

Synthesis of a π -extended TTF–perylene diimide donor–acceptor dyad

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Abstract

A donor–acceptor dyad containing perylene diimide as the electron acceptor and π -extended tetrathiafulvalene as electron donor has been successfully synthesized by means of a Wittig reaction. Cyclic voltammetry and absorption spectroscopy show that both electroactive units preserve their nature, whereas preliminary photophysical investigations show a strong fluorescence quenching.

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Photoinduced electron transfer has a great importance in both life and science. It is the fundamental process in which photosynthesis settles and it also constitutes the basis of molecular electronics.¹ In this respect, the unique features that organic semiconductors offer, for example the tuning of absorption and emission properties, REDOX behaviour or HOMO–LUMO band gaps by easy structural modifications, have prompted the synthesis of a variety of molecular architectures combining electron donor fragments covalently linked to accepting units and exhibiting the transfer of one electron from the donor to the acceptor unit after photoexcitation.²

Perylene diimide (PDI) derivatives have evolved into one of the most fascinating materials in both industry and academics due to their good chemical, thermal and photostability.³ Specially remarkable for the construction of systems showing photoinduced electron transfer are its good electron accepting ability and high absorption of light in the visible. Thus, PDIs have been recently linked to conjugated polymers,⁴ [60]fullerene,⁵ oligophenylene-vinyls,⁶ pyrenes,⁷ oligothiophenes,⁸ phthalocyanines,⁹

porphyrins¹⁰ or tetrathiafulvalene (TTF)¹¹ as the donor counterpart aiming the induction of photoinduced electron transfer. These dyads are often claimed as promising candidates for the construction of organic solar cells,¹² either as active layers or to be used as light-harvesting antenna,¹³ or as models for the investigation of the fundamentals of photoinduced electron transfer.

One important aspect to consider in these dyads is the stabilization of the charge separated state (PDI^{•-}–Donor^{•+}). The employment of TTF¹⁴-based donors in combination with PDIs can be specially useful,¹¹ as TTF undergoes aromatization upon oxidation, affording thermodynamically stable radical cationic and dicationic species. In this respect, the substitution of TTF by its π -extended analogue, exTTF, could be advantageous, considering the additional improvement in the stability of radical ion pairs produced by exTTF.¹⁵ In fact, exTTF has been employed in the synthesis of D–A dyads showing long lifetime charge separated states.¹⁶ This fact has been rationalized in terms of the aromaticity and planarity that are gained in the dicationic state of exTTF.

Thus, we decided to synthesize the dyad exTTF–PDI **5**, in which a PDI electron accepting unit has been covalently attached to an electron donor exTTF through a relatively rigid vinyl-benzene spacer. The presence of long alkyl chains in the PDI unit assures the solubility of dyad **5**, thus

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enabling its complete characterization by NMR, electrochemical and light absorption and emission techniques.

The synthesis of dyad **5** was carried out following the synthetic procedure depicted in Scheme 1. Although, in general, perylenediimides are attached to a variety of systems by the direct condensation between perylenemonoimide-monoanhydrides and amino-functionalized compounds we have employed an alternative approach, namely a Wittig reaction between the appropriately functionalized PDI unsymmetrical diimide **3** and the corresponding triphenylphosphonium salt of exTTF **4**.¹⁷ The presence in **1**, readily affordable from the parent monoanhydride by treatment with ammonium acetate,¹⁸ of an acidic imido hydrogen enables its further and convenient functionalization. Thus, Williamson reaction between **1** and 4-(bromomethyl)benzaldehyde (**2**)¹⁹ in the presence of cesium carbonate as the base and a catalytic amount of sodium iodide afforded the perylenediimide derivative **3**, functionalized with an aldehyde group. Subsequent Wittig reaction between **3** and exTTF triphenylphosphonium salt **4** gave dyad **5** in a moderate 65% yield.

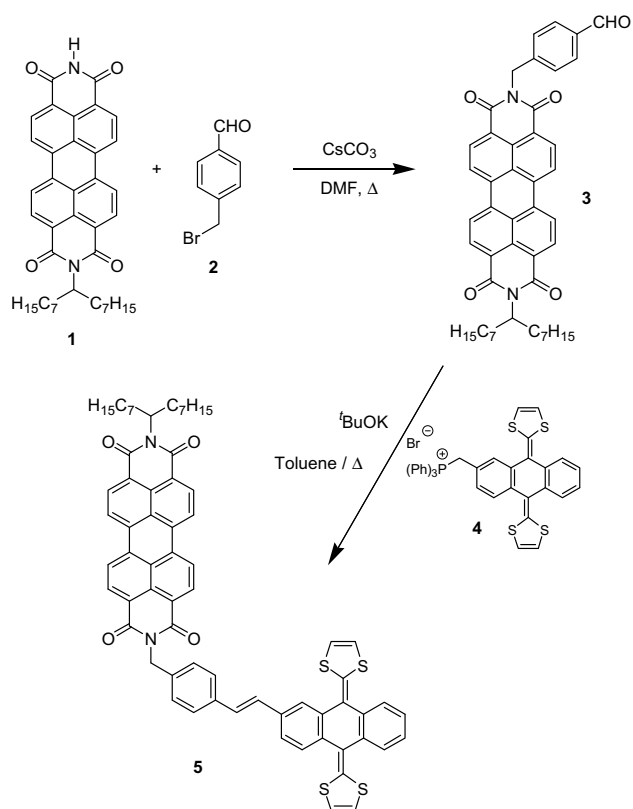
The presence of long and branched alkyl chains in the perylenediimide moiety of dyad **5** provides good solubility in common organic solvents and enables its complete characterization not only by the standard spectroscopic techniques,²⁰ but also by cyclic voltammetry and absorption and emission spectroscopy.

Thus, the ¹H NMR spectrum of dyad **5** displays at low fields the characteristic duplets arising from the perylene-

diimide aromatic core. The vinyl protons of the exTTF moiety appear as a singlet around 6.30 ppm and the additional signals of both the aromatic anthracene core of exTTF and the vinyl-benzene spacer are displayed as complex overlapping duplets and multiplets. One important issue to be considered in compound **5** is the stereochemistry of the vinylic double bond. Although Wittig reactions are known to generally proceed without control on the stereochemistry of the final alkene, in contrast to other olefination reactions such as Wittig-Horner or McMurry couplings, it has been reported that the use of the triphenylphosphonium salt **4** in similar Wittig reactions exclusively affords the *trans* isomer, probably due to the bulky character of the exTTF fragment.¹⁶ Experimental evidence of the *trans* configuration arises from the observation of an olefinic coupling of ca. 16 Hz, which can be related to the *trans* configuration. In the ¹³C NMR spectrum the carbonyl imide group of the PDI moiety is clearly visible at 163 ppm together with those signals of the aromatic carbons in the sp² region, the methylene and methyne groups linked to the nitrogen (55 ppm) and the signals of the alkyl chains.

The electrochemical behaviour of dyad **5** has been investigated by cyclic voltammetry in dichloromethane solutions, and this technique shows the ambipolar behaviour of this material. Thus, at negative values, the two distinct one-electron reversible waves ($E_{\text{red}}^{1/2} = -1.09$ and -1.29 V) corresponding to the successive reduction of the PDI moiety to yield PDI⁻ and PDI²⁻ species are clearly visible (see Fig. 1).

For comparison, the reference compound *N,N'*-(1-hexylheptyl)perylenediimide gives peaks at $E_{\text{red}}^{1/2} = -1.11$ and -1.31 V under the same experimental conditions, which is also similar to the values reported earlier for PDI compounds.^{4,21} At positive potentials, a quasireversible oxidation process can be detected, at $E_{\text{ox}}^{1/2} = -0.20$ V, which can be attributed to the oxidation of the exTTF unit to



Scheme 1. Synthesis of PDI-exTTF dyad **5**.

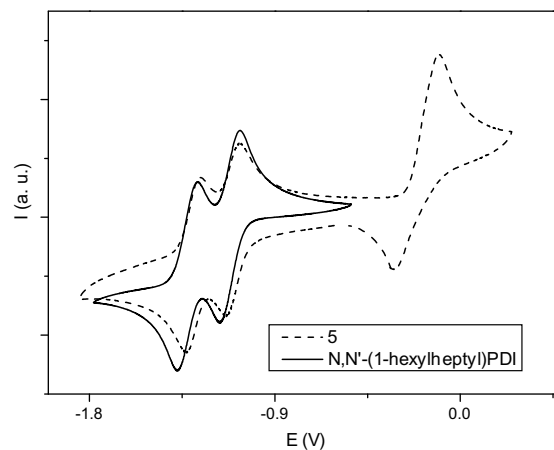


Fig. 1. Cyclic voltammogram of dyad **5** along with reference *N,N'*-(1-hexylheptyl)PDI (10^{-2} M, Pt as working and counter electrode, TBAPF₆ (0.1 M) as supporting electrolyte and a scan rate of 200 mV s^{-1} at room temperature. The ferrocene/ferrocenium (Fc/Fc⁺) couple was used as internal reference and showed a peak at $+0.35 \text{ V}$ vs Ag/Ag⁺).

the corresponding aromatic and thermodynamically stable dication exTTF^{2+} .²² The similar values observed for the oxidation and the reduction processes of the two electroactive moieties in dyad **5** compared to the reference compounds suggest that there is no significant ground state interaction between the electron-donating exTTF unit and the electron-accepting PDI fragment. Many PDI derivatives substituted at the imide nitrogen have already been investigated and it has been observed that the imide substituent has a negligible influence on the electronic properties of perylene diimides because of the presence of nodes of the HOMO and LUMO at the imide nitrogen.^{3c} Thus, perylene diimides can be regarded as closed chromophoric systems whose electronic properties remain unaltered by the imide substituent.²³

Thus, in these systems, the PDI and exTTF units can be regarded as independent chromophoric systems whose electronic properties remain unaltered in spite of their covalent attachment, as it is also observed in the UV–vis spectra.

The UV–vis absorption spectra of the donor–acceptor dyad **5** together with that of references *N,N'*-(1-hexylheptyl)perylene diimide and exTTF in diluted (ca. $5 \cdot 10^{-6}$ M) dichloromethane solutions are depicted in Figure 2. The absorption spectrum of exTTF–PDI dyad **5** consists of the approximate superposition of the absorption features of its constitutive units, confirming the minimal interaction between the chromophores in the ground state, in agreement with the electrochemical behaviour. No new intramolecular charge-transfer bands above 600 nm were detected in dyad **5**. The absorption spectrum of dyad **5** shows characteristic bands arising from the presence of the PDI groups, with maxima at 527, 489, and 455 nm, the latter overlapping with the lowest energy band from exTTF.

Fluorescence emission spectra of PDI–exTTF dyad **5** and *N,N'*-(1-hexylheptyl)PDI were measured in diluted dichloromethane solutions at fixed optical density using an excitation wavelength of 480 nm. The emission features

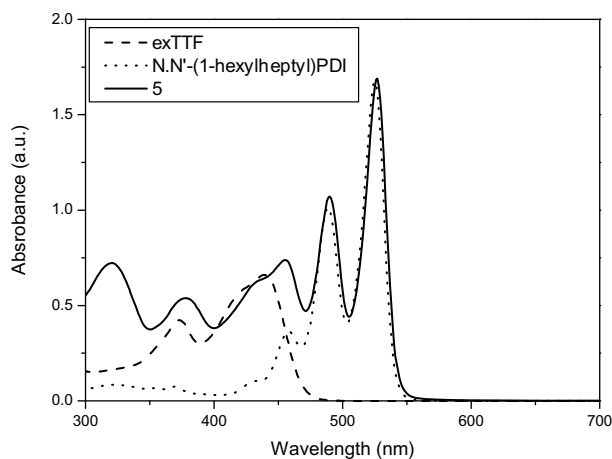


Fig. 2. UV–vis spectra of dyad exTTF–PDI **5** (solid line), *N,N'*-(1-hexylheptyl)perylene diimide (dotted line), and exTTF (dashed) in dichloromethane solution.

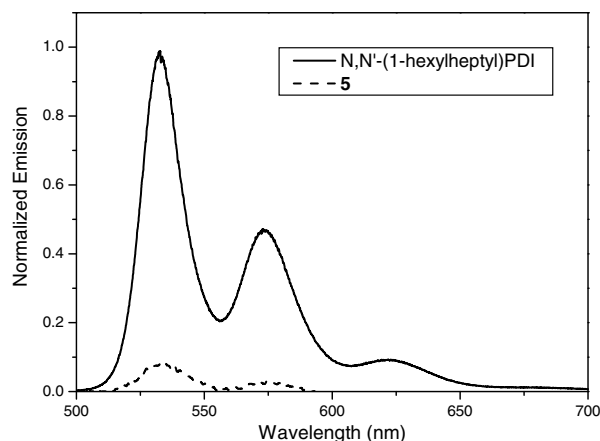


Fig. 3. Fluorescence spectrum of dyad **5** along with reference *N,N'*-(1-hexylheptyl)PDI.

are in approximate mirror symmetry to the corresponding absorption features. This result implies that the fluorescence of dyad **5** is due to the PDI units. The fluorescence properties of the perylene diimide chromophore are greatly affected by the presence of the exTTF moiety. Thus, a quantitative quenching (ca. 92%) of the PDI fluorescence emission was observed in dyad PDI–exTTF in comparison with the fluorescence spectrum of reference *N,N'*-(1-hexylheptyl)PDI (Fig. 3).

To explain this strong fluorescence quenching, energy transfer can be ruled out as the PDI fragment has a smaller optical bandgap than the exTTF moiety, that is, there is a minimal spectral overlap between the absorption spectrum of the exTTF moiety and the fluorescence spectrum of the PDI fragment. Quenching by the PDI → exTTF energy transfer process due to the Förster mechanism will be prohibited, according to the energy level of both units (2.33²⁴ and 2.7 eV for exTTF¹⁵). Thus, we ascribe the large fluorescence intensity reduction in dyad **5** to photoinduced electron transfer (PET) processes between the PDI and exTTF units. Indeed, a PET process is energetically favourable as the corresponding free energy ΔG_{PET} was estimated to be -2.60 eV using the Weller equation.²⁵ However, time-resolved absorption spectral studies (PIA) will be needed to provide further evidence for the above assumption.

Acknowledgements

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