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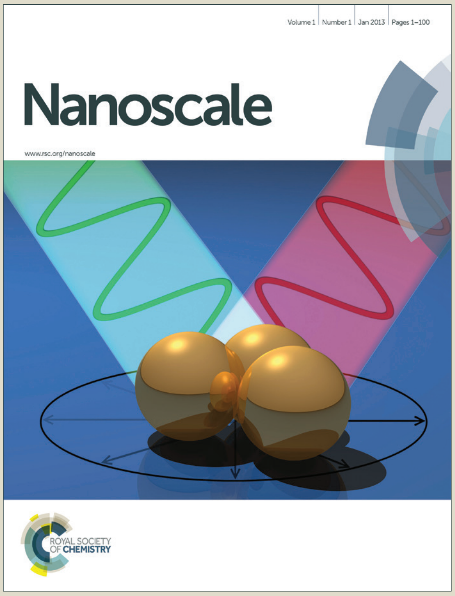

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Does a Nitrogen Matter?: Synthesis and Photoinduced Electron Transfer of Perylenediimide Donors Covalently Linked to $C_{59}N$ and C_{60} Acceptors

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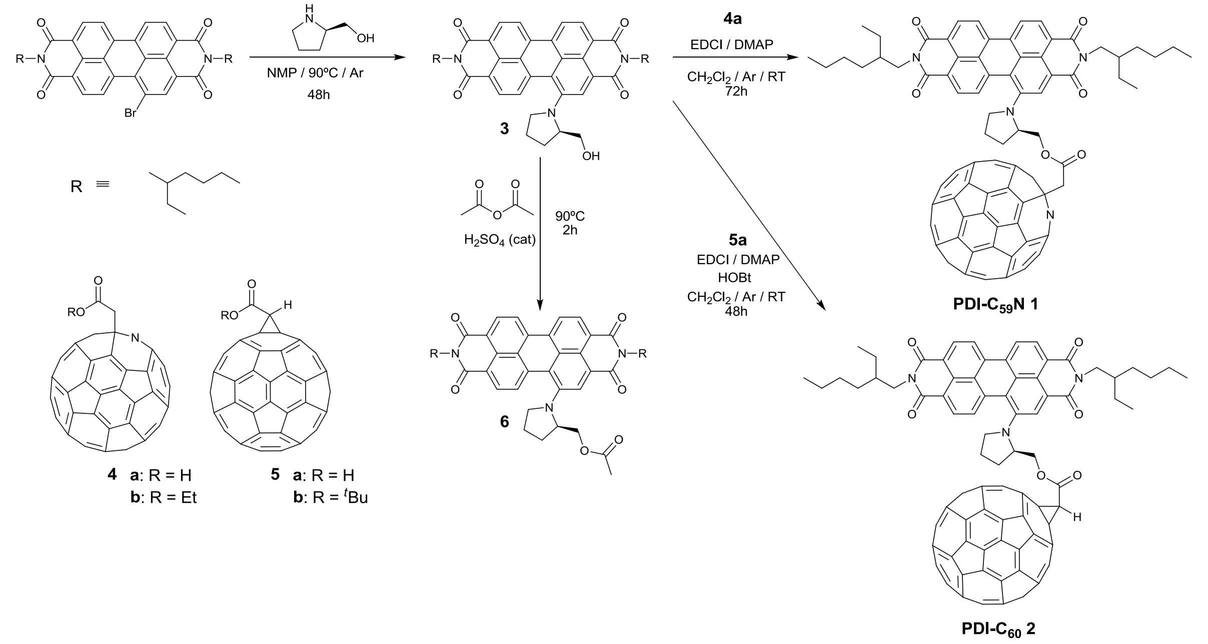
The first perylenediimide (PDI) covalently linked to an azafullerene ($C_{59}N$) is described. PDI-$C_{59}N$ and PDI-C_{60} dyads where PDI acts as an electron-donor moiety have been synthesized by connection of the balls to the PDI 1-bay position. Photoexcitation of the PDI unit in both systems results in formation of the charge-separated state by photoinduced electron transfer from the singlet excited state of the PDI moiety to the $C_{59}N$ or to the C_{60} moiety. The charge-separated state has a lifetime of 400 ps in the case of PDI-$C_{59}N$ and 120 ps for PDI-C_{60} dyad in benzonitrile at 298 K. This result has significant implications for the design of organic solar cells based on covalent donor–acceptor systems using $C_{59}N$ as an electron acceptor, indicating that longer-lived charge-separated states can be attained using $C_{59}N$ systems instead of C_{60} systems.

Introduction

The seeking for efficient molecular systems, based on the covalent combination of suitable and versatile building blocks, capable to mimic the photoinduced electron transfer that naturally occurs in photosynthesis, has been a constant in material science.[1] In a simplistic definition, a molecular system which combines an electron-acceptor moiety with an electron-donor counterpart, able to be excited by the action of light, can be considered as a potential photosynthetic system, and therefore useful for photovoltaic applications. [60]Fullerene, due to its extraordinary electron-acceptor character and its fascinating chemical versatility, has been one of the most utilized electron-acceptor building blocks[2] for that purpose and, thus, several efficient artificial photosynthetic [60]fullerene-based systems have been described, using different chromophores as photoexcitable electron-donor counterparts.[3] Performances of these donor-acceptor materials can be improved by selecting an appropriate electron-donor counterpart, but also by replacing one or more carbon atoms of the fullerene cage by heteroatoms, affording the so-called heterofullerenes.[4] The substitution of a tetravalent carbon atom of the three dimensional network by a trivalent nitrogen atom is one of the most interesting alterations. This simple modification leads to azafullerene $C_{59}N$, a fullerene-based building block with an improved electron-acceptor character, when it is compared to that of pristine C_{60} fullerene.[5] A number of different azafullerene-based donor-acceptor covalent compounds have been previously described, showing interesting photophysical properties that make them ideal candidates to be incorporated in organic photovoltaic devices. Hirsch et al. described the synthesis of an azafullerene-ferrocene dyad, that shows strong electronic coupling between the ferrocene and azafullerene moieties in the ground state.[6] Additional $C_{59}N$-based dyads carrying photoactive units such as porphyrin[7] and pyrene,[8] were also prepared. More recently, azafullerene-electron-donor dyads, using phthalocyanine[9] and corrole[10] units, have been reported to undergo photoinduced electron transfer upon selective irradiation of the electron-donor moiety.

On the other hand, perylenediimides (PDI) compose an outstanding family of perylene derivatives that, due to an extreme synthetic versatility and an easily tunable electronic character, have become one of the most promising classes of molecular materials in organic photovoltaic devices.[11] In this context, we can find only few examples where PDI derivatives have been successfully employed like an electron-donor moiety in fullerene-based systems, eventually undergoing photoinduced electron and/or energy transfer.[12]

Here we present the synthesis, characterization and photophysical properties of a new photoexcitable molecular system, consisting of an electron-donor PDI moiety, carrying a pyrrolidinyl substituent in the 1-bay position, which also acts as linker to the $C_{59}N$ counterpart (Scheme 1). The obtained donor-acceptor PDI-$C_{59}N$ dyad **1**, upon selective excitation of the PDI subunit in benzonitrile, shows efficient intramolecular photoinduced electron transfer, generating a 400 ps-lived charge-separated state (CSS). Together with two covalently linked porphyrin-$C_{59}N$ dyads,[7] is the longest CSS lifetime value



Scheme 1. Synthetic routes for preparing PDI-$C_{59}N$ and PDI-C_{60} dyads **1** and **2** as well as PDI-based reference material **6**.

obtained so far for a $C_{59}N$-based donor-acceptor dyad in a polar solvent. Moreover, in order to study the effect of the nitrogen atom on the photophysics, the analogous PDI-C_{60} dyad **2** (Chart 1) was synthesized, as reference material, obtaining a 3-times shorter CSS lifetime than PDI-$C_{59}N$ dyad **1**, thus, highlighting the role of nitrogen in the photoinduced electron- transfer processes.

Synthesis and characterization

Initially, PDI-$C_{59}N$ and PDI-C_{60} dyads **1** and **2** were synthesized as described in Scheme 1. Firstly, *(R)*-1-(2'-hydroxymethylpyrrolidin-*N*-yl)PDI **3** was obtained upon nucleophilic aromatic substitution on *N,N'*-di(2-ethylhexyl)-1-bromoperylene-3,4,9,10-tetracarboxy diimide [13] by *(R)*-2-hydroxymethylpyrrolidine in 51% yield. Then, esterification reaction of PDI-based **3** with azafullerenylacetic acid **4a**[9] gave rise to PDI-$C_{59}N$ dyad **1** in 8% yield. A similar esterification process, involving 2,2-[60]fullerenylacetic acid **5a** [14] and PDI-based **3** was followed, affording in 43% yield PDI-C_{60} dyad **2**. Furthermore, PDI derivative **6** was also synthesized in 75% yield, through an acylation of **3** with acetic anhydride in acidic media, in order to be used as reliable reference to evaluate optical, electrochemical and photophysical properties.

All new compounds were fully characterised using standard analytical techniques such as ^{1}H and ^{13}C NMR, HR-MS, FT-IR, electronic absorption and photoluminescence. Figure 1 compares the aromatic region of the ^{1}H NMR spectra for **1**, **2** and **6** in $CDCl_3$ as solvent. Taking as reference the C1 of the PDI core (the substituted one), and comparing the signals of analogous hydrogens in compounds **1**, **2** and **6**, it is worth noting that the chemical displacement of the nearby hydrogens (H^2, H^{11} and H^{12}) is significantly shifted in dyad's spectra, while the contrary trend is observed in the displacement of H^5, H^6, H^7 and H^8. For example, H^2 signal goes from 8.69 to 9.19 and 9.18 ppm (in **2** and **1** respectively), while H^6 goes from 8.45 to 8.40 ppm. Furthermore, the fullerene influence is slightly larger when $C_{59}N$ is present instead of C_{60}, and it can be recognised in H^{12} displacement, which changes from 8.11 ppm in **6,** to 8.29 and 8.40 ppm in dyads **2** and **1**, respectively. Figure 2 shows the aliphatic regions of the spectra, where some differences can also be found due to the presence of the covalently attached fullerene. For example, the signals corresponding to the hydrogens labelled as H^B, H^C and H^E, which appear as broad signals in the spectrum of PDI-based **6**, split into two in the corresponding spectra of PDI-fullerene dyads **1** and **2**. All these differences in the ^{1}H NMR spectra of dyads and reference material can be explained by

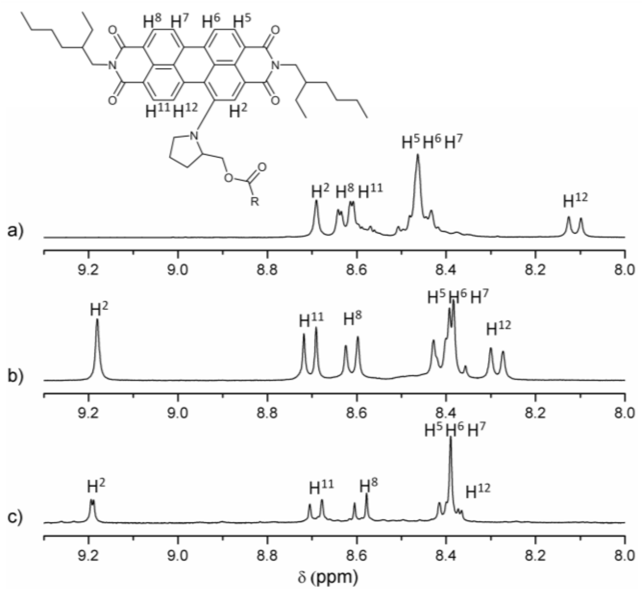


Figure 1. Partial ^{1}H NMR (9.30-8.00 ppm) spectra of a) reference PDI-based reference material **6**, b) PDI-C_{60} dyad **2**, and c) PDI-$C_{59}N$ dyad **1**.

considering the electron-withdrawing character of the fullerene sphere, which is more intense in the case of $C_{59}N$ as compared with C_{60}, and also assuming a pseudo-fixed molecular conformation in PDI-fullerene dyads caused by an electrostatic interaction between the PDI and the fullerene moiety including a concave-convex interaction[12c,15] that causes a different influence of the sphere on the chemical shift of the pyrrolidine-linker geminal protons. HR MALDI-TOF (negative mode) experiments clearly confirm the structure of PDI-$C_{59}N$ and PDI-C_{60} dyads **1** and **2**, respectively, showing base peaks due to the molecular ions at 1476.463 amu and 1474.302 amu, with isotopical distributions that exactly match the simulated isotope patterns for $C_{106}H_{52}N_4O_6$ and $C_{107}H_{51}N_3O_6$, respectively (see SI, Fig. S1).

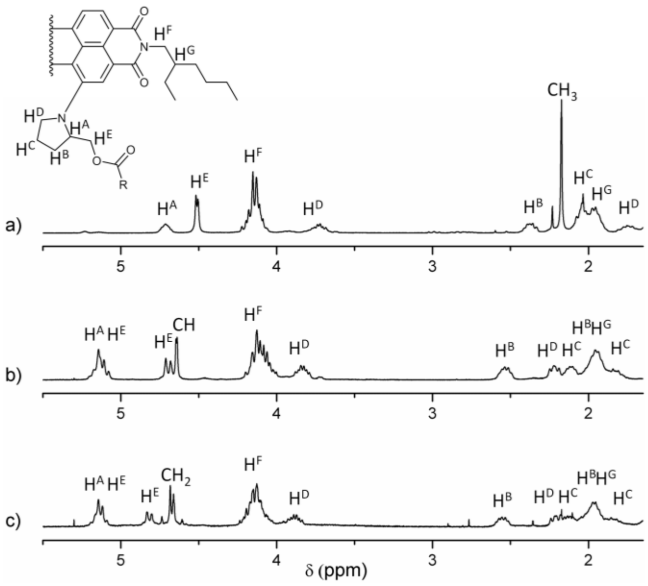


Figure 2. Partial ^1H NMR (5.50-1.60 ppm) spectra in $CDCl_3$ as solvent of a) PDI-based reference material **6**, b) PDI-C_{60} dyad **2**, and c) PDI-$C_{59}N$ dyad **1**.

Photophysical and electrochemical properties.

Figure 3 shows the overlapped UV-vis spectra of dyads **1** (solid black line) and **2** (solid grey line) and PDI **6** as reference compound (dotted line) using dichloromethane as solvent. The absorption spectra of PDI-$C_{59}N$ and PDI-C_{60} dyads **1** and **2** are characterised by three sets of absorption maxima centred around 320, 430 and 630 nm. The band around 430 nm (431 and 427 in PDI-$C_{59}N$ and PDI-C_{60} spectra, respectively) can be attributed to transitions 1-0 and 0-0 in the PDI species,[16] while the one centred at 630 nm (631 and 628 in PDI-$C_{59}N$ and PDI-C_{60} spectra, respectively) consists of a broad charge transfer (CT) band that usually appears in bay amino-substituted PDI compounds. The latter band appears as a consequence of an electron transfer between the electron-donor pyrrolidine and the electron-acceptor PDI units,[17] and therefore is very sensitive to changes in the electronic character of the entire molecule. When those spectra are compared to the absorption profile of reference compound PDI **6**, some differences can be found. One of these differences, directly related to the electronic interaction between the electroactive moieties, is a bathochromic displacement of the band centred at 624 nm, which now appears at 628 and 631 nm in PDI-C_{60} and PDI-$C_{59}N$, respectively. This fact reveals the electronic influence of the fullerene sphere on the perylene subunit in the ground state, slightly more intense in the case of $C_{59}N$, as it has been already pointed out in the comparison of ^1H NMR spectra (*cf*. Figs. 1 and 2).

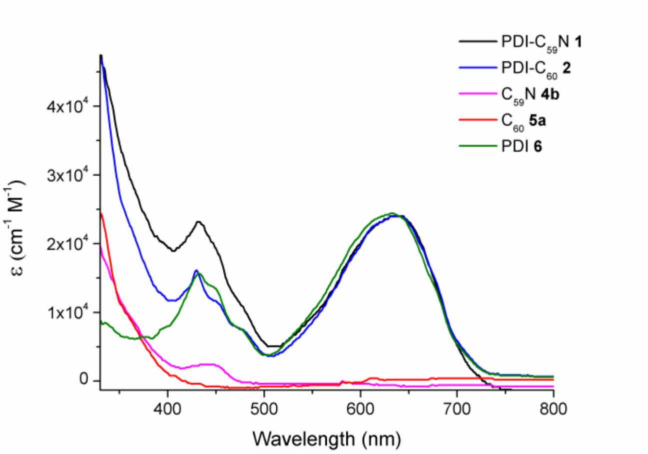


Figure 3. UV/vis spectra of PDI-$C_{59}N$ and PDI-C_{60} dyads **1** and **2**, reference compounds **4b** and **5a** and PDI-based reference material **6** registered in benzonitrile as solvent.

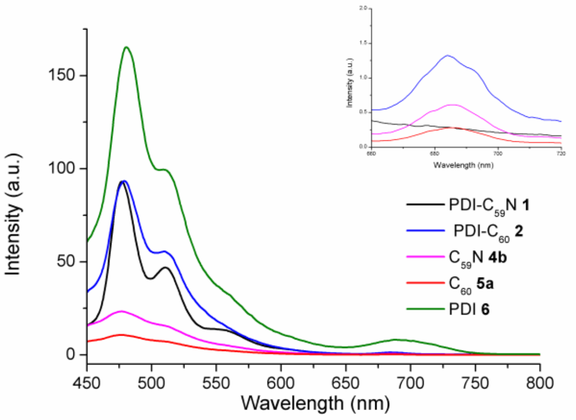


Figure 4. Fluorescence spectra of PDI-$C_{59}N$ and PDI-C_{60} dyads **1** and **2**, reference compounds **4b** and **5a** and PDI-based reference material **6**, obtained in benzonitrile ($4x10^{-6}$M; λ_{exc}=429 nm).

On the other hand, Figure 4 shows the fluorescence emission spectra of PDI-$C_{59}N$ and PDI-C_{60} dyads **1** and **2**, reference compounds **4b** and **5a** and PDI-based reference material **6**, when selectively excited at 429 nm. As it can be seen, the fluorescence spectrum of **6** clearly shows two different emission bands, centred at 529 nm and 683 nm. When the emission spectra of PDI-$C_{59}N$ and PDI-C_{60} dyads **1** and **2** are compared to that of the reference compound, the first band is partially quenched and hypsochromically shifted (505 nm) while the second one is extinguished. These effects are slightly more pronounced in the case of PDI-$C_{59}N$ dyad **1**. The latter is indicative of intradyad electronic interactions between the two components of the dyad (i.e., PDI and fullerene) at the excited state. The strong fluorescence quenching of the 683 nm band in both **1** and **2** as compared to **6**, supports electron and/or energy transfer as the decay mechanism of the PDI-centred singlet excited state.

The electrochemical data of PDI-$C_{59}N$ and PDI-C_{60} dyads **1** and **2**, respectively, as well as **6**, **4b** and **5b** as reference materials for PDI $C_{59}N$, and C_{60}, respectively, in benzonitrile using Fc/Fc$^+$ as internal standard are listed in Table 1 (see differential pulse voltammograms in SI, Fig. S13). The measurements for PDI **6** reference compound reveal a one-electron oxidation and two one-electron reduction processes centred at 0.58, -1.15 and -1.35 V respectively, while the measurements for fullerene reference compounds show two one-electron reversible reduction processes at -1.01 and -1.42 V. The voltammograms of dyads **1** and **2** are very similar, in spite of the nitrogen atom in dyad **1**, and can be considered as a combination of the already mentioned electrochemical processes assigned to PDI and fullerene electroactive moieties. A slight influence of the fullerene sphere (either $C_{59}N$ and C_{60}) over the PDI moiety can be recognised, and it is highlighted by a 20-30 mV anodic displacement of the oxidation wave and a 40 mV cathodic displacement of the second reduction process, which is attributed to the PDI counterpart. As contrary to previous results reported by us,[9,10] the similar first reduction values obtained for PDI-C_{60} and PDI-$C_{59}N$ might come from the use of different solvents. Based on the redox data shown in Table 1 and neglecting the Coulombic interactions, the electrochemical band gap for **1** is calculated 1.59 eV (1.61 eV for **2**).

Table 1. Redox potentials of PDI-$C_{59}N$ and PDI-C_{60} dyads **1** and **2**, and **6**, **4b** and **5b** as reference materials for PDI, $C_{59}N$, and C_{60}, respectively. The values are *versus* Fc/Fc$^+$ and extracted from differential pulse voltammograms of PhCN solutions containing Bu_4NPF_6 (0.10 M) as a supporting electrolyte.

	E^3_{red} (V)	E^2_{red} (V)	E^1_{red} (V)	E_{ox} (V)
PDI-**6**	-1.35	-1.15		0.55
PDI-C_{60} **2**	-1.39	-1.19	-1.03	0.58
PDI-$C_{59}N$ **1**	-1.38	-1.19	-1.01	0.58
C_{60}-ref **5b**	-1.42		-1.01	
$C_{59}N$.ref **4b**	-1.42		-1.01	

Femtosecond laser flash photolysis on a deaerated benzonitrile solution of **1** and **2** indicates the formation of a charge-separated state, providing solid evidence for the electron-transfer deactivation mechanism in **1** and **2**, after selective excitation of the perylene moiety. The transient absorption spectrum taken at 1 ps after laser pulse irradiation of the absorption band of the PDI moiety at 490 nm exhibits an absorption maximum at 900 nm, which is assigned to the singlet excited state of $C_{59}N$ of PDI-$C_{59}N$ dyad **1** (Fig. 5a). No indication of the PDI singlet excited state was observed in spite of the selective excitation of PDI, indicating that the rate of energy transfer from the singlet excited state of the PDI moiety to the $C_{59}N$ moiety is too fast to be followed even with the use of femtosecond laser flash photolysis (fmwh = 130 fs). Then, electron transfer from PDI to the singlet-excited state of $C_{59}N$ takes place to form PDI$^{\bullet+}$–$C_{59}N^{\bullet-}$ as the charge-separated state. The transient absorption band decayed with a rate constant of 5.5 x 10^{10} s^{-1} giving rise to an absorption band at λ_{max} = 1030 nm due to $C_{59}N^{\bullet-}$ radical anion,[9, 10] which indicates the formation of the charge-separated state. From the decay of the absorption band at 1030 nm, a 400 ps lifetime (k = 2.5 x 10^9 s^{-1}) was obtained for the charged-separated state (Fig. 5b), being that the first example of a charge-separated state in a donor-acceptor dyad based on PDI and azafullerene.

When benzonitrile was replaced by toluene, the rate constant of charge separation became much larger (3.9 × 10^{11} s^{-1}), whereas the rate constant of charge recombination became smaller (1.3 × 10^9 s^{-1}) as shown in Fig. S14 (ESI). The faster charge separation in toluene that in benzonitrile may result from the smaller solvent reorganization energy of toluene than that of a much polar benzonitrile in the Marcus normal region, where the charge separate becomes faster with decreasing the solvent reorganisation energy of electron transfer.[1d,18] By the same token, the slower charge recombination in toluene than in benzonitrile results from the smaller solvent reorganisation energy of toluene than that of benzonitrile in the Marcus inverted region, where the charge recombination becomes slower with decreasing the solvent reorganisation energy of electron transfer.[1d,18]

On the other hand, a similar transient absorption spectral change was observed for PDI-C_{60} dyad **2** as shown in Fig. 6a. The transient absorption recorded at 1 ps after femtosecond laser pulse irradiation is assigned to the singlet excited state of C_{60}, indicating that ultrafast energy transfer from the singlet excited state of PDI to the C_{60} moiety also occurs in PDI-C_{60}. Then, electron transfer from PDI to the singlet excited state of C_{60} takes place to form the charge-separated state. The rate constant for electron transfer is determined to be 8.6 x 10^{10} s^{-1} from the rise of the absorbance at 1000 nm (Inset of Fig. 7b). This rate is slightly faster than that of PDI-$C_{59}N$ (vide supra). The lifetime of the charge-separated state was determined to be 120 ps from the decay of absorbance at 1000 nm as shown in Fig. 6b It is worth to mention the much shorter lifetime of the CSS in PDI-C_{60}, less than one third of that in PDI-$C_{59}N$, pointing out to the remarkable influence of the nitrogen

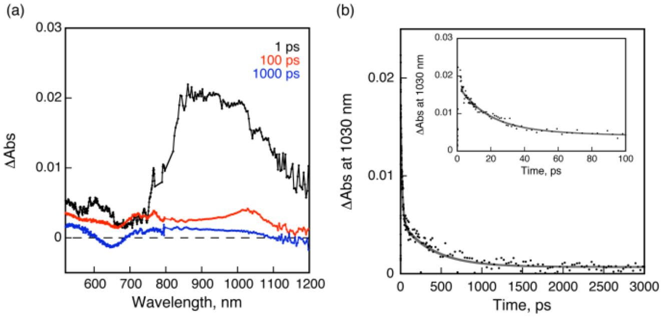


Fig. 5 (a) Transient absorption spectra of $C_{59}N$–PDI (0.5 mM) in deaerated PhCN after femtosecond laser excitation at 510 nm; (b) Time profile of the absorbance at 1030 nm. Inset: decay time profile for the short time range. Gray line is drawn by the double exponential curve fitting.

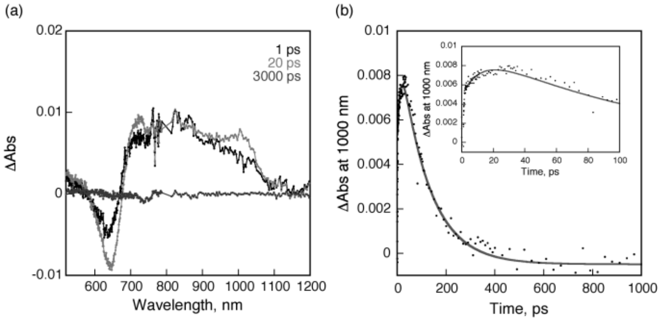


Fig. 6 (a) Transient absorption spectra of C_{60}–PDI (0.5 mM) in deaerated PhCN after femtosecond laser excitation at 510 nm; (b) Time profile of the absorbance at 1000 nm. Inset: rise and decay time profile for the short time range. Gray line is drawn by the double exponential curve fitting.

atom in $C_{59}N$, which is not explained only by an increased electron-accepting character as the reduction potentials of **1** and **2** indicate. In both cases, the decay of the charge-separated state by back electron transfer yields the ground state rather than the triplet excited state of PSI as indicated by no triplet transient absorption of **1** and **2** in nanosecond laser flash photolysis measurements (Figs. S14 in ESI).

Experimental

General Information

All chemicals were reagent grade, purchased from commercial sources, and used as received, unless otherwise specified. Column chromatography: SiO_2 (40–63 mm) TLC plates coated with SiO_2 60F254 were visualized by UV light and. **2** and **6** crude products were finally purified by a Combiflash Rf chromatography system (Teledyne Technologies, Inc., Thousand Oaks, CA), while **1** crude product was finally purified by preparative HPLC (Japan Analytical Industry Co Ltd., utilising a Buckyprep 20x250 column with toluene as eluent at 10 mL/min flow rate). NMR spectra were measured with a Bruker AC 300. UV/vis spectra were recorded with a Helios Gamma spectrophotometer. Fluorescence spectra were recorded with a PerkinElmer LS 55 Luminescence Spectrometer and IR spectra with a Nicolet Impact 400D spectrophotometer. Mass spectra were obtained from a Bruker Microflex matrix-assisted laser desorption/ionization time of flight (MALDI-TOF).

Tert-butyl (2,2-[60]fullerenyl)acetate **5b**[14] and ethyl (2-azafullerenyl)acetate **4b**, **6** used as C_{60} and $C_{59}N$ reference compounds, respectively, in electrochemistry measurements, were prepared as reported earlier.

Electrochemistry

Differential pulse voltammetry measurements were performed in a conventional three-electrode cell using a μ-AUTOLAB type III potentiostat/galvanostat at 298 K, over PhCN deaerated sample solutions (~0.5 mM), containing 0.10 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as supporting electrolyte. A glassy carbon (GC) working electrode, Ag/$AgNO_3$ reference electrode and a platinum wire counter electrode were employed. Ferrocene/ferrocenium was used as an internal standard for all measurements.

Synthesis

Synthesis of *N,N'*-di(2-ethylhexyl)-1-[*(R)*-2-(hydroxymethyl)-pyrrolidinyl]perylene-3,4,9,10-tetracarboxy diimide (3). Over a heated solution (90 ℃) of *(R)*-2-(hydroxymethyl)pyrrolidine (500 mg, 4.95 mmol), in NMP (10 ml), 100 mg (0.14 mmol) of *N,N'*-di(2-ethylhexyl)-1-bromoperylene-3,4,9,10-tetracarboxy diimid[19] suspended in 100 ml of NMP were slowly added under Ar atmosphere. When the addition is completed, the mixture was left at 90 ℃ continuously stirring for 48 h. The crude product was added over 400 ml of NaOH 1M, vacuum filtered and washed with distilled water, in order to eliminate the undesirable NMP used as solvent. The crude material was finally purified by column chromatography (SiO_2, Hx→Hx/AcOEt 3:1) to obtain 52 mg (51%) of the desired product as green powder. ^1H NMR (300 MHz, , 25 ℃): 8.46 (1H, s, H-PDI), 8.42-8.35 (2H, m, 3xH-PDI), 8.18 (1H, d, *J*= 8.2 Hz, H-PDI), 8.02-7.89 (2H, m, 2xH-PDI), 7.55-7.47 (1H, m, 2xH-PDI), 4.51-4.39 (1H, m, C$\underline{H}$N-pyrrolidine), 4.31 (1H, t, *J*=12.7 Hz, C$\underline{H}$H-OH), 4.21-4.03 (4H,m, 2xCH_2-N-alkyl chain), 3.98 (1H, t, *J*=12.7 Hz, CH$\underline{H}$-OH), 3.57-3.41 (1H, m, CH$\underline{H}$N-pyrrolidine), 2.30-2.09 (2H, m, CH_2-pyrrolidine), 2.07-1.91 (2H, m, CH$\underline{H}$-pyrrolidine + CH-alkyl chain), 1.90-1.76 (1H, m, CH-alkyl chain), 1.71-1.59 (2H, m, C$\underline{H}$HN-pyrrolidine + C$\underline{H}$H-pyrrolidine) 1.54-1.21 (16H, m, 8xCH_2-alkyl chain) and 1.06-0.78 (12H, m, 4xCH_3-alkyl chain) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, 25 ℃):164.2, 163.9, 163.3, 163.3, 147.2, 134.8, 134.2, 132.0, 131.5, 129.7, 129.7, 128.3, 128.1, 126.6, 126.2, 124.6, 123.2, 123.0, 122.5, 122.3, 120.6, 120.0, 118.0, 116.2, 62.0, 60.2, 56.2, 44.3, 43.9, 38.1, 38.1, 37.8, 30.9, 30.7, 29.6, 28.8, 28.6, 27.9, 25.2, 24.1, 24.0, 23.1, 14.1, 10.7 and 10.6 ppm; IR-FT (KBr) ν/cm^{-1}: 3467, 2956, 2927, 2858, 1691, 1652, 1586, 1427, 1338, 1242, 807, 748; UV/vis (CH_2Cl_2), λ_{max}/nm (log ε): 431 (4.16), 637 (4.36); HR-MS (MALDI-TOF, dithranol): *m/z*=713.349, [M]$^-$, calcd for $C_{45}H_{51}N_3O_5$: 713.383

Synthesis of *N,N'*-di(2-ethylhexyl)-1-[*(R)*-2-(acetylmethyl)-pyrrolidinyl]perylene-3,4,9,10-tetracarboxy diimide (6). 20 mg of **3** (0.03 mmol) were dissolved in 1 ml of acetic anhydride with a catalytic amount of H_2SO_4 (1 drop). The mixture was left, continuously stirred, at 90 ℃ for 2h. The crude product was added over 200 ml of NaOH 1M, extracted with CH_2Cl_2 and, after evaporation of the solvent, purified by Combiflash chromatography (0−5% of AcOEt in CH_2Cl_2). 17 mg of the desired product (75 %) were obtained as green powder. ^1H NMR (300 MHz, $CDCl_3$, 25 ℃): 8.69 (1H, s, H-PDI), 8.63 (1H, d, *J*= 8.1 Hz, H-PDI), 8.62 (1H, d, *J*= 8.0 Hz, H-PDI), 8.52-8.41 (3H, m, 3xH-PDI), 8.11 (1H, d, *J*= 8.1 Hz, H-PDI), 4.72 (1H, br s, C$\underline{H}$N-pyrrolidine), 4.51 (2H, d, *J*=3.93 Hz, CH_2-O), 4.23-4.05 (4H, m, 2xCH_2-N-alkyl chain), 3.78-3.68 (1H, m, CH$\underline{H}$N-pyrrolidine), 2.42-2.32 (2H, m, CH_2-pyrrolidine), 2.17 (3H, s, CH_3-C=O), 2.11-1.88 (4H, m, CH_2-pyrrolidine + 2xCH-alkyl chain), 1.50-1.24 (16H, m, 8xCH_2-alkyl chain) and 1.01-0.84 (12H, m, 4xCH_3-alkyl chain) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, 25 ℃): 170.9, 164.3, 164.1, 147.8, 135.9, 135.2, 133.2, 131.3, 129.2, 129.1, 127.6, 127.5, 124.6, 124.0, 123.9, 123.3, 122.9, 122.6, 122.1, 121.0, 119.8, 118.9, 65.3, 57.5, 56.4, 44.5, 38.1, 31.0, 29.1, 28.9, 25.4, 24.3, 23.2, 21.0, 14.3, 10.9, 10.8; IR-FT (KBr) 2956, 2927, 2857, 1744, 1693, 1654, 1587, 1419, 1336, 1240, 808, 748 ν/cm^{-1}; UV/vis (CH_2Cl_2), λ_{max}/nm (log ε):332 (3.80), 430 (4.17), 624 (4.36); HR-MS (MALDI-TOF, dithranol): *m/z*=755.385, [M]$^-$, calcd for $C_{45}H_{51}N_3O_5$: 755.393.

Synthesis of *N,N'*-di(2-ethylhexyl)-1-[*(R)*-2-([60]fullereneacetylmethyl)pyrrolidinyl]perylene-3,4,9,10-tetracarboxy diimide (2) Over a suspension of 2,2-([60]fullerenyl)acetic acid[14] (25 mg, 0.034 mmol), **3** (24 mg, 0.034 mmol) and 1-hydroxybenzotriazole (HOBt, 9 mg, 0.067 mmol) in dry dichloromethane (25 mL) at 0 °C under Ar, EDCI (19.5 mg, 0.102 mmol) and DMAP (3 mg, 0.025 mmol) were added. The mixture was left, continuously stirred, at room temperature for 48h. The reaction was then quenched with HCl 1M, extracted with CH_2Cl_2 and, after evaporation of solvent, the crude product was purified by Combiflash chromatography (0−5% of AcOEt in $CHCl_3$). 20 mg of the desired product (43 %) were obtained as green powder. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): 9.18 (1H, s, H-PDI), 8.70 (1H, d, *J*= 8.2 Hz, H-PDI), 8.61 (1H, d, *J*= 8.0 Hz, H-PDI), 8.45-8.35 (3H, m, 3xH-PDI), 8.29 (1H, d, *J*= 8.2 Hz, H-PDI), 5.21-5.06 (2H, m, C*H*N-pyrrolidine + C*H*H-O_2C), 4.70 (1H, d, *J*= 9.3 Hz, CH*H*-O_2C), 4.65 (1H, s, O_2C-CH=C_{60}), 4.22-3.99 (4H, m, 2xCH_2-N-alkyl chain), 3.90-3.76 (1H, m, C*H*HN-pyrrolidine), 2.60-2.48 (1H, m, NCH-CH*H*-pyrrolidine), 2.27-1.76 (6H, m, CH*H*N-pyrrolidine + NCH-C*H*H-pyrrolidine + CH_2-pyrrolidine + 2xCH-alkyl chain), 1.50-1.22 (16H, m, 8xCH_2-alkyl chain) and 1.01-0.82 (12H, m, 4xCH_3-alkyl chain) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): 165.8, 164.3, 164.0, 163.9, 148.8, 148.0, 147.0, 145.5, 145.4, 145.2, 145.1, 145.0, 144.9, 144.8, 144.6, 144.5, 144.4, 144.3, 144.2, 144.1, 143.9, 143.7, 143.6, 143.5, 143.4, 143.3, 143.1, 142.9, 142.8, 142.7, 142.5, 142.2, 142.1, 142.0, 141.9, 141.8, 141.2, 141.0, 140.7, 140.2, 140.0, 139.9, 139.2, 136.3, 136.1, 135.6, 135.1, 133.6, 131.5, 131.1, 129.5, 129.0, 127.8, 127.5, 124.9, 124.5, 124.0, 123.7, 123.1, 122.5, 122.1, 121.1, 120.0, 119.4, 70.2, 70.0, 68.9, 57.1, 44.5, 44.4, 44.3, 38.5, 38.2, 38.0, 30.9, 28.9, 28.8, 28.7, 25.4, 24.2, 23.3, 23.2, 14.3 and 10.9; IR-FT (KBr) 2951, 2923, 2854, 1740, 1693, 1655, 1417, 1333, 1242, 1182, 1152, 807, 747, 527 ν/cm^{-1}; UV/vis (CH_2Cl_2), λ_{max}/nm ($\log\varepsilon$): 327 (4.60), 428 (4.18), 628 (4.35); HR-MS (MALDI-TOF, dithranol): *m/z*=1473.302, $[M]^-$, calcd for $C_{107}H_{51}N_3O_6$: 1473.378.

Synthesis of *N,N'*-di(2-ethylhexyl)-1-[*(R)*-2-(azafullereneacetylmethyl)pyrrolidinyl]perylene-3,4,9,10-tetracarboxy diimide (1). Over a suspension of 2-(azafullerenyl)acetic acid **6** (20 mg, 0.026 mmol), **3** (19 mg, 0.026 mmol) and DMAP (2.5 mg, 0.021 mmol) in dry dichloromethane (20 mL) at 0 °C under N_2, EDCI (15 mg, 0.078 mmol) was added and the mixture was left stirring at r.t. for 72 hours. Then, the solvent was evaporated; the residue was then re-dissolved in *o*-dichlorobenzene (25 mL) and passed through silica column chromatograph (toluene→toluene/ethyl acetate 9:1). The first green fraction was collected and further purified in preparative HPLC (buckyprep, toluene, 10 ml/min. R.t. = 18.6 min) yielding **1** as green dust (3 mg, 8%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): 9.19 (1H, s, H-PDI), 8.69 (1H, d, *J*= 8.1 Hz, H-PDI), 8.59 (1H, d, *J*= 8.0 Hz, H-PDI), 8.44-8.35 (4H, m, 4xH-PDI), 5.21-5.27 (2H, m, C*H*N-pyrrolidine + C*H*H-O_2C), 4.87-4.77 (1H, m; CH*H*-O_2C), 4.71 (1H, d, *J*= 16.2 Hz, O_2C-C*H*H-C59N), 4.63 (1H, d, *J*= 16.2 Hz, O_2C-CH*H*-C59N), 4.24-4.03 (4H,m, 2xCH_2-N-alkyl chain), 3.95-3.83 (1H, m, C*H*HN-pyrrolidine), 2.62-2.48 (1H, m, NCH-CH*H*-pyrrolidine), 2.28-1.76 (6H, m, CH*H*N-pyrrolidine + NCH-C*H*H-pyrrolidine + CH_2-pyrrolidine + 2xCH-alkyl chain), 1.48-1.22 (16H, m, 8xCH_2-alkyl chain) and 1.02-0.80 (12H, m, 4xCH_3-alkyl chain) ppm; ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): 169.5, 164.5, 164.3, 164.1, 164.0, 154.7, 154.4, 148.5, 147.8, 147.6, 147.5, 147.4, 147.1, 147.0, 146.7, 146.6, 146.5, 146.4, 146.3, 145.9, 145.8, 145.7, 145.1, 145.0, 144.8, 144.6, 144.3, 143.8, 143.6, 143.5, 142.7, 142.1, 141.7, 141.6, 141.1, 140.9, 140.8, 140.6, 139.4, 139.2, 137.0, 136.9, 135.8, 135.2, 134.2, 133.7, 133.6, 131.6, 131.1, 129.4, 129.0, 127.9, 127.6, 124.8, 124.3, 124.1, 123.9, 123.8, 123.6, 123.0, 122.4, 122.0, 121.0, 120.0, 119.2, 78.4, 68.4, 57.4, 57.1, 46.9, 44.5, 44.3, 38.2, 37.9, 30.9, 29.8, 29.1, 28.9, 28.8, 28.7, 25.3, 24.2, 23.3, 23.2, 14.3, 10.9 and 10.8 ppm; IR-FT (KBr) ν/cm^{-1}: 3425, 2953, 2925, 2856, 1747, 1694, 1656, 1588, 1421, 1334, 1242, 1185, 808, 748, 525; UV/vis (CH_2Cl_2), λ_{max}/nm ($\log\varepsilon$): 321(4.59), 431 (4.27), 632 (4.37); HR-MS (MALDI-TOF, dithranol): *m/z*=1476.463, $[M]^-$, calcd for $C_{106}H_{52}N_4O_6$: 1476.389

Conclusions

We have synthesized for the first time a dyad where a perylenediimide unit is connected to $C_{59}N$. Taking advantage of the electron donor character of the mono pyrrolidinyl PDI derivative synthesised, PDI-$C_{59}N$ dyad undergoes efficient intramolecular photoinduced electron transfer to afford a 400 ps-lived CS state in PhCN. PDI-C_{60} has also been synthesized, as reference compound, affording 3 times shorter CSS lifetime than PDI-$C_{59}N$ dyad to address the influence of the nitrogen in the photoinduced electron-transfer process. The present results have significant implications for the design of organic solar cells based on covalent donor–acceptor systems using $C_{59}N$ as acceptor and shows that the longer-lived charge-separated states can be attained using $C_{59}N$ systems instead of C_{60} systems.

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Notes and references

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