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Synthesis and Photophysical Properties of Electron-Rich Perylenediimide-Fullerene Dyad

Yuki Shibano,[†] Tomokazu Umeyama,[†] Yoshihiro Matano,[†] Nikolai V. Tkachenko,*,[‡] Helge Lemmetyinen,[‡] and Hiroshi Imahori*,[†,§]

Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan, Fukui Institute for Fundamental Chemistry, Kyoto University, 34-4, Takano-Nishihiraki-cho, Sakyo-ku, Kyoto 606-8103, Japan, and Institute of Materials Chemistry, Tampere University of Technology, P.O. Box 541, Korkeakoulunkatu 8, FIN-33101, Tampere, Finland

imahori@scl.kyoto-u.ac.jp; nikolai.tkachenko@tut.fi

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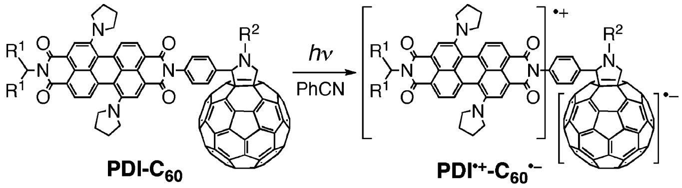
ABSTRACT



An electron-rich perylenediimide-C_{60} dyad has been prepared to explore a new type of donor–acceptor system. Time-resolved absorption measurements in benzonitrile revealed unambiguous evidence for the formation of a charge-separated state consisting of perylene diimide radical cation and C_{60} radical anion via photoinduced electron transfer, showing a new class of artificial photosynthetic models in terms of charge separation.

Recently, a wide variety of donor−acceptor linked molecules have been prepared to develop artificial photosynthetic systems toward the realization of highly efficient solar energy conversion.[1] The key points for the efficient conversion are a high light-harvesting ability and fast charge separation (CS) and slow charge recombination (CR), which allow the systems to generate a long-lived charge-separated state in a high quantum yield. Fullerenes are one of the most attractive electron acceptors[2] because they bear small reorganization energies[3] that accelerate CS and decelerate CR. A disadvantage of fullerenes is small molar absorption coefficients in the visible region. Thus, porphyrins have been frequently employed as a donor of such combinations owing to the intense Soret band in the blue and moderate Q-bands in the green regions, as well as relatively small reorganization energies.[4] Actually, porphyrin-fullerene linked systems have successfully exhibited the efficient formation of a long-lived charge-separated state.[2,3,5] However, taking into account solar energy distribution on the earth surface, the light-harvesting properties of porphyrins are insufficient as a donor.

[†] Kyoto University.

[‡] Tampere University of Technology.

[§] Fukui Institute for Fundamental Chemistry.

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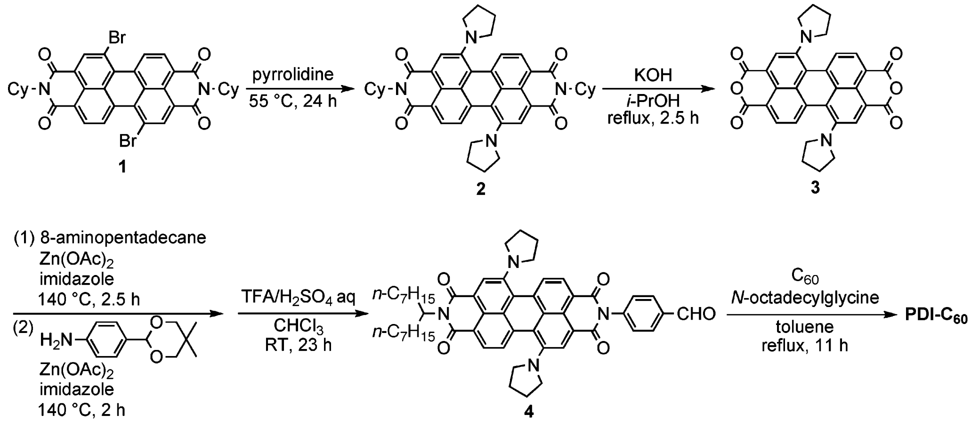
Scheme 1



Perylene diimides (PDI) are well-known as chemically, thermally, and photophysically stable and good light-harvesting dyes. Owing to their outstanding properties, they have been regarded as potential candidates for optical devices such as organic light-emitting diodes,[6] photovoltaic devices,[7] and optical switches.[8] So far several perylenediimide-C$_{60}$ linked systems have been reported.[9] However, energy transfer (EN) to C$_{60}$ is a main relaxation pathway of the excited singlet state of PDI as a result of the poor electron-donating ability of the perylenediimide. As such, no unambiguous evidence for electron transfer (ET) from the excited singlet state of PDI to C$_{60}$ has been presented.

We report herein synthesis and photophysical properties of a novel perylenediimide-C$_{60}$ linked dyad **PDI-C$_{60}$**. It is known that the electronic structures of perylenediimides are highly affected by introducing electron-donating or electron-withdrawing groups at a perylene core.[6−8] Bearing this in mind, we introduced electron-donating amine substituents into the perylene core.[10] Such substitution is expected to facilitate photoinduced ET from the excited singlet state of the PDI to the C$_{60}$ as a result of the low oxidation potential of the PDI moiety. More importantly, the electron-donating substituents would shift the absorption bands due to the PDI moiety to the longer wavelength regions, improving the light-harvesting properties in the visible and near-infrared regions.[11] To increase the solubility, a swallow-tail secondary alkyl group[12] and long alkyl group were introduced into one imide end of the PDI and the pyrrolidine ring on the C$_{60}$, respectively.

The synthetic scheme is shown in Scheme 1. According to Wasielewski's method,[10a] the bispyrrolidine-substituted PDI **2** was synthesized by treating the *N*,*N*′-dicyclohexyl-1,7-dibromoperylene-3,4:9,10-tetracarboxylic acid bisimide **1** with a large amount of pyrrolidine. Under our conditions, **2** was contaminated by monopyrrolidinated PDI. The desired product was separated by alumina chromatography (CHCl$_3$/hexane = 1:1) to give **2** in 52% yield. The saponification of **2** by using the reported procedure[10b] gave the 1,7-dipyrrolidinylperylene bisanhydride **3** in 83% yield. Cross-condensation of 8-aminopentadecane, **3**, and formyl-protected aniline, followed by acid-catalyzed deprotection, afforded **4** in 17% yield. The perylenebisimide-C$_{60}$ dyad **PDI-C$_{60}$** was obtained in 56% yield by 1,3-dipolar cycloaddition using C$_{60}$ and *N*-octadecylglycine in toluene.[13] Compounds **PDI-ref** and **C$_{60}$-ref**[14] (Figure 1) were also synthesized as references.

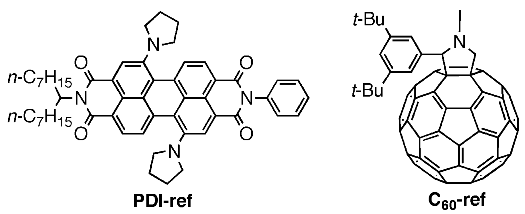


Figure 1. Reference compounds **PDI-ref** and **C$_{60}$-ref**.

The products were characterized on the basis of their ^{1}H, ^{13}C NMR, mass, and IR spectra (Supporting Information).

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UV−vis−NIR absorption spectra of **PDI-C$_{60}$**, **PDI-ref**, and **C$_{60}$-ref** were measured in benzonitrile (Figure 2). The dyad **PDI-C$_{60}$** reveals strong absorption at 700 nm and relatively weak absorption at 430 nm that come from the PDI moiety, together with strong absorption at the UV region from the C$_{60}$ moiety. The spectrum of **PDI-C$_{60}$** is virtually the superposition of the spectra of **PDI-ref** and **C$_{60}$-ref**, suggesting that there is no significant interaction between the PDI and C$_{60}$ moieties in the ground state. It is noteworthy that the spectral shapes of **PDI-C$_{60}$** in the NIR region, namely, the strong absorption at 700 nm and a shoulder at 650 nm, reveal that **6** exists as a monomer rather than as a π−π stacked aggregate in solution, because the H-aggregates of pyrrolidine-substituted PDI are known to exhibit the inverse spectral shapes in the NIR region, stronger absorption at 650 nm and a shoulder at 700 nm.[15]

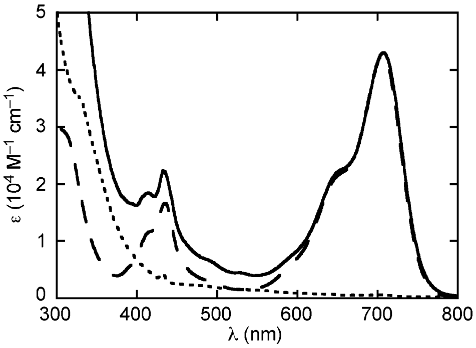

Figure 2. Absorption spectra of **PDI-C$_{60}$** (solid line), **PDI-ref** (dashed line), and **C$_{60}$-ref** (dotted line) in benzonitrile.

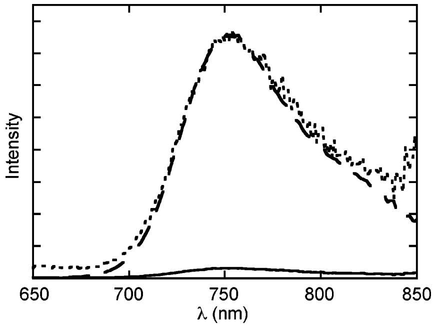

Figure 3. Fluorescence spectra of **PDI-C$_{60}$** (solid line) and **PDI-ref** (dashed line) in benzonitrile at λ_{ex} = 430 nm where the absorbances of the compounds are identical. The spectrum of **PDI-C$_{60}$** is also normalized at 750 nm for comparison (dotted line).

Figure 3 shows the steady-state fluorescence spectra of **PDI-C$_{60}$** and **PDI-ref** measured in benzonitrile with excitation wavelength (λ_{ex}) of 430 nm where the absorbances are identical. The shape of the spectrum of **PDI-C$_{60}$** is almost identical to that of **PDI-ref**, indicating that there is no significant interaction between the PDI and C$_{60}$ moieties in the excited state. The fluorescence from the C$_{60}$ moiety could not be confirmed because of the overlapping of the two emission at 700−800 nm and the low fluorescence quantum yield of the C$_{60}$. The fluorescence intensity of **PDI-C$_{60}$** is significantly reduced compared to that of **PDI-ref** in benzonitrile, indicating that the excited singlet state of the PDI moiety (^{1}PDI*) is strongly quenched by the C$_{60}$ moiety. The energy level of the excited singlet state (E_{00}) of the PDI is determined as 1.70 eV in benzonitrile from the absorption and fluorescence spectra of **PDI-ref** in benzonitrile.

The first oxidation potential (E_{ox}) of the PDI moiety and the first reduction potential (E_{red}) of the C$_{60}$ moiety were measured in benzonitrile containing 0.1 M Bu$_4$NPF$_6$ as supporting electrolyte using differential pulse voltammetry. The redox potentials of **PDI-C$_{60}$** (E_{ox} = +0.82 V, E_{red} = −0.41 V vs NHE) are almost the same as those of **PDI-ref** (E_{ox} = +0.81 V vs NHE) and **C$_{60}$-ref** (E_{red} = −0.41 V vs NHE), supporting only a minor electronic interaction between the PDI and the C$_{60}$ moieties in the ground state. The free energy change ($-\Delta G_{CS}$) for photoinduced ET from the ^{1}PDI* to the C$_{60}$ in benzonitrile is calculated to be 0.47 eV, implying that CS is possible.

Femto- to picosecond transient absorption spectra of the dyad **PDI-C$_{60}$** in benzonitrile were recorded using the pump−probe technique. The excitation wavelength (λ_{ex} = 415 nm) ensures the selective excitation of the PDI moiety. We could not excite the C$_{60}$ moiety selectively because of the extensive overlapping of the absorption spectra of the C$_{60}$ and the PDI moieties. Multiexponential global fittings were applied to transient-absorption decay curves (Figure S3, Supporting Information) at different wavelengths. The component spectra are shown in Figure S4 (Supporting Information). Three-exponential fitting gave a reasonably small mean square deviation value. The minor short-lived component (τ = 7 ps) stems from the thermal vibrational relaxation of the PDI excited singlet state. The longest lifetime component (τ = 170 ps) exhibits a characteristic spectrum resembling that of the major component of **PDI-ref** that arises from the lowest singlet excited state of the PDI moiety. The middle lifetime component (τ = 60 ps) has negative absorption at 1020 and at 880 nm, respectively, and has positive absorption at around 700 nm. This spectrum well agrees with the inverse of the differential spectrum of the charge-separated state (PDI$^{\bullet+}$-C$_{60}$$^{\bullet-}$). The recalculated differential spectra of ^{1}PDI* and PDI$^{\bullet+}$-C$_{60}$$^{\bullet-}$ states (Figure 4) also confirm the formation of the charge-separated state via photoinduced ET from the excited singlet state of the PDI to the C$_{60}$ (see S3−S5, Supporting Information, for the details). Namely, the spectrum of PDI$^{\bullet+}$-C$_{60}$$^{\bullet-}$ has ground-state bleaching at 720 nm and broad positive absorption bands at 880 and 1020 nm due to the PDI radical cation[15] and C$_{60}$ radical anion,[2,3,5]

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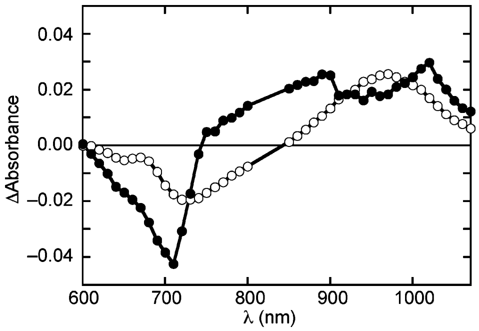

Figure 4. Recalculated transient absorption spectra of **PDI-C_{60}** in benzonitrile. Lines with open circles and close circles represent the spectra of ^{1}PDI* and PDI$^{•+}$-$C_{60}^{•-}$ states, respectively.

respectively, whereas the spectrum of ^{1}PDI* exhibits ground-state bleaching at 720 nm and broad positive absorption band at 980 nm. Thus, the time constant of CS (τ_{CS} = 170 ps) is larger than that of CR (τ_{CR} = 60 ps) (S5).[16] The rather slow CS and fast CR may result from large reorganization energy of the perylenediimide moiety.

In conclusion, we have successfully synthesized a novel perylenediimide-C_{60} dyad in which electron-donating amine substituents are introduced into the perylenediimide moiety to facilitate photoinduced electron transfer. By femto- to picosecond transient absorption measurements, the formation of the charge-separated state has been demonstrated unambiguously in perylenediimide-C_{60} linked dyads for the first time. Thus, our perylenediimide-C_{60} dyad is highly promising as a new class of artificial photosynthetic models and photovoltaic materials.

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Supporting Information Available: Experimental details (S1−S2) and kinetic analysis of transient absorption spectra of **PDI-C_{60}** (S3−S5). This material is available free of charge via the Internet at http://pubs.acs.org.

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