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Comparison of Reorganization Energies for Intra- and Intermolecular Electron Transfer**

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The reorganization energy (λ), which is a sum of two terms, inner-sphere reorganization energy, λ_i, and outer-sphere reorganization energy, λ_o, imposes probably the most far-reaching impact on biological electron-transfer (ET) systems.[1] In particular, the primary ET processes in photosynthesis are all characterized by small reorganization energies.[2] This situation allows, for instance, forward ET processes to proceed under nearly optimal conditions, that is, near the top region of the Marcus parabola, whereas the highly exergonic and energy-wasting back-ET process is shifted deeply into the inverted region. To achieve small reorganization energies, it is highly desirable for the construction of artificial photosynthetic systems to employ donor–acceptor couples, which offer room for the delocalization of the charges—electrons or

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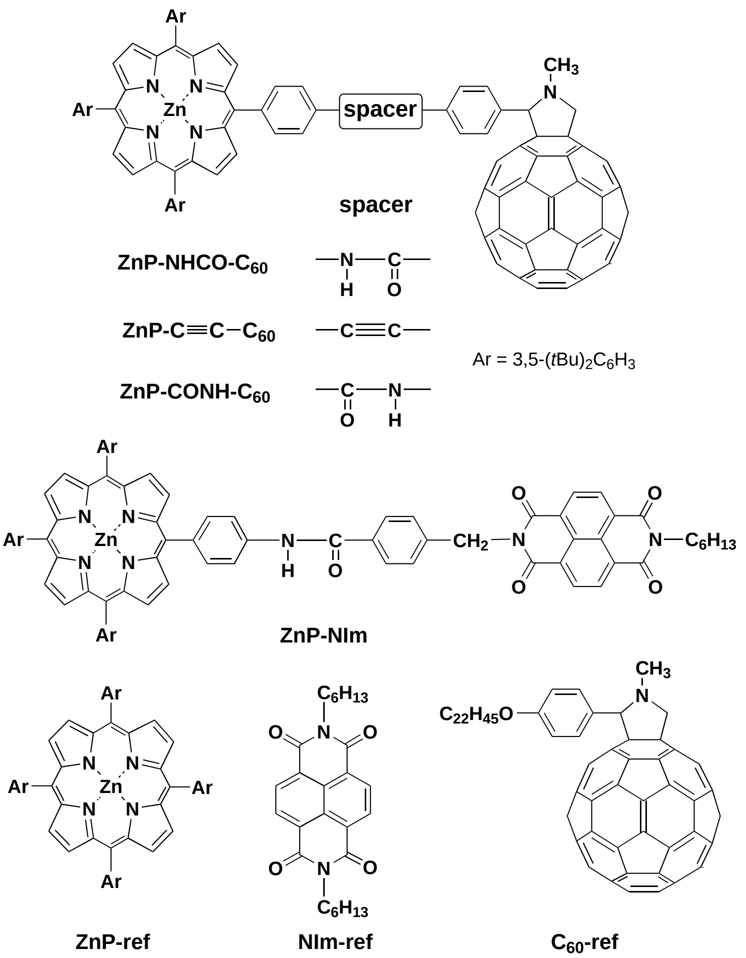
holes—within their structure. In this context, the exceptionally small λ values of porphyrin–fullerene donor–acceptor ensembles, a fact that relates to their delocalized π-electron systems, have great potential.[3] A quantitative comparison of λ values for intramolecular ET processes of a large 3D π acceptor (i.e., fullerenes) with those of conventional 2D acceptors (i.e., quinones and diimides), which have similar redox potentials and intervening spacers has, however, yet to be reported, mainly as a result of the synthetic challenges involved.[4–6]



Scheme 1.

Herein we report the first comprehensive assay of λ values for intramolecular ET involving a 3D acceptor (spherical C_{60}) and a 2D acceptor (planar naphthalenediimide (NIm); Supporting Information: S1). For this purpose we designed a series of porphyrin-linked C_{60} and NIm ensembles, endowed with similar rigid spacers (-NHCO-, -C≡C-, -CONH-)[3c, 7–9] as shown in Scheme 1. In addition, we report a quantitative analysis of λ values in intramolecular ET versus intermolecular ET.

Details on the synthesis and characterization of the compounds are provided in the Supporting Information (S2). Importantly, the first reduction potentials of **C_{60}-ref** (−1.02, −1.04, −0.92 V versus Fc/Fc$^+$ (Fc = ferrocene) in THF, PhCN, and DMF, respectively)[3c] are virtually the same as those of **NIm-ref** (−1.15, −1.05, −0.91 V versus Fc/Fc$^+$ in THF, PhCN, and DMF, respectively).

Time-resolved transient absorption spectra of the different dyads were measured by pico- and nanosecond laser photolysis in THF, PhCN, and DMF. Upon excitation of, for example, **ZnP-NHCO-C_{60}** with a 532 nm laser pulse (18 ps) in THF, a characteristic broad band at 680 nm assigned to the zincporphyrin radical cation (**$ZnP^{\bullet+}$**)[10] appeared. Concomitantly, the porphyrin singlet excited state (^{1}**ZnP***) absorption at 460 nm decayed, which suggests the transformation of ^{1}**ZnP*-NHCO-C_{60}** into **$ZnP^{\bullet+}$-NHCO-$C_{60}^{\bullet-}$**. The presence of **$C_{60}^{\bullet-}$** (1000 nm) and **$ZnP^{\bullet+}$** (680 nm) in the molecule was further substantiated by an independent set of complementary nanosecond experiments (Figure 1). By fitting the rise and decay of the fingerprint absorptions to a first-order rate law, the charge separation (CS) rates evolving from ^{1}**ZnP*** to **C_{60}** ($k_{ET(CS)}$) and the charge recombination (CR) rates within the **$C_{60}^{\bullet-}$/$ZnP^{\bullet+}$** pairs ($k_{ET(CR)}$) were determined. In THF, the exact values were $2.2 \times 10^{10}\,s^{-1}$ and $2.0 \times 10^{6}\,s^{-1}$, respectively. Hereby, the $k_{ET(CS)}$ value agrees well with the corresponding value ($2.0 \times 10^{10}\,s^{-1}$) obtained from the fluorescence lifetime measurements. A similar behavior was also observed for **ZnP-C≡C-C_{60}** ($k_{ET(CS)} = 3.7 \times 10^{10}\,s^{-1}$, $k_{ET(CR)} = 1.5 \times 10^{6}\,s^{-1}$) and **ZnP-CONH-$C_{60}$** ($k_{ET(CS)} = 1.3 \times 10^{10}\,s^{-1}$, $k_{ET(CR)} = 3.7 \times 10^{5}\,s^{-1}$).[3c]

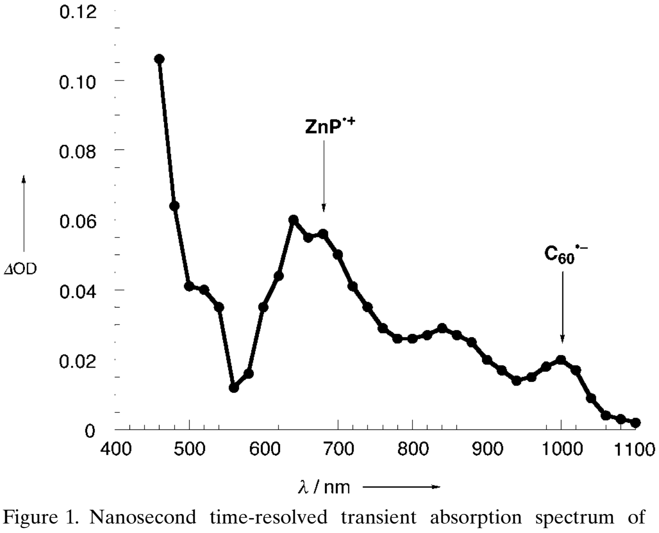


Figure 1. Nanosecond time-resolved transient absorption spectrum of **ZnP-NHCO-C_{60}** excited at 532 nm in THF (absorption ratio of **ZnP**:**C_{60}** = 3:1).

Importantly, in all **ZnP-C_{60}** dyads, the value of charge separation, $k_{ET(CS)}$, is much larger than the value of charge recombination, $k_{ET(CR)}$. This result infers that the CS processes for **ZnP-C_{60}** dyads are in the Marcus top region whereas the CR processes are in the Marcus inverted region.[3c] Conversely, the $k_{ET(CR)}$ value in the corresponding NIm-based dyad, **ZnP-NIm**, is much larger than the $k_{ET(CS)}$ value as determined by the picosecond transient absorption spectrum[11] and the decay of the ^{1}**ZnP*** fluorescence (Supporting Information: S3). This situation means that the CS processes for **ZnP-NIm** are in the Marcus normal region whereas the CR processes are in the Marcus top region. The $k_{ET(CS)}$ and $k_{ET(CR)}$ values of **ZnP-NIm** in THF were determined as $3.9 \times 10^{8}\,s^{-1}$

and 2.0×10^{10} s^{-1}, respectively. In more polar PhCN and DMF, a behavior resembling ET was noted for all of the dyads investigated (Table 1).

Table 1. Rate constants (k_{ET}) for charge separation (CS) and charge recombination (CR) and the free energy changes ($-\Delta G^0_{ET}$)[a] in porphyrin–fullerene and porphyrin–naphthalenediimide dyads.

	THF ($\varepsilon_s = 7.58$)		Benzonitrile ($\varepsilon_s = 25.2$)		DMF ($\varepsilon_s = 36.7$)	
	$-\Delta G^0_{ET}$ [eV]	k_{ET} [s^{-1}]	$-\Delta G^0_{ET}$ [eV]	k_{ET} [s^{-1}]	$-\Delta G^0_{ET}$ [eV]	k_{ET} [s^{-1}]
ZnP-NHCO-C$_{60}$						
CS	0.70	2.2×10^{10}[b]	0.70	2.8×10^{10}	0.89	1.3×10^{10}[b]
CR	1.37	2.0×10^{6}	1.34	2.4×10^{6}	1.17	3.4×10^{6}
ZnP-C≡C-C$_{60}$						
CS	0.67	3.7×10^{10}[c]	0.69	3.0×10^{10}	[d]	3.0×10^{10}[c]
CR	1.40	1.5×10^{6}	1.35	2.1×10^{6}	[d]	2.5×10^{6}
ZnP-CONH-C$_{60}$						
CS	0.65	1.3×10^{10}[e]	0.66	9.5×10^{9}[e]	0.85	1.3×10^{10}[e]
CR	1.42	3.7×10^{5}[e]	1.38	1.3×10^{6}[e]	1.21	1.8×10^{6}[e]
ZnP-NIm						
CS	0.57	3.9×10^{8}	0.69	[d]	0.90	3.5×10^{8}[b]
CR	1.50	2.0×10^{10}	1.35	[d]	1.16	[d]

[a] $-\Delta G^0_{CR} = E_{ox}(D/D^{\bullet+}) - [-E_{red}(A/A^{\bullet-})]$, $-\Delta G^0_{CS} = \Delta E_{0\text{-}0} - (-\Delta G^0_{CR})$ where E_{ox} ($D/D^{\bullet+}$) and E_{red} ($A/A^{\bullet-}$) are the first oxidation potential of donor and the first reduction potential of acceptor, respectively, and $\Delta E_{0\text{-}0}$ is energy of the 0-0 transition between the lowest excited state and the ground state. [b] From ref. [8]. [c] From ref. [9]. [d] Not determined. [e] From ref. [3c].

In the next step we quantified the driving-force dependence on the ET rate constants (k_{ET}), by Equation (1), where V represents the electronic coupling matrix element.[1] This equation is rewritten to give Equation (2) which is also applied to evaluate the electron-transfer rate constant (k_{ET}).

$$k_{ET} = \left(\frac{4\pi^3}{h^2 \lambda k_B T}\right)^{1/2} V^2 \exp\left[-\frac{(\Delta G^0{}_{ET} + \lambda)^2}{4 \lambda k_B T}\right] \tag{1}$$

$$k_B T \ln k_{ET} + \frac{\Delta G^0{}_{ET}}{2} = k_B T \ln\left[\left(\frac{4\pi^3}{h^2 \lambda k_B T}\right)^{1/2} V^2\right] - \frac{\lambda}{4} - \frac{(\Delta G^0{}_{ET})^2}{4\lambda} \tag{2}$$

The driving forces ($-\Delta G^0_{ET}$) for the intramolecular ET processes were determined accurately, based on the first oxidation potential of the zincporphyrin donor and the first reduction potential of the fullerene/naphthalenediimide acceptors in THF, PhCN, and DMF, together with the energy level of the porphyrin singlet excited state. According to Equation (2), a plot of $k_B T \ln k_{ET} + (\Delta G^0_{ET}/2)$ versus $(\Delta G^0_{ET})^2$ for **ZnP-NHCO-C$_{60}$**, **ZnP-C≡C-C$_{60}$**, and **ZnP-CONH-C$_{60}$** gives a linear correlation (Supporting Information: S4).[12] The λ and V values are obtained from the intercept and the slope as $\lambda = 0.59 \pm 0.15$ eV and $V = 7.9 \pm 1.7$ cm^{-1}, respectively. A linear correlation was also obtained for **ZnP-NIm** (Supporting Information: S4) which afforded a much larger λ value ($\lambda = 1.41 \pm 0.33$ eV) together with a similar V value (7.8 ± 3.2 cm^{-1}).[13] Such an extraordinary large difference in λ between the C$_{60}$ and NIm dyads is the reason why the ratio of $k_{ET(CS)}$ to $k_{ET(CR)}$ is reversed in the two donor–acceptor systems (Table 1). This result is the first quantitative manifestation that the λ value of a 3D electron acceptor (C$_{60}$) is, indeed, much smaller than the value of a typical 2D acceptor (NIm).

However, our current conclusion is in sharp contradiction to a previous hypothesis concerning the λ value for an intermolecular electron self-exchange reaction of tBuC$_{60}{}^{-}$/tBuC$_{60}{}^{\bullet}$.[14] In particular, the value of 0.64 eV in PhCN/benzene (1:7 v/v) is quantitatively similar to that seen for the BQ$^{\bullet-}$/BQ couple (BQ = benzoquinone), 0.74 eV in PhCN.[14] To shed light on this apparent discrepancy, the λ value of intermolecular electron self-exchange between (**ZnP-ref**)$^{\bullet+}$/**ZnP-ref** and between (**NIm-ref**)$^{\bullet-}$/**NIm-ref** was determined by analyzing line-width variations in the ESR spectra (Supporting Information: S5).[15–17] The line width (ΔB_{pp}) increased with increasing **NIm-ref** concentration (Supporting Information: S6). From the slope of the linear correlation the electron self-exchange rate constant (k_{ex}) was determined.[16, 18] The Arrehenius plot of k_{ex} at various temperatures (Supporting Information: S7) afforded the activation parameters ($\Delta H^{\ddagger} = 4.2$ kJ mol^{-1} and $\Delta S^{\ddagger} = -14$ J K^{-1}mol^{-1}). The λ values of **ZnP-ref**$^{\bullet+}$/**ZnP-ref** and **NIm-ref**$^{\bullet-}$/**NIm-ref** were determined from the rate constant in MeCN at 298 K as 0.30 eV and 0.34 eV, respectively. Both of these λ values are substantially smaller than the value of tBuC$_{60}{}^{-}$/tBuC$_{60}{}^{\bullet}$ (0.64 eV). With the λ values of the electron self-exchange reaction of each component in hand, the λ values of intermolecular ET were estimated as the average of the two λ values of electron self-exchange reactions. Importantly, the λ value of the intermolecular ET from **ZnP-ref** to **NIm-ref** (0.32 eV) is appreciably smaller than that seen for the **ZnP-ref/C$_{60}$-ref** couple (0.47 eV).

In summary, our results clearly infer that intermolecular ET between a planar naphthalenediimide (NIm) acceptor and a planar zincporphyrin (ZnP) donor takes place at short separation distances rendering the reorganization energy small. In contrast to such a 2D π system, intermolecular ET involving a spherical 3D π system (C$_{60}$) is likely to occur at larger distances. An important asset is the effective radius of the acceptor moiety: Even if C$_{60}$ is held at the same critical distance (i.e., van der Waals contact) as NIm, because of the strong π–π interactions, the effective center-to-center separation is significantly larger. In the case of intramolecular ET systems, the fixed distance, by which the donor and acceptor are separated, allows the intrinsic reorganization energies of a planar and a spherical acceptor to be distinguished. This study has provided for the first time insights into the intrinsic reorganization energies of electron transfer, which relate to different molecular shapes.

Experimental Section

Details on the synthesis and characterization of the compounds are provided in the Supporting Information (S2). Time-resolved fluorescence spectra of the compounds were measured by a single-photon counting method using a second-harmonic generation (SHG, 524 nm) of a semiconductor YLF laser (Lightwave 131-1047-300, FWHM = 20 ps) as an excitation source.[19] Picosecond transient absorption spectra of **ZnP-NIm** were measured by means of a picosecond dye laser (FWHM 12 ps) pumped by the second harmonic of a repetitive mode-locked Nd^{3+}:YAG laser (Quantel, Picochrome YG-503 C/PTL-10).[19] The 590-nm output of the dye laser (Rhodamine 6G) was used for excitation. Picosecond laser flash photolysis experiments for **ZnP-C_{60}** dyads were carried out with 532-nm laser pulses from a mode-locked, *Q*-switched Quantel YG-501 DP ND:YAG laser system (pulse width ~18 ps, 2–3 mJ/pulse).[3c] The white continuum picosecond probe pulse was generated by passing the fundamental output through a D_2O/H_2O solution. Nanosecond laser-flash photolysis experiments were performed with laser pulses from a Quanta-Ray CDR Nd: YAG system (532 nm, 6 ns pulse width) in a front face excitation geometry.[3c] A Xe lamp was triggered synchronously with the laser. A monochromator (SPEX) in combination with either a Hamamatsu R 5108 photomultiplier or a fast InGaAs-diode was employed to monitor transient absorption spectra.

Tetramethyl-*p*-benzoquinone (Me_4Q) radical anion was prepared by proportionation reactions of Me_4Q with the dianion obtained by deprotonation of the corresponding hydroquinone with tetrabutylammonium hydroxide.[14] The self-exchange rate constants between the reference compounds and the corresponding radical anions in CH_3CN at various temperatures are directly determined by analyzing line-width variations of the ESR spectra.[14] Typically, an aliquot of a stock solution of the Me_4Q radical anion (5.0×10^{-4} M) was added to an ESR tube containing a deaerated CH_3CN solution of various concentrations of **NIm-ref** (5.0×10^{-4} M to 2.0×10^{-3} M) under an atmospheric pressure of Ar. The ESR spectra of the **NIm-ref** radical anion were measured at various temperature (−40 to 25 °C) with a JEOL X-band spectrometer (JES-RE1XE). The ESR spectra were recorded under nonsaturating microwave power conditions. The magnitude of modulation was chosen to optimize the resolution and the signal-to-noise (S/N) ratio of the observed spectra, when the maximal slope line width (ΔB_{pp}) of the ESR signals was unchanged with the larger modulation. The *g* values and the hyperfine coupling constants were calibrated with a Mn^{2+} ion marker. The **ZnP-ref** radical cation was produced by the chemical oxidation of **ZnP-ref** with $[Ru(bpy)_3]^{3+}$ ions (bpy = 2,2′-bipyridine).[20]

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[12] The Marcus plots for **ZnP-CONH-C_{60}** involving CS from the excited porphyrin and **C_{60}** singlet states, and CS from the excited **C_{60}** triplet state, and CR from **$C_{60}^{\bullet-}$** to **$ZnP^{\bullet+}$** have been reported.[3c] The plots in THF, PhCN, and DMF fit well to a single parabolic Marcus curve on the basis of Equation (1), which implies that the classical Marcus theory is valid for both the CS and CR processes in the porphyrin–fullerene linked systems. This result supports the idea that reorganization energies of porphyrin–fullerene systems are virtually the same in the three solvents because of the charge delocalization in porphyrin and fullerene moieties, which would mask the solvent effects on the reorganization energies.[3c,4d] Thus, the λ values are assumed to be similar in **ZnP-NHCO-C_{60}**, **ZnP-C≡C-C_{60}**, and **ZnP-CONH-C_{60}**.

[13] The *V* values of **ZnP-NHCO-C_{60}**, **ZnP-C≡C-C_{60}**, **ZnP-CONH-C_{60}** (7.9 ± 1.7 cm^{-1}), and **ZnP-NIm** (7.8 ± 3.2 cm^{-1}) are found to be similar. This result agrees with the similarity in the intervening spacer moieties. We have also reported the linear correlation of logarithmic k_{ET} versus edge-to-edge distance (R_{ee}) in porphyrin–fullerene linked systems (i.e., porphyrin–fullerene dyads, triads, and tetrad) including **ZnP-CONH-C_{60}** where the decay coefficient factor (β) is 0.6 $Å^{-1}$. Since the R_{ee} values (11.9 Å) are the same in the two systems, the similar *V* values are consistent with the distance dependence of k_{ET}. H. Imahori, D. M. Guldi, K. Tamaki, Y. Yoshida, Y. Sakata, S. Fukuzumi, *J. Am. Chem. Soc.* **2001**, *123*, 6617.

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