Long-range Photoinduced Electron Transfer Mediated by Oligo-*p*-phenylenebutadiynylene Conjugated Bridges

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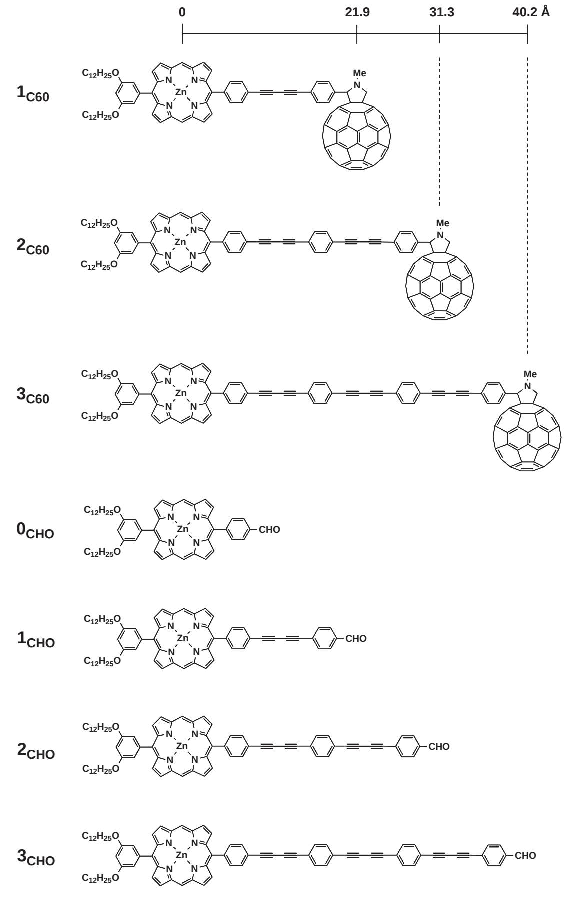
A series of novel zinc porphyrin/C_{60} dyads connected by 20–40 Å long intervening modules involving π-conjugated *p*-phenylenebutadiynylene oligomers underwent long-range photoinduced electron transfer with an attenuation factor (β) of 0.25 $Å^{-1}$.

Photoinduced electron-transfer reactions mediated by π-conjugated oligomers have attracted attention not only in view of the understanding of biological photosynthetic events but also for the fabrication of photofunctional molecular devices.[1] So far, a variety of π-conjugated molecules such as oligomeric *p*-phenylenes,[2] alkynylenes,[3] and *p*-phenyleneethynylenes[4] have been studied as intervening modules, where attenuation factors (β) of these π-conjugated molecules are in a range of 0.1–0.57 $Å^{-1}$, suggesting a superexchange mechanism for the electron-transfer processes. Otsubo and co-workers have reported a very small attenuation factor (0.03 $Å^{-1}$) for oligothiophenes,[5] which is close to those of oligophenylenevinylenes (0.04 $Å^{-1}$) in an electron-transfer process via electron hopping.[6] Here, we report photochemical properties of oligomeric *p*-phenylenebutadiynylenes.[7] Because of their conformational simplicity along with good capabilities for terminal functionalization and chain elongation, they are expected as useful building blocks for functional molecular and supramolecular architectures. However, their photochemical properties, in particular, electron-transfer properties, have never been reported.

In order to evaluate electronic properties of oligo-*p*-phenylenebutadiynylenes, we synthesized a series of zinc porphyrin/C_{60} dyads $\mathbf{1_{C60}}$–$\mathbf{3_{C60}}$ (Scheme 1) and unambiguously characterized by MALDI-TOF mass spectrometry along with ^{1}H NMR and absorption spectroscopies.[8] In these molecular systems, the zinc porphyrin and fullerene units are expected to serve as electron donor (D) and acceptor (A), respectively.[9] Compounds $\mathbf{1_{C60}}$–$\mathbf{3_{C60}}$ were sufficiently soluble in halogenated and aromatic solvents, owing to the presence of a 3,5-didodecyloxyphenyl group at the zinc porphyrin moiety. Molecular mechanics calculations allowed estimation of the center-to-center distances between the zinc porphyrin and C_{60} moieties in $\mathbf{1_{C60}}$, $\mathbf{2_{C60}}$, and $\mathbf{3_{C60}}$ as 21.9, 31.3, and 40.2 Å, respectively (Scheme 1). For references, we prepared $\mathbf{0_{CHO}}$–$\mathbf{3_{CHO}}$ that are devoid of the electron-accepting fullerene unit.[8] As predicted from molecular orbital calculations (PM3), the ground-state D–A interaction, if any, is negligibly small in $\mathbf{1_{C60}}$–$\mathbf{3_{C60}}$,[10] since the $\lambda_{\max}$ values of compounds $\mathbf{1_{C60}}$–$\mathbf{3_{C60}}$ and $\mathbf{0_{CHO}}$–$\mathbf{3_{CHO}}$ in the Soret absorption region were nearly identical to one another. In contrast, the luminescence profile was highly dependent on the molecular structure. By reference to $\mathbf{1_{CHO}}$, compound $\mathbf{1_{C60}}$, upon excitation at the



Scheme 1. Schematic structures of dyads $\mathbf{1_{C60}}$–$\mathbf{3_{C60}}$ and their reference compounds $\mathbf{0_{CHO}}$–$\mathbf{3_{CHO}}$.

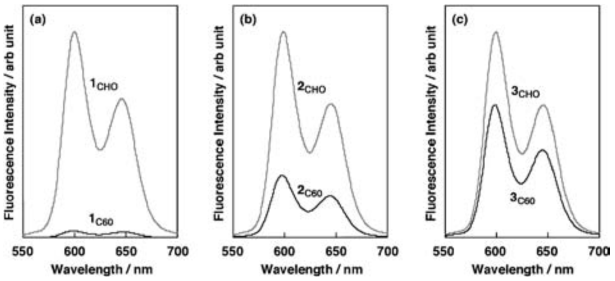


Figure 1. Steady-state fluorescence spectra of (a) $\mathbf{1_{C60}}$ and $\mathbf{1_{CHO}}$, (b) $\mathbf{2_{C60}}$ and $\mathbf{2_{CHO}}$, and (c) $\mathbf{3_{C60}}$ and $\mathbf{3_{CHO}}$ upon excitation at 422 nm in benzonitrile at 20 °C. All the spectra were normalized to a constant absorbance ($A = 0.2$) at the excitation wavelength.

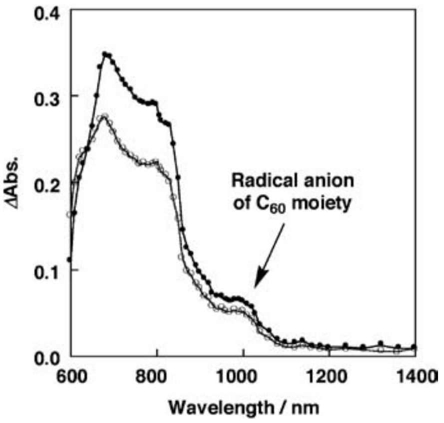


Figure 2. Transient absorption spectra of $\mathbf{3_{C60}}$ in benzonitrile at 25 °C taken 0.1 (●) and 1.0 (○) μs after a 532 nm, 6 ns, 10 mJ pulse under Ar.

Soret absorption band (422 nm) in benzonitrile, showed a notable quenching (96%) of the fluorescence emission from the zinc porphyrin moiety (Figure 1a). As the center-to-center distance between the zinc porphyrin and C_{60} moieties became larger from 21.9 ($\mathbf{1_{C60}}$) to 31.3 ($\mathbf{2_{C60}}$) to 40.2 Å ($\mathbf{3_{C60}}$), the efficiency of fluorescence quenching was decreased from 96 to 69 to 33% (Figure 1).

We also conducted time-resolved fluorescence spectroscopy of $\mathbf{1_{C60}}$–$\mathbf{3_{C60}}$ in benzonitrile at 25 °C. As expected from their steady-state fluorescence-quenching profiles (Figure 1), the fluorescence lifetime (τ) of the zinc porphyrin moiety became considerably longer from $\mathbf{1_{C60}}$ (0.092) to $\mathbf{2_{C60}}$ (0.78) to $\mathbf{3_{C60}}$ (1.83 ns), whereas those of $\mathbf{1_{CHO}}$ (2.28), $\mathbf{2_{CHO}}$ (2.30), and $\mathbf{3_{CHO}}$ (2.28 ns) were all close to that of $\mathbf{0_{CHO}}$ (2.33) and obviously longer than the lifetimes of the C_{60}-appended series.[8] Noteworthy, the fluorescence lifetime of $\mathbf{3_{C60}}$ is a little but definitely shorter than that of $\mathbf{3_{CHO}}$, suggesting the occurrence of a long-range (40 Å) electronic D–A communication even in $\mathbf{3_{C60}}$, the largest member of the family.[5,6] Since neither the C_{60} moiety nor the conjugated wire fluoresced upon excitation of the zinc porphyrin moiety, the fluorescence quenching observed for $\mathbf{1_{C60}}$–$\mathbf{3_{C60}}$ is most likely due to a D–A electron transfer, rather than energy transfer. Accordingly, transient absorption spectra of $\mathbf{1_{C60}}$–$\mathbf{3_{C60}}$ (Figure 2; $\mathbf{3_{C60}}$) displayed a characteristic absorption at around 1000 nm due to a radical anion of the C_{60} moiety. The decay profiles of the radical anion allowed evaluation of the lifetimes of the charge-separated states of $\mathbf{1_{C60}}$, $\mathbf{2_{C60}}$, and $\mathbf{3_{C60}}$ as 0.9, 1.0, and 2.2 μs, respectively.[8]

From the fluorescence lifetimes of the zinc porphyrin moiety in $\mathbf{1_{C60}}$–$\mathbf{3_{C60}}$ and reference compounds $\mathbf{1_{CHO}}$–$\mathbf{3_{CHO}}$, the rate constants of electron transfer (k_{et}) in $\mathbf{1_{C60}}$–$\mathbf{3_{C60}}$ were calculated as 10.4×10^9, 0.85×10^9, and $0.11 \times 10^9\ s^{-1}$, respectively.[11] As shown in Figure 3, plots of the $\ln k_{et}$ values against the center-to-center distances (d) between the zinc porphyrin and C_{60} moieties showed a negative linear correlation. Using equation $k_{et} = A\exp(-\beta d)$,[12] the attenuation factor β of oligomeric *p*-phenylenebutadiynylene was evaluated as $0.25\ Å^{-1}$, which is larger than that of polyyne ($0.1\ Å^{-1}$)[3] but smaller than those of oligomeric *p*-phenylene ($0.4\ Å^{-1}$)[2] and *p*-phenyleneethynylene (0.36–$0.57\ Å^{-1}$).[4] When compared with the case of electron hopping observed for oligo-*p*-phenylenevinylenes, the β value evaluated is much larger, indicating that the electron transfer in $\mathbf{1_{C60}}$–$\mathbf{3_{C60}}$ takes place via superexchange rather than electron hopping.

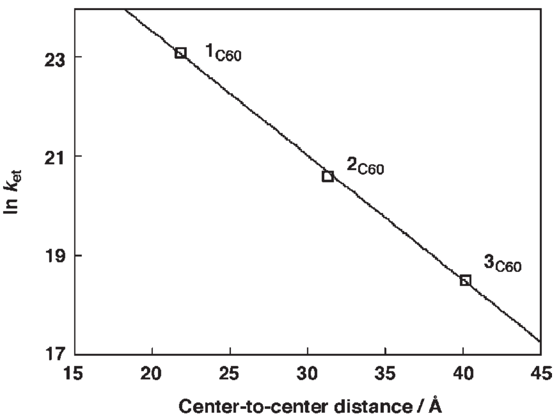


Figure 3. Distance dependence of electron-transfer rate constant (k_{et}) from zinc porphyrin to C_{60} moieties in $\mathbf{1_{C60}}$–$\mathbf{3_{C60}}$.

In conclusion, we have demonstrated the first example of a long-range photoinduced electron transfer between zinc porphyrin and C_{60} units connected via oligomeric *p*-phenylenebutadi ynylenes as intervening modules. Along with the conformational simplicity and synthetic availability, the relatively small attenuation factor ($0.25\ Å^{-1}$) of oligo-*p*-phenylenebutadiynylenes suggests their potential utility for molecular electronics.

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10 Square wave voltammetry of $\mathbf{1_{C60}}$, having C_{60} in the closest proximity to the zinc porphyrin moiety (P_{Zn}) among $\mathbf{1_{C60}}$–$\mathbf{3_{C60}}$, showed the first oxidation potential of the P_{Zn} moiety as 0.49 V (vs Fc/Fc$^+$), which is identical to that observed for reference $\mathbf{1_{CHO}}$ without C_{60}. See Supporting Information.

11 k_{et} values were calculated from the following equation: $k_{et} = (1/\tau_{C60}) - (1/\tau_{CHO})$, where τ_{C60} and τ_{CHO} are the fluorescence lifetimes of $\mathbf{1_{C60}}$–$\mathbf{3_{C60}}$ and $\mathbf{1_{CHO}}$–$\mathbf{3_{CHO}}$, respectively.

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