A Paradigmatic Change: Linking Fullerenes to Electron Acceptors

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ABSTRACT: The potential of Lu₃N@C₈₀ and its analogues as electron acceptors in the areas of photovoltaics and artificial photosynthesis is tremendous. To this date, their electron-donating properties have never been explored, despite the facile oxidations that they reveal when compared to those of C₆₀. Herein, we report on the synthesis and physicochemical studies of a covalently linked Lu₃N@C₈₀–perylenebisimide (PDI) conjugate, in which PDI acts as the light harvester and the electron acceptor. Most important is the unambiguous evidence—in terms of spectroscopy and kinetics—that corroborates a photoinduced electron transfer evolving from the ground state of Lu₃N@C₈₀ to the singlet excited state of PDI. In stark contrast, the photoreactivity of a C₆₀–PDI conjugate is exclusively governed by a cascade of energy-transfer processes. Also, the electron-donating property of the Lu₃N@C₈₀ moiety was confirmed through constructing and testing a bilayer heterojunction solar cell device with a PDI and Lu₃N@C₈₀ derivative as electron acceptor and electron donor, respectively. In particular, a positive photovoltage of 0.46 V and a negative short circuit current density of 0.38 mA are observed with PDI/Ca as anode and ITO/Lu₃N@C₈₀ as cathode. Although the devices were not optimized, the sign of the V_OC and the flow direction of J_SC clearly underline the unique oxidative role of Lu₃N@C₈₀ within electron donor–acceptor conjugates toward the construction of novel optoelectronic devices.

INTRODUCTION

Empty fullerenes such as C₆₀ and C₇₀ are spherical building blocks of nanometer dimensions and have been widely used as electron acceptors in artificial photosynthesis and photovoltaics because of their excellent electrochemical and photophysical properties.¹ However, in contrast to its nice electron-accepting property, the electron-donating property of C₆₀ is very poor, which relates primarily to its high oxidation potential of 1.26 V vs that of ferrocene/ferricenium (Fc⁰/+).⁴ In fact, the very poor electron-donating property of C₆₀ only occurs with the help of either strong oxidants/acceptors or scandium ions that can bind with the electron transfer product.⁵ Such limitations impede, however, its application as a widely applicable electron donor.

Endohedral metallofullerenes (EMFs) are types of special fullerene derivatives. Their unique physicochemical properties and rich electrochemical properties, in particular, relate to a significant hybridization effect of the encapsulated metallic cluster.⁶⁻⁷ Recently, a variety of EMFs have been integrated into various photoactive conjugates or hybrids, and these EMFs reveal their distinctive photophysical behaviors.⁷⁻⁸ Some of them, especially nitride cluster fullerenes (NCFs) such as M₃N@C₂₋₄, have been found to be superior electron acceptors when compared to C₆₀.⁹ Still, electron transfer oxidations of NCFs have been seldom probed,¹⁰ despite the fact that their one-electron oxidation potentials are generally much lower than those found in C₆₀. Specifically, the oxidation potential of Lu₃N@C₈₀ is 0.62 V lower than that of C₆₀. Therefore, we postulate its better electron donor properties and easier photoinduced electron transfer oxidations. For further confirmation, herein, we attach an electron acceptor to Lu₃N@C₈₀, which is aiming to power a photoinduced electron transfer oxidation of Lu₃N@C₈₀. In particular, a perylene dye, namely 1,6,7,12-tetrachloro-3,4,9,10-perylene-diimide (PDI), is used as electron acceptor due to its outstanding light-harvesting and electron-accepting features.¹¹ Importantly, a photoinduced
electron transfer oxidation of Lu₃N@C₈₀ is identified in the physicochemical studies of the Lu₃N@C₈₀−PDI conjugate (1) (see Figure 1), which is in contrast to the analogues C₆₀−PDI conjugate (2). Also, we further explored the electron-donating potential of Lu₃N@C₈₀ derivatives in a photovoltaic device.

RESULTS AND DISCUSSION

The syntheses of 1 and 2 were carried out via [1 + 2]-cycloaddition reaction of PDI diazo compounds, which were generated in situ by a Bamford–Stevens reaction between PDI tosylhydrazone (9) and sodium methoxide (Schemes S1−S3, Supporting Information). In fact, the thermal reaction of C₆₀ with 9 gave rise to the [6,6]-closed (2) and [5,6]-open (3) isomers of C₆₀−PDI, while only the [6,6]-open isomer (1) of Lu₃N@C₈₀−PDI was found in the reaction with Lu₃N@C₈₀. All of the compounds were isolated and purified by HPLC. However, only 1 and 2 were thermodynamically stable and, thus, further studied.

MALDI-TOF mass and NMR experiments—see Supporting Information—served as the basis for the structural characterization of 1 and 2. The mass spectra of 1 in positive and negative modes show distinct peaks at m/z of 2358 and 2356 that are respectively assigned to the [1 + 2H]²⁺ and [1]⁻ ions, whereas the mass peak of 2 at m/z of 1576 is only observed in negative mode. The ¹H NMR spectra of 1 and 2 reveal the signals for the perylene moiety at around 8.6 ppm together with the aromatic protons of the phenylmethane moiety and the protons of the alkyl chains. In the ¹³C NMR spectra of 1, the signals between 98 and 94 ppm are assigned to the bridgehead atoms, reflecting their sp² character due to the [6,6]-open addition pattern, which are quite different from those of 2 at 79 ppm. The signal at 51 ppm corresponds to the spiro carbon of 1 in analogy to that of 2.

Figure 2 summarizes the absorption spectra of all of the PDI-containing compounds, that is, 1, 2, 8, and 10, at room temperature. Common to these spectra are features at 430, 487−490, and 522−524 nm. In addition, in 1 the Lu₃N@C₈₀ features emerge at 405 and 675 nm, while in 2 the features at 330, 433, and 695 nm are C₆₀ centered. However, the absorption spectrum of 1 differs slightly from the linear superimpositions of the individual components. Red shifts of the absorption maxima, which range from 1 to 3 nm (see Supporting Information, Figure S18), document the electronic communications/short intramolecular distances between PDI and Lu₃N@C₈₀.

The electrochemical properties of 1 and 2 were investigated by means of differential pulse voltammetry (DPV) and cyclic voltammetry (CV) (Table 1, Figures S19 and S20, see Supporting Information). Using 8 and 10 as references allows for the accurate assignment of the individual redox steps. 1 shows in the cathodic direction four one-electron reduction steps. The first and second reductions (i.e., −0.86 and −1.08 V) relate to Lu₃N@C₈₀ centered processes. In the anodic direction, only one oxidation step is observed for 1. This oxidation (i.e., +0.57 V) is due to the formation of the π-radical cation of Lu₃N@C₈₀.

Figure 1. Schematic structures of conjugates 1 and 2 as well as those for compounds 8, 10, 11.

Figure 2. UV−vis absorption spectra of 1, 2, 8, and 10 in toluene. Inset shows enlarged absorptions between 550 and 800 nm.
Table 1. Redox Potentials of PDI—Fullerene Conjugates 1, 2, and Reference Compounds\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th>(E_{1/2})</th>
<th>(E_{1/2}^{\text{red}})</th>
<th>(E_{1/2}^{\text{ox}})</th>
<th>(E_{1,2}^{\text{red}})</th>
<th>(E_{1,2}^{\text{ox}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.57\textsuperscript{b}</td>
<td>−0.86</td>
<td>−1.08</td>
<td>−1.41\textsuperscript{b}</td>
<td>−1.87</td>
</tr>
<tr>
<td>2</td>
<td>1.21</td>
<td>−0.89</td>
<td>−1.13</td>
<td>−1.52</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>−0.89</td>
<td>−1.12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.55\textsuperscript{b}</td>
<td>−1.46\textsuperscript{b}</td>
<td>−1.94</td>
<td></td>
<td></td>
</tr>
</tbody>
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\textsuperscript{a}All the potentials, in volts, were measured relative to the Fc/Fc\textsuperscript{+} couple by means of DPV. \textsuperscript{b}Quasi-reversible process determined via CV.

For 2, three one-electron reduction steps emerge in the cathodic direction. In particular, reductions at −0.89, −1.13, and −1.52 V correspond to the formation of the PDI π-radical anion, the PDI dianion/C\textsubscript{60} π-radical anion and the C\textsubscript{60} dianion, respectively. In the anodic direction, the π-radical cation formation of C\textsubscript{60} sets in at +1.21 V for 2. The fact that the one-electron reduction and the one-electron oxidation of 1 differ slightly from those seen for 8 (i.e., −0.89 V) and 10 (+0.55 V), respectively, points to appreciable ground state interactions between PDI and Lu\textsubscript{3}N@C\textsubscript{80}. In 2, on the other hand, no particular differences were noted.

Next, the structures of 1 and 2 were optimized using DFT method at the M06-2X/3-21G−SDD level\textsuperscript{13,14} with a Gaussian 09 package\textsuperscript{15} and the corresponding energy-minimum conformers are shown in Figure S23 (see Supporting Information). Common is the close proximity between PDI and Lu\textsubscript{3}N@C\textsubscript{80} or C\textsubscript{60}. Shortest intramolecular distances of around 2.8 Å are indicative for significant through-space interactions. In addition, 1 and 2 reveal similar MO distributions (Figure 3) that is, localization of the HOMO on Lu\textsubscript{3}N@C\textsubscript{80} or C\textsubscript{60} and that of the LUMO on PDI. Upon closer inspection, the calculated MOs agree well with the electrochemistry data. In particular, a HOMO, which is 0.45 eV higher in 1 than in 2, relates to the easier oxidation of Lu\textsubscript{3}N@C\textsubscript{80} relative to C\textsubscript{60}. The LUMO of 1, on the other hand, is 0.19 eV lower than that of 2, reflecting a slightly easier PDI reduction in 1 as compared to that in 2. Implicit is a redistribution of electron density, that is, from Lu\textsubscript{3}N@C\textsubscript{80} to PDI.

To attribute our spectral observation (vide infra) spectroelectrochemical experiments, that is, the formation of the PDI π-radical anion and Lu\textsubscript{3}N@C\textsubscript{80} π-radical cation, were deemed necessary. Spectroelectrochemical experiments were performed in either deaerated toluene/acetonitrile mixtures (4:1 v/v) or in deaerated o-DCB. The differential absorption spectrum following the conclusion of the spectroelectrochemical reduction of PDI is shown in Figure 4. Sets of maxima at 444, 675, 756, and 918 nm as well as minima at 489 and 522 nm are formed under pseudo-first-order conditions. On the other hand, Lu\textsubscript{3}N@C\textsubscript{80} oxidation experiments led to differential absorption changes that include maxima at 585 and 730 nm and a broad tail that reaches out into the near-infrared.

Fluorescence assays with 1, 2, and 8 disclose a rather strong fluorescence quenching in the earlier two. The fluorescence quantum yields were 0.91 (toluene, chlorobenzene, benzonitrile) for 8, 0.045 (toluene), 0.038 (chlorobenzene), 0.033 (benzonitrile) for 2, and 0.017 (toluene), 0.015 (chlorobenzene), 0.014 (benzonitrile) for 1. Notably, the weak fluorescent features of C\textsubscript{60} and Lu\textsubscript{3}N@C\textsubscript{80} with quantum yields of less than 10\textsuperscript{−4} hamper any meaningful analysis. In conclusion, we postulate a rapid PDI excited state deactivation in 1 and 2.

Decisive insights into the excited state deactivation of PDI in 1 and 2, in general, and into the corresponding photoproducts, in particular, came from transient absorption measurements. To this end, 8 reveals upon femtosecond excitation at 530 nm differential absorption changes that include transient maxima at 755, 800, 875, and 970 nm as well as transient minima at 490 and 515 nm—Figure 5. These features relate to the singlet–singlet transitions of photoexcited PDI, which decay with a

![Table 1](https://dx.doi.org/10.1021/ja3039695|jacs.2012.134.12190–12197)

![Figure 3](https://dx.doi.org/10.1021/ja3039695|jacs.2012.134.12190–12197)

![Figure 4](https://dx.doi.org/10.1021/ja3039695|jacs.2012.134.12190–12197)
lifetime of 4.0 ± 0.2 ns. It is, however, the ground state rather than the triplet excited state that is populated due to an inefficient intersystem crossing. In addition, a minimum evolves in the range of no ground state absorption, that is, at 595 nm. Complementary nanosecond excitation at 532 nm further corroborates the spin-allowed ground state recovery, that is, the lack of an appreciable transient (not shown).

Excitation of 2 at 530 nm results in the exclusive formation of the PDI singlet excited state. Notable is the light partition of C60 vs PDI at the excitation wavelength (1:24). Transient maxima at 755, 790, 880, and 970 nm as well as transient minima at 490 and 515 nm are formed instantaneously despite the presence of C60—Figure 6. However, the presence of C60 exerts an impact on the PDI singlet excited state lifetime, namely a rapid decay with an underlying lifetime of 35 ± 5 ps. At the conclusion of this decay, only a broad feature around 880 nm remains discernible in the near-infrared region of the spectrum. In the visible region, which is initially dominated by the ground state bleaching of PDI, an additional band is noticeable at 460 nm. Owing to the similarity of the aforementioned features (i.e., 460 and 880 nm) with those known for the C60 singlet excited state and the exclusive excitation of PDI at 530 nm we postulate an exothermic transduction of singlet excited state energy. In most C60 derivatives, the deactivation of the C60 singlet excited state is dominated by intersystem crossing (1.5 ± 0.1 ns) to the energetically lower-lying triplet excited state. In this regard, it is important to note that in 2, the 880 nm transition decays with kinetics that are hardly faster (1.4 ± 0.1 ns) than the inherent intersystem crossing dynamics of C60. Interestingly, we did not find the characteristic C60 triplet feature—a strong triplet—triplet transition at 700 nm with an extinction coefficient of 15.000 M−1 cm−1—at the end of the C60 singlet excited state deactivation. On the contrary, minima at 490 and 515 nm as well as a maximum at 565 nm were concluded. Earlier we have established that such features are reliable attributes of the PDI triplet excited state. From this we infer that the C60 triplet (1.5 eV), once formed, undergoes a thermodynamically allowed transfer of triplet excited state energy to PDI (1.2 eV). Nearly, similar kinetics at the 565 nm maximum (1.4 ± 0.1 ns), which allowed us to follow the generation of the PDI triplet excited state, further furnishes the following kinetic assignment—the rate-determining step in the PDI triplet excited state formation is the C60 centered intersystem crossing. The only component seen in the complementary nanosecond experiments—following 532 nm excitation—was that of the PDI triplet formed with quantum yields of 0.52 and 1.0 in toluene and chlorobenzene as inferred from singlet oxygen quantum yields—Figure S24 in Supporting Information.
Exciting 2 at 387 nm forms the singlet excited state of \( C_{80} \) directly. The latter undergoes intersystem crossing to the corresponding triplet excited state. Nevertheless, the differential absorption changes that are recorded at the end of the intersystem crossing process resemble those of the PDI triplet excited state. Most notable are the 565 nm maximum the 480/525 nm minima seen at time delays of about 4 ns and beyond—Figure S25 (Supporting Information). Such an observation is in line with the sequence of a slow intersystem crossing and a fast triplet—triplet energy transfer.

When 1 was examined subsequent to laser excitation at 530 nm, the same singlet excited state features, which were observed in the cases of 2 and 8, developed at the conclusion of the laser excitation—Figure 7. This, again, attests to the successful PDI excitation. However, instead of seeing the slow intersystem crossings, the PDI singlet excited state decays ultrafast with lifetimes less than 1.0 ps (see Figure 7). Simultaneously with the latter decay, new transitions grow-in in the visible, namely maxima around 575, 700, 760, and 890 nm, and in the near-infrared, namely a broad near-infrared tail. On the basis of a spectral comparison—vide infra—we ascribe the visible bands to the PDI \( \pi \)-radical anion (PDI\(^{\cdot -}\)), while the near-infrared band corresponds to the Lu\(_3\)N@C\(_{80}\) \( \pi \)-radical cation \( [(\text{Lu}_3\text{N@C}_{80})\text{PDI}]^{\cdot +}\). In accordance with these results, we propose that in 1 electron transfer evolves from the electron-donating Lu\(_3\)N@C\(_{80}\) to the PDI singlet excited state to yield \( [(\text{Lu}_3\text{N@C}_{80})\text{PDI}]^{\cdot +}\), for which we estimate, on the basis of electrochemical data, an energy of 1.43 eV. Notably, \( \text{(Lu}_3\text{N@C}_{80})\text{PDI}]^{\cdot +}\) is metastable and decays with a lifetime of 120 ± 10 ps in toluene, 100 ± 10 ps in chlorobenzene and 45 ± 5 ps in benzonitrile. For 1, the PDI triplet excited state emerges as the product of charge recombination. Again, in complementary nanosecond experiments—following 532 nm excitation—the only product that was monitored was that of the PDI triplet—Figure S26. As singlet oxygen quantum yields suggest, the triplet is formed with quantum yields of 0.58, 0.97, and 0.23 in toluene, chlorobenzene, and benzonitrile, respectively.

In contrast to the aforementioned, 387 nm photoexcitation of 1 generates the relatively short-lived (50 ± 2 ps) singlet excited state of 1. However, its energy (1.70 eV) is insufficient to power the electron transfer that has been seen to evolve from the PDI singlet excited state. As a matter of fact, the corresponding triplet excited state fingerprint at 570 nm develops and remains stable on the experimental time scale of our setup, that is, 8 ns. All of the different electron- and energy-transfer pathways occurring upon photoexcitation of 1 or 2 are summarized in energy diagrams: see Figure 8.

To further corroborate the photoinduced oxidation of Lu\(_3\)N@C\(_{80}\) in the presence of the electron-accepting PDI, bilayer-structured solar cell devices were prepared by utilizing, in contrast to previous studies,\(^{36}\) 10 as an electron donor and a tetrachlorinated perylenebisimide derivative—(1,6,7,12-tetrachloro-\( N,N'\text{-dil-(4-pyridyl)perylene-3,4,9,10-tetracarboxylic} \) diimide)\(^{19}\) (11)—as an electron acceptor. The fabricated devices had the following configurations: indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene:poly(styrene sulfonate) (PEDOT:PSS) (50 nm)/10 (30 nm)/11 (40 nm)/Ca (15 nm)/Ag (80 nm). Doctor blading was employed for depositing the hole-transporting PEDOT:PSS and the electron-donating layer of 10, whereas the electron-accepting layer constituted by 11 as well as the Ca/Ag cathode were deposited by thermal evaporation followed by postannealing. Figure 9 shows the current density (\( J \)) vs voltage (\( V \)) curves under illumination and in the dark for a 10/11 device. Under simulated 1 sun AM 1.5G radiation (100 mW/cm\(^2\)), a short circuit current density (\( J_{SC} \)) of 0.38 mA, an open circuit voltage (\( V_{OC} \)) of 0.46 V, a fill factor (FF) of 30.24%, and an efficiency (\( \eta \)) of 0.054% were determined. It is important to note that the devices were not optimized in terms of layer thicknesses or thermal annealing conditions. Nevertheless, our preliminary results clearly under-
energy back and forth between PDI and C_{60}. Overall, the facile oxidation of Lu\textsubscript{3}N@C_{60} is believed to be sufficient in driving this unprecedented electron transfer event. In preliminary assays, we have applied Lu\textsubscript{3}N@C_{60}-PCBM (10) as an electron donor in a bilayer heterojunction solar cell device with PDI derivative (11) as electron acceptor. Although the overall efficiencies were rather moderate with values of 0.054% (i.e., under nonoptimized conditions) the electron-donating property of Lu\textsubscript{3}N@C_{60} was undoubtedly confirmed, that is, a positive photovoltage of 0.46 V and a negative short circuit current density of 0.38 mA with PDI/Ca as anode and ITO/Lu\textsubscript{3}N@C_{60} as cathode. This work, therefore, discloses a new way of using NCFs as electron donors toward the construction of optoelectronic devices integrating n-type semiconductors.

**EXPERIMENTAL SECTION**

**Spectroscopy.** All NMR spectra were recorded respectively on a Bruker AC 300 spectrometer or Bruker AV 500 spectrometer with a CryoProbe system, locked on deuterated solvents and referenced to the solvent peak. The 1D (\textsuperscript{1}H, \textsuperscript{13}C and DEPT45/135) and 2D experiments (COSY and HMQC) were performed by means of standard experimental procedures of the Bruker library. Absorption spectra of all samples were recorded in toluene with a Shimadzu UV-3150 spectrometer using a quartz cell and 1-nm resolution. Matrix-assisted laser desorption—ionization time-of-flight (MALDI-TOF) mass spectra were recorded with a Bruker BIFLEX-III mass spectrometer using 1,1,4,4-tetraphenyl-1,3-butadiene as the matrix. The measurements were performed in both positive and negative ion modes.

**Steady-State Emission.** The spectra were recorded on a FluoroMax 3 fluorometer (vis detection) and on a Fluorolog spectrometer (NIR detection). Both spectrometers were built by HORIBA Jobin Yvon. The measurements were carried out at room temperature under argon atmosphere.

**Time Resolved Absorption.** Femtosecond transient absorption studies were performed with 387 and 530 nm laser pulses (1 kHz, 150 fs pulse width) from an amplified Ti:Sapphire laser system (Clark-MXR, Inc.), the laser energy was 200 nJ. Nanosecond laser flash photolysis experiments were performed with (355 and) 532 nm laser pulse from a Quanta-Ray CDR Nd:YAG system (6 ns pulse width) in a front face excitation geometry.

**Time Resolved Emission.** Fluorescence lifetimes were measured by using a Fluorolog (Horiba Jobin Yvon).

**Electrochemistry.** Differential pulse voltammetry (DPV) and cyclic voltammetry (CV) were carried out in o-DCB using a BAS CV-50 instrument. A conventional three-electrode cell consisting of a platinum working electrode, a platinum counter-electrode, and a saturated calomel reference electrode (SCE) was used for both measurements. 0.05 M (n-Bu\textsubscript{4})NPF\textsubscript{6} was used as the supporting electrolyte. All potentials were recorded against a SCE reference electrode and corrected against Fc/Fc\textsuperscript{+}. DPV and CV were measured at a scan rate of 20 and 50 mV s\textsuperscript{-1}, respectively.

**Materials.** All chemicals were of reagent grade and purchased from Wako. Lu\textsubscript{3}N@I\textsubscript{1}-C_{60} (>99%) was purchased from Luna Co.. Preparative and analysis HPLC were performed on semi preparative Buckyprep column (\textalpha\textsubscript{3} 10 × 100 mm, Cosmisorb), semi-preparative SPBB column (\textalpha\textsubscript{3} 10 mm × 100 mm, Cosmisorb) and Buckyprep column and Buckyclutcher column (\textalpha\textsubscript{3} 4.6 mm × 100 mm, Cosmisorb), respectively. Toluene was used as eluent.

**Spectroelectrochemistry.** The spectroelectrochemical measurements were done on a Varian Cary 5000 UV—vis—NIR spectrophotometer connected to a Princeton PGstat 263A using a home-made cell with three-electrode configuration. A light transparent platinum gauze, a platinum plate, and a silver wire were employed as the working, counter, and reference electrodes, respectively, in an analyte solution of o-dichlorobenzene containing 0.05 M tetrabutylammonium-hexafluorophosphate as supporting electrolyte.
ASSOCIATED CONTENT

Supporting Information

Experimental details including the reaction schemes, synthesis of other compounds, HPLC profiles, mass spectra, CV, DPV curves, 1D and 2D NMR spectra, NMR chemical shifts, DFT-optimized structures of 1 and 2, transient absorption spectra of 2 and 1, complete ref 15. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(17) We assume that stimulated PDI fluorescence is the origin of this feature.
