompt the remarkable impact that one extra carbon between the two constituents exerts on photoinduced processes, that is, charge recombination dynamics in the normal versus inverted region.

Over the last decade, the field of organic solar cells has attracted major research interest among scientists from different research fields. Mastering the performances of such solar devices implies the cooperative alliance of different research disciplines, namely organic synthesis, photophysical characterization, and device fabrication. Such a multidisciplinary approach secured nowadays the role of fullerene derivatives as the most employed n-type material for photovoltaic applications.¹ Fullerenes not only possess outstanding electron accepting properties, but also form long-lived charge separated states in combination with electron donating polymers and/or molecules.² However, it is well-known that they exhibit weak absorption cross sections throughout the visible part of the solar spectrum, which limits the sunlight capture and, therefore, restricts the efficiencies in terms of photon-to-electron conversion. A promising alternative to fullerenes is subphthalocyanines (SubPcs).^{3,4} These non-planar aromatic structures are able to absorb light throughout most of the visible part with very high extinction coefficients. In addition, they act either as electron donors or as electron acceptors.⁵

While a great deal of research effort has focused on exploring the performances of SubPcs as electron donors, detailed investigations that shed light on their accepting capabilities still remain scarce.

On the other hand, π -extended tetrathiafulvalenes (exTTFs) are non-aromatic compounds that gain aromaticity upon oxidation and feature excellent electron abilities.⁶ This renders them especially interesting for the design of electron donor–acceptor conjugates/hybrids. As a matter of fact, a myriad of investigations have demonstrated the outstanding electronic communication between exTTFs and carbon-based materials such as fullerenes and carbon nanotubes among others.⁷

Taking the aforementioned into concert, we were interested to investigate the performances of SubPcs as electron acceptors, when combined with exTTF derivatives. In this context, dodecafluorosubphthalocyanines–exTTFs conjugates (SubPc–exTTF) **1** and **2** were synthesized using spacers of different lengths (see Fig. 1). Steady state measurements revealed that in the ground state SubPcs and exTTFs act as independent constituents **1** and **2**. Moreover, by means of transient absorption spectroscopy the excited state interactions between the constituents were investigated in detail.

Fig. 1 Synthesis of SubPc–exTTF **1** and **2**.

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† This article is part of the *ChemComm* 'Porphyrins and phthalocyanines' web themed issue.

‡ Electronic supplementary information (ESI) available: Experimental details for compounds **1**, **2** and **5**. HOMO and LUMO representations for compounds **1** and **2**. See DOI: 10.1039/c2cc31167d

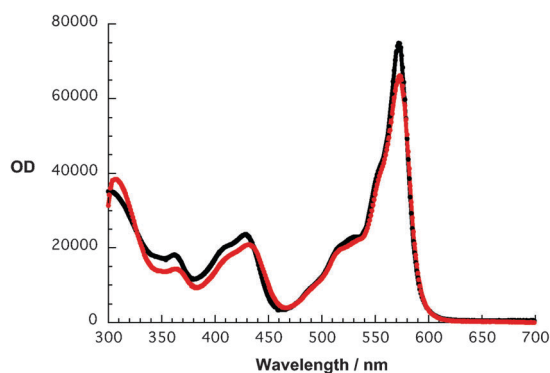


Fig. 2 Absorption spectra of **1** in toluene (black spectrum) and benzonitrile (red spectrum).

ExTTFs **3** and **4** were synthesized according to previously reported procedures based on that published by Bryce and Marshall.^{8–10} SubPc precursor **5** was obtained in 93% yield, by condensation of tetrafluorophthalonitrile in the presence of BBr_3 in chlorobenzene adapting a procedure described by van Lier and colleagues.¹¹ Substitution of the bromine atom of **5** by exTTFs **3** and **4** in refluxing toluene gave rise to the final products **1** and **2**, which possess different linker lengths. After purification by silica gel column chromatography, **1** and **2** were obtained in 27 and 12% isolated yields, respectively. Both compounds were characterized by ^1H NMR, ^{13}C NMR spectroscopy, UV-vis spectrophotometry as well as mass spectrometry. MALDI-TOF mass spectra of **1** and **2** show peaks at 1106.1 and 1020.0, respectively, corresponding to $[\text{M}]^+$. A peak at 611.1, which corresponds to the loss of exTTF, was observed for **2**.

First insights into the electronic interactions in SubPc–exTTF—in the ground state and excited state—came from steady state measurements. Here, **1** and **2** were tested and compared in solvents of very different polarity (Fig. 2 and Fig. S10 (ESI \dagger)).

Basically, the absorption spectra of **1** and **2** consist in the superposition of their constituents, namely SubPc and exTTF. In particular, **1** shows two main absorption maxima at around 430 and at 574 nm, which correspond to exTTF and SubPc, respectively. While the impact of the solvent polarity on the optical band gap of the SubPc moiety is negligible, the absorption maximum of the exTTF shifts from 429 to 432 nm upon changing the solvent from toluene to benzonitrile. In **2**, the solvent polarity imposes a slightly stronger impact on the absorption features (Fig. S10, ESI \dagger). For example, the exTTF centered maximum undergoes a bathochromic shift from 431 to 436 nm upon increasing the polarity, while the maximum of SubPc absorption blue shifts from 575 to 570 nm.¹²

Regarding the steady-state fluorescence of **1**, only the SubPc characteristic pattern in the form of a very weak fluorescence band at 582 nm evolved with quantum yields of 1.1×10^{-3} in toluene and 1.0×10^{-3} in benzonitrile. Please note that the quantum yield of a SubPc reference is 0.67.¹³ Likewise in **2** the only appreciable fluorescence is that of SubPc with maxima at 581 and 579 nm, and slightly higher fluorescence quantum yields of 0.12 and 0.18 in toluene and benzonitrile, respectively. It is important to note the lack of any detectable emissive features originating from exTTF in either **1** or **2**.

The aforementioned experiments were complemented by fluorescence lifetime measurements of the SubPc fluorescence

in the reference as well as in **1** and **2**. In the SubPc reference the fluorescence lifetime is strictly mono-exponential with a lifetime of 3.2 ns.¹³ In stark contrast, the SubPc fluorescence lifetimes in **1** and **2** are bi-exponential with a very weak long-lived component of around 2 ns and a dominant short-lived component of less than 0.1 ns. In summary, all these initial results are, *a priori*, first indications for a fast excited state deactivation process, well *via* electron and/or energy transfer.

Transient absorption spectroscopy based on pump–probe experiments helped to provide spectroscopic and kinetic evidence of a charge transfer mechanism between photoexcited SubPc and exTTF. The transient absorption changes of a SubPc reference relate to its first singlet excited state, showing a broad transient absorption maximizing around 500 and 910 nm, whereas a minimum at 575 nm correlates with the bleaching of Q-band absorption of the SubPc. This transient decays *via* intersystem crossing to the first triplet excited state showing a transient absorption maximum at 1175 nm. The lifetime of the first singlet excited state obtained from a monoexponential fit of the decay at 910 nm is 1.5 ± 0.1 ns—a value that agrees well with previous reports.¹⁴

When probing **1** the same singlet excited state characteristics of SubPc were found—despite the presence of the electron donating exTTF—upon photoexcitation at either 387 or 550 nm.

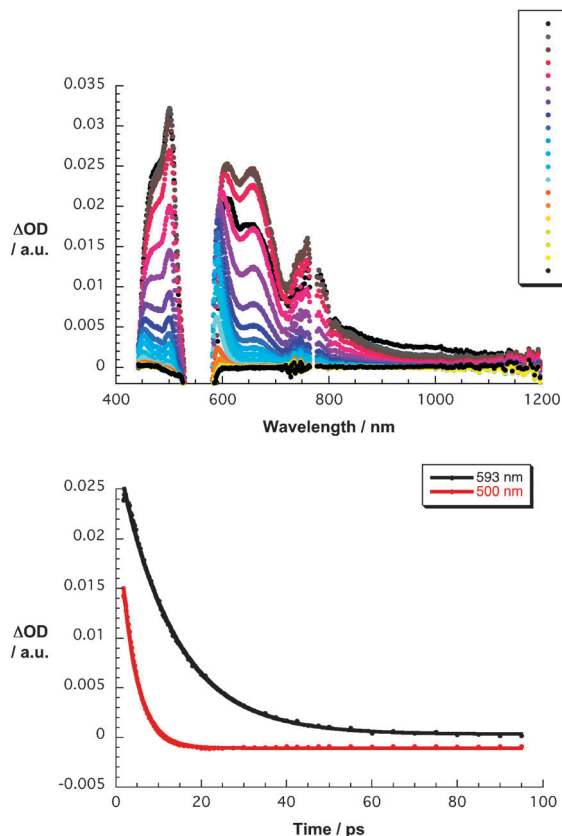


Fig. 3 Upper part: differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump–probe experiments (550 nm) of **1** in benzonitrile with several time delays between 1.1 and 210 ps at room temperature—see figure legend for details. Lower part: time absorption profiles of the spectra at 500 (red spectrum) and 593 nm (black spectrum) monitoring the charge separation and charge recombination dynamics.

The SubPc singlet excited state features decay much faster in **1** compared to SubPc and give rise to the formation of new transient absorption bands maximizing at 455, 500, 590, and 670 nm (Fig. 3). On the one hand, the maximum at 670 nm is assigned to the one electron oxidized form of exTTF.¹⁵ The maxima at 455, 500, and 590 nm, on the other hand, match the absorption of the one electron reduced form of SubPc.¹⁶ In summary, transient absorption spectroscopy testifies the formation of radical ion pair states in **1**, in which in accordance with the frontier orbital calculations (see Fig. S11, ESI†), SubPc is one-electron reduced and exTTF is one-electron oxidized. Next, the formation and decay dynamics of these radical ion pair states were derived by two-exponential fitting of the 500 and 595 nm absorptions. To this end, the charge separation and the charge recombination dynamics were 3.1 and 1.7 as well as 13 and 18 ps in toluene and benzonitrile, respectively. As the product of charge recombination, the triplet excited state of SubPc finally evolves.

Regarding the excited state characteristics of **2**, a reaction pattern develops that is quantitatively identical to that seen for **1**. In particular, within 3 ps the singlet excited state of SubPc transforms into radical ion pair states in toluene and benzonitrile, respectively. Like in **1**, the latter features maxima at 455, 500, 590, and 670 nm. The lifetimes of the radical ion pair state were 15 ps in toluene and 7 ps in benzonitrile and, as such, a reflection of the different spacers. Again, the SubPc triplet excited state is formed as a product of charge recombination.

In a nutshell, we have demonstrated the unique light harvesting and electron accepting features of dodecafluorophthalocyanine covalently linked extended TTFs. In fact, a rapid electron transfer yields a radical ion pair state, whose lifetime was found to be influenced by the nature of the linker. Most importantly, implementation of an additional carbon moves the charge recombination dynamics from the normal to the inverted region of the Marcus parabola.

Financial support from the MICINN and MEC, Spain (CTQ-2011-24187/BQU, CTQ2011-24652/BQU, CONSOLIDER-INGENIO 2010 CDS 2007-00010 Nanociencia Molecular, PRI-PIBUS-2011-1128, PRI-PIBUS-2011-1067, PLE2009-0070), and CAM (MADRISOLAR-2, S2009/PPQ/1533) and the Deutsche Forschungsgemeinschaft (SFB 583 and FCI), is acknowledged. LE thanks the National Science Foundation for an International Collaboration in Chemistry award, grant CHE-1124075, for generous support.

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