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Inter- and Intramolecular Photoinduced Electron Transfer of Flavin Derivatives with Extremely Small Reorganization Energies

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Abstract: Photoinduced electron transfer (ET) of a series of aromatic electron donors (D) to the singlet or triplet excited state of a flavin analogue (10methylisoalloxazine: MeFl) and intermolecular back electron transfer (BET) from MeFl⁻⁻ to D⁺⁺ in benzonitrile (PhCN) has been investigated in light of the Marcus theory of ET. The rate constants of intermolecular photoinduced ET (k_{et}) from D to the singlet excited state (1MeFl*) and the triplet excited state (3MeFl*) were determined by fluorescence quenching and enhanced decay rates of triplet-triplet (T–T) absorption by the presence of D, respectively. The k_{et} values increase with an increase in the ET driving force to reach the diffusion-limit value that remains constant with a further increase in the ET driving force. Nanosecond laser flash photolysis was performed to determine the rate constants of intermolecular BET (k_{bet}) from MeFl⁻ to D⁺ in PhCN. In contrast to the case of k_{et} , the driving force dependence of k_{bet} shows a pronounced decrease towards the highly exothermic region. The reorganization energy (λ) of intermolecular BET is determined to be 0.68 eV by applying the Marcus equation in the inverted region, where the k_{bet} value decreases with increasing

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the BET driving force. The slowest BET was observed for BET from MeFl⁻⁻ to N,N-dimethylaniline radical cation (DMA⁺⁺) with the k_{bet} value of $3.5 \times 10^{6} \text{ m}^{-1} \text{ s}^{-1}$, which is 1600 times smaller than the diffusion rate constant in PhCN $(5.6 \times 10^9 \text{ m}^{-1} \text{ s}^{-1})$. Then, DMA was linked to the 10-position of isoalloxazine to synthesize a DMA-flavin linked dyad (10-[4'-(N,N-dimethylamino)phenyl]-isoalloxazine: DMA-Fl). Photoexcitation of DMA-Fl results in photoinduced ET from the DMA moiety to the singlet excited state of Fl moiety to form the charge-separated (CS) state (DMA⁺-Fl⁻) that has an extremely long lifetime (2.1 ms) in PhCN at 298 K.

Introduction

Natural photosynthesis applies photoinduced electron-transfer (ET) systems, where a relay of photoinduced ET reactions evolves among chlorophyll (electron donor) and quinone (electron acceptor) moieties embedded in a transmembrane protein matrix, to attain a lifetime of the final chargeseparated (CS) state as long as seconds.^[1] The long-lived CS state leads to conversion of light into usable chemical

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inspired from the natural photosynthetic systems to develop electron donor-acceptor (D-A) linked molecules that undergo photoinduced ET reactions to afford charge-separated (CS) states.^[2-17] The Marcus theory of electron transfer^[18] has provided rational design of D-A linked molecules. The most important prediction of the Marcus theory of ET is that the ET rate is expected to decrease in the strongly exergonic region.^[18] Such a strongly exergonic region is generally referred to as the Marcus inverted region,^[18] which has been observed in a number of D-A linked systems.^[12-17] The magnitude of the reorganization energy (λ) is known to be the key parameter to control the ET process. The smaller λ value promotes the forward photoinduced ET process, but retard the back electron transfer (BET) process when the driving force for BET $(-\Delta G_{\text{BET}})$ is larger than the λ value. Thus, the CS lifetimes can be finely controlled by the λ value, which is determined by the choice of the electron donor and acceptor pair, the type of linkage between the electron donor and acceptor molecules.^[18]

energy.^[1] Extensive efforts have so far been devoted being

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We have previously reported that D–A compounds, which afford the long-lived CS state in glassy solution at 77 K, however, the CS state decays with the diffusion rate via intermolecular charge recombination (CR) between two CS states in solution at 298 K.^[14,16] Artificially, none of reported molecules has ever afforded a CS state over millisecond in solution at 298 K. Formation of a truly longer-lived CS state in solution at 298 K requires slower intermolecular CR than intramolecular CR.

It has generally been believed that intermolecular ET reactions exhibit a Rehm–Weller behavior: the ET rate increases with an increase in the ET driving force to reach a diffusion limit, which remains unchanged no matter how exergonic ET might be.^[19,20] This is the main reason for ignoring the Marcus inverted region for the intermolecular ET reaction. Recently, however, there have been reports on observation of the Marcus inverted region for ET reactions with a small λ value.^[21–24] Thus, if a chromophore with an extremely small λ value for the inter- and intramolecular ET is utilized, an extremely long-lived intramolecular CS state in D–A dyad would be formed in solution at 298 K.

In this context, flavin may be a good candidate as a chromophore with an extremely small λ value of electron transfer, because the flavin cofactor is one of the most important coenzymes for electron transportation and an important photoreceptor in biological systems.^[25,26] Flavin is a tricyclic heteronuclear organic ring based on pteridine whose biochemical source is the vitamin riboflavin. The redox reactivity of flavins is the most drastically changed by the photoexcitation as compared to the ground state. Thus, photochemistry of flavoenzymes and flavin analogues has been the subject of intense research in photocatalysts for the photobioprocesses.[27-29] logical redox Besides, the flavin chromophore has a strong absorption band at visible region acting as a photosensitizer.^[30] Despite the versatile role of flavin as a photosensitizer, there has been to the best of our knowledge no report on photoinduced ET in D-A dyads using a flavin chromophore.

We report herein the dynamics for inter- and intramolecular photoinduced ET and BET reactions of a flavin analogue (10-methylisoalloxazine: MeFl shown below) by using the time-resolved spectroscopic measurements, which have revealed the evidence of the Marcus inverted region for the intermolecular BET reactions for the first time. *N*,*N*-Dimethylaniline that afforded the slowest intermolecular BET rate in photoinduced ET with MeFl was linked to the isoalloxazine at 10-position to synthesize an *N*,*N*-dimethylaniline–flavin linked dyad (10-[4'-(N,N-dimethylamino)phen-yl]–isoalloxazine: DMA–Fl). The longest lifetime of the CS





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state of DMA-Fl was successfully observed in solution at 298 K.

Results and Discussion

Photoinduced electron transfer from electron donors to MeFI: Irradiation of the absorption band of 10-methylisoalloxazine (MeFI) at 440 nm results in fluorescence at $\lambda = 500$ nm in deaerated PhCN (see Supporting Information S1).^[30] The steady-state fluorescence emission of the singlet excited state of MeFI (¹MeFI*) was efficiently quenched by the addition of triphenylamine (TPA) in PhCN via photoinduced ET from TPA to ¹MeFI* as confirmed later (see Supporting Information S2a). The observed quenching rate constant (k_{et}) was derived from the slope of the Stern–Volmer (SV) plot and lifetime of ¹MeFI* (see inset of Supporting Information S2a). The fluorescence lifetime (τ_0) was determined from the time-resolved fluorescence decay to be 9.4 ns in PhCN (see Supporting Information S2b).

Fluorescence decays of MeFl were also measured in the presence of various concentrations of TPA as shown in Figure 1 b. The fluorescence lifetime (τ) was significantly shortened by the addition of TPA (see Supporting Information S2b). The quenching rate constant was obtained from the linear plot (see inset of see Supporting Information S2b) of τ_0/τ versus concentration of TPA ($5.8 \times 10^9 \,\mathrm{M^{-1} \, s^{-1}}$), which agrees with the value ($5.9 \times 10^9 \,\mathrm{M^{-1} \, s^{-1}}$) determined from the steady-state fluorescence quenching in PhCN (see inset of see Supporting Information S2a). Similarly, the $k_{\rm et}$ values for other electron donors (D) are determined from the SV plots, which are listed in Table 1.

Photoinduced ET can be examined not only from D to ¹MeFl* but also from D to the triplet excited state (³MeFl*). The energy of ³MeFl* was determined from phosphorescence spectrum of MeFl in 2-methyltetrahydrofuran glass at 77 K to be 1.96 eV (see Supporting Information S3).^[30,32] The one-electron reduction potential of ³MeFl* was estimated from the one-electron reduction potential of MeFl (-0.83 V vs. SCE) and the triplet energy (1.96 eV) to be 1.30 V versus SCE. Thus, photoinduced ET from D ($E_{ox} < 1.30$ V vs. SCE) to ³MeFl* can be energetically feasible. The reaction pathway of photoinduced ET from D to ³MeFl* becomes dominant under experimental conditions of low concentrations of D because of the much longer lifetime of ³MeFl* as compared to ¹MeFl*.

Figure 1 a shows a transient absorption spectrum in a PhCN solution at 1.6 μ s after the laser pulse excitation at 440 nm containing MeFl and *N*,*N*,*N'*,*N'*-tetramethylbenzidine (TMBZ; E_{ox} =1.03 V vs. SCE). Transient absorption at 1050 nm is assigned to TMBZ'+, which was confirmed by comparison with the spectrum obtained by the one-electron oxidation of TMBZ with [Fe(bpy)₃]³⁺ as an oxidant (see Supporting Information S4). The time profile of rise in absorption at 1050 nm obeys pseudo-first order kinetics, and the observed pseudo-first-order rate constant (k_{obs}) increases linearly with increasing concentration of TMBZ (inset of Figure 1b). The k_{et} value of photoinduced ET from TMBZ

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Figure 1. a) Transient absorption spectrum of MeFl $(6.0 \times 10^{-5} \text{ M})$ in the presence of TMBZ $(4.0 \times 10^{-4} \text{ M})$ in deaerated PhCN at 298 K taken at 1.6 µs after nanosecond laser excitation (λ = 440 nm, 13 mJ per pulse). b) Time profile at 1050 nm. Inset: Plot of k_{obs} versus [TMBZ]. The k_{obs} values were determined from the decay time profiles of ³MeFl* ($6.0 \times 10^{-5} \text{ M}$) with various concentration of TMBZ.

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where e is elementary charge, ${}^{1}E^{*}$, ${}^{3}E^{*}$, E_{ox} and E_{red} are the energies of the 1 MeFl* (2.60 eV), 3 MeFl* (1.96 eV), ${}^{[30,33]}$ the one-electron oxidation potentials of D and the one-electron reduction potential of MeFl (-0.83 V vs. SCE), respectively. The electrostatic stabilization term is neglected in a highly polar solvent such as PhCN in Equations (1) and (2). Since the E_{ox} values of D in PhCN have been determined by electrochemical measurements (see Experimental Section), the $-\Delta G_{el}(S)$ and $-\Delta G_{el}(T)$ values are determined by using Equations (1) and (2) as listed in Tables 1 and 2, respectively.

Figure 2 shows a plot of $\log k_{\rm et}$ versus $(-\Delta G_{\rm et}(S)$ or $-\Delta G_{\rm et}(T))$ in PhCN, the $\log k_{\rm et}$ value increases with a decrease in the $(-\Delta G_{\rm et}(S) \text{ or } -\Delta G_{\rm et}(T))$ value to reach a plateau value corresponding to the diffusion rate constant $(5.6 \times 10^9 \,\mathrm{m^{-1} \, s^{-1}})^{[34]}$ in PhCN as the photoinduced ET becomes energetically more favorable (i.e., more exergonic).^[19,20]

Photoinduced ET from D to ¹MeFl* and the subsequent reactions are shown in Scheme 1, where k_{diff} and k_{diff} are diffusion and dissociation rate constants in the encounter complex, (D MeFl*).^[34] The rate constant of forward intramolecular photoinduced ET in the encounter complex, (D MeFl*) to (D⁺⁺ MeFl⁺⁻) is denoted as k_{ET} , whereas the rate constant complex, (D MeFl*) to (D⁺⁺ MeFl⁺⁻) is denoted as k_{ET} , whereas the rate constant of the forward intermolecular photoinduced ET (D + MeFl*) to (D⁺⁺ + MeFl⁺⁻) is denoted as k_{et} . Likewise the rate constant of the back ET (BET) to the ground state by intramolecular and bimolecular BET are denoted as k_{BET} and k_{bet} , respectively. The observed rate constant of intermolecular photoinduced ET (k_{et}) is given by Equation (3).

to ³MeFl* is determined from the slope of the linear plot of k_{obs} versus concentration of TMBZ to be $5.6 \times 10^9 \text{ m}^{-1} \text{ s}^{-1}$. Similarly k_{et} values of various electron donors were determined and the results are listed in Table 2.

Driving force of photoinduced ET from D to ¹MeFl* $(-\Delta G_{et}(S) \text{ in eV}; S \text{ denotes sin$ $glet excited state}) \text{ and } ^{3}MeFl*$ $<math>(-\Delta G_{et}(T) \text{ in eV}; T \text{ denotes}$ triplet excited state) are given by Equations (1) and (2),

$$-\Delta G_{\rm et}(\mathbf{S}) = {}^{1}E^{*} - e(E_{\rm ox} - E_{\rm red})$$
(1)
$$-\Delta G_{\rm et}(\mathbf{T}) = {}^{3}E^{*} - e(E_{\rm ox} - E_{\rm red})$$

Table 1. Oxidation potentials of electron donors (E_{ox}), free energy changes of intermolecular photoinduced ET from ¹MeFl* to electron donors (D) ($-\Delta G_{et}(S)$) and rate constants of photoinduced ET (k_{et}) from ¹MeFl* to D in PhCN.

Entry	Electron donor	$E_{\rm ox}$ vs. SCE in PhCN [V]	$-\Delta G_{\rm et}({ m S})^{[{ m a}]} [{ m eV}]$	$k_{\rm et}^{[b]} [{\rm M}^{-1} {\rm s}^{-1}]$
1	1,2,3-trimethylbenzene	1.88	-0.11	7.3×10^{6}
2	1,2,4-trimethylbenzene	1.79	-0.02	2.8×10^{8}
3	1,2,3,4-tetramethylbenzene	1.70	0.07	1.2×10^{9}
4	1,2,3,5-tetramethylbenzene	1.69	0.08	1.2×10^{9}
5	1,2,4,5-tetramethylbenzene	1.65	0.12	2.3×10^{9}
6	hexamethylbenzene	1.53	0.24	3.4×10^{9}
7	4-methoxybenzene	1.46	0.31	4.0×10^{9}
8	trans-stilbene	1.40	0.37	4.6×10^{9}
9	1,2,3-trimethoxybenzene	1.32	0.45	3.7×10^{9}
10	1,4-dimethoxybenezene	1.21	0.56	5.4×10^{9}
11	1,2,4-trimethoxybenzene	0.93	0.84	5.8×10^{9}
12	triphenylamine	0.83	0.94	5.9×10^{9}
13	N,N-dimethylaniline	0.68	1.09	5.6×10^{9}
14	phenothiazine	0.50	1.27[0.18] ^[c]	5.5×10^{9}
15	bis(ethylenedithiol)tetrathiafulvalene	0.40	1.37[0.13] ^[c]	5.5×10^{9}
16	N, N, N', N'-tetramethylbenzidine	0.27	1.50[0.35] ^[c]	5.9×10^{9}
17	N, N, N', N'-tetramethylphenylenediamine	0.03	1.74[0.22] ^[c]	5.7×10^{9}

[a] Driving force of intermolecular photoinduced ET from electron donors (D) to ¹MeFl* producing D⁺⁺ and MeFl⁻⁻, determined from the one-electron oxidation potentials of electron donors, the one-electron reduction potential of MeFl ($E_{red} = -0.83$ V vs. SCE in PhCN) and the energy of ¹MeFl* (2.60 eV in PhCN) by using Eq. (1). [b] The experimental error is ± 5 %. [c] Driving force of intermolecular photoinduced ET from D to ¹MeFl* to produce the doublet excited state (D^{++*}) and MeFl⁻⁻, determined by subtracting the energy of the low-lying excited state of D^{++*} ($^{2}E^{*}$)^[31] from those of photoinduced ET producing the ground state (D⁺⁺ and MeFl⁻⁻).

(2)

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Table 2. Free energy changes of intermolecular photoinduced ET from D to ${}^{3}MeFl^{*}$ ($-\Delta G_{et}(T)$) and back ET ($-\Delta G_{bet}$), the rate constants of intermolecular photoinduced ET from D to ${}^{3}MeFl^{*}$ (k_{et}) and intermolecular BET (k_{bet}) from MeFl⁻ to D⁺ in PhCN, and the molar absorption coefficients of D⁺ (ε).

Entry	Electron donor ^[a]	$-\Delta G_{ m et}({ m T})^{[{ m b}]}$ [eV]	$-\Delta G_{ m bet}$ [eV]	k_{et} [m ⁻¹ s ⁻¹]	k_{bet} [$M^{-1}S^{-1}$]	$arepsilon^{[ext{c}]} \left[ext{M}^{-1} ext{cm}^{-1} ight] \ (\lambda_{ ext{max}} \left[ext{nm} ight])^{[ext{d}]}$
13	DMA	0.62	1.51	4.8×10^{9}	3.5×10^{6}	3.4×10^2 (650)
14	PTZ	0.80	1.33	5.8×10^{9}	1.8×10^{8}	7.1×10^2 (758)
15	BEDT-TTF	0.90	1.23	5.4×10^{9}	1.4×10^{9}	7.3×10^3 (998)
16	TMBZ	1.03	1.10	5.6×10^{9}	4.8×10^{9}	4.8×10^4 (1075)
17	TMPD	1.27	0.86	5.5×10^{9}	5.8×10^{9}	8.3×10^3 (620)

[a] DMA: *N*,*N*-dimethylaniline, PTZ: phenothiazine, BEDT-TTF: bis(ethylenedithiol)–tetrathiafulvalene, TMBZ: *N*,*N*',*N*'-tetramethylbenzidine, and TMPD: *N*,*N*,*N*',*N*'-tetramethylphenylenediamine. [b] Determined from the reduction potential of MeFl ($E_{red} = -0.83$ V vs. SCE in PhCN) and the value of triplet excited state of MeFl (³MeFl*=1.96 eV in PhCN) by using Eq. (2). [c] Determined from UV-visible spectra of radical cations of aromatic electron donors obtained by the oxidation with [Fe(bpy)₃](PF₆)₃ (bpy=2,2'-bipyridine) in deaerated MeCN at 298 K. [d] Values in parentheses are absorption maxima of radical cations.

$$k_{\rm et} = k_{\rm ET} k_{\rm diff} / (k_{\rm ET} + k_{\rm -diff}) \tag{3}$$

The dependence of $k_{\rm et}$ on $-\Delta G_{\rm et}$ ($-\Delta G_{\rm et}(S)$ or $-\Delta G_{\rm et}(T)$) for adiabatic outersphere ET has well been established by Marcus as given by Equation (4), where $k_{\rm B}$ is the Boltzmann constant, *h* is the Planck constant

$$k_{\rm ET} = (k_{\rm B}T/h)\exp(-(\Delta G_{\rm et} + \lambda)^2/4\lambda k_{\rm B}T)$$
(4)

and λ is the reorganization energy of electron transfer.^[18] Equations (3) and (4) are derived Equations (5) and (6):

$$k_{\rm et} = \frac{k_{\rm diff} Z \exp\left(-\frac{\Delta G_{\rm et} + \lambda)^2}{4\lambda k_{\rm B} T}\right)}{k_{\rm -diff} + Z \exp\left(-\frac{(\Delta G_{\rm et} + \lambda)^2}{4\lambda k_{\rm B} T}\right)}$$
(5)

$$\frac{1}{k_{\rm et}} = \frac{1}{k_{\rm diff}} + \frac{1}{Z \exp[-(\lambda/4)(1 + \Delta G_{\rm et}/\lambda)^2/k_{\rm B}T]}$$
(6)

where $Z [=(k_{\rm B}T/h) (k_{\rm diff}/k_{\rm -diff})]$ is the collision frequency which is taken as $1 \times 10^{11} \,\mathrm{m^{-1} \, s^{-1} \, l^{[18]}}$ The $k_{\rm diff}$ value in PhCN is taken as $5.6 \times 10^9 \,\mathrm{m^{-1} \, s^{-1} \, l^{[34]}}$

The driving-force dependence of $log k_{et}$ is shown in Figure 2. The $k_{\rm et}$ values increase with increasing the ET driving force to reach the k_{diff} value. This region is well reproduced using Equation (6) as indicated by the solid curve in Figure 2, where the λ value is taken as 0.59 eV in PhCN, which is the smallest value for intermolecular photoinduced ET reactions ever reported in such a polar solvent (for example, 0.66 eV for $C_{60}\!/C_{60}\!\stackrel{-}{-}$ in PhCN^{[24]} and 0.88 eV for 9-(AcrPh⁺)/AcrPh[•] phenyl-10-methylacridinium ion in MeCN).^[34] The calculated dependence of $k_{\rm et}$ on $-\Delta G_{\rm et}$ using Equation (6) predicts a decrease in the k_{et} value from a diffusion-limited value with increasing the driving force of electron transfer ($-\Delta G_{et} > 1.0 \text{ eV}$), provided that the λ value is constant (0.59 eV). However, the observed k_{et} values remains diffusion-limited up to $-\Delta G_{\rm et} = 1.74$ eV. The absence of a Marcus inverted region has well been recognized in forward photoinduced electron-transfer reactions as mentioned in Introduction.^[19,20] The reason is discussed in the next section.

Intermolecular charge recombination: In contrast to the case of photoinduced ET reactions of MeFl, the existence of the Marcus inverted region is clearly shown in the BET reactions (see below). A transient absorption spectrum observed at 48 µs after the laser pulse excitation of a PhCN solution of MeFl with *N*,*N*-dimethylaniline (DMA) is shown in Figure 3a. The observed transient absorption at 370 nm is assigned to



Figure 2. Driving force dependence of $\log k_{\rm et}$ for intermolecular photoinduced ET from electron donors to ¹MeFI* ($-\Delta G_{\rm et}(S)$: \odot and \bullet) and ³MeFI* ($-\Delta G_{\rm et}(T)$: \blacktriangle), and $\log k_{\rm bet}$ for intermolecular back ET ($-\Delta G_{\rm bet}$: \bullet) in PhCN at 298 K. \odot : represents highly exergonic ET reactions directly to ground-state products (radical cations of electron donors and MeFI⁻); \bullet : represents the much less exergonic ET reactions to produce the excited states of radical cations of electron donors and MeFI⁻. The solid and broken lines represent best fit to Eq. (6) with $\lambda = 0.59$ and 0.68 eV, respectively. Numbers refer to the electron donors in Table 1 and Table 2.



Scheme 1.

MeFl^{--[35]} being overlapped with that due to DMA⁺⁺.^[36] The observed absorption band at 620 nm is diagnostic of DMA⁺⁺, as indicated by the reference spectrum of DMA⁺⁺ (see Supporting Information S5). The decay time profile of absorb-

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ance (Figure 3b) obeys second-order kinetics as indicated by the second-order plot (see inset of Figure 3b), which afford the same slope at different laser powers (13 and 9 mJ per pulse) in PhCN at 298 K. The rate constant of intermolecular BET (k_{bet}) from MeFI⁻ to DMA⁺⁺ is determined from the slope and the inset of Figure 3b to be $3.5 \times 10^6 \,\mathrm{m^{-1} s^{-1}}$. This k_{bet} value is 1700 times smaller than the k_{diff} value in PhCN. Similarly, the other k_{bet} values are determined from the second-order decay plots by using the molar absorption coefficients of the radical cations of aromatic electron-donor compounds, which are determined by the one-electron oxidation with $[Fe(bpy)_3]^{3+}$ as an oxidant (see Supporting Information S6–S12). The k_{bet} values are listed in Table 2 with the values of the BET driving force $(-\Delta G_{bet})$.



Figure 3. a) Transient absorption spectrum of MeFl $(6.0 \times 10^{-5} \text{ M})$ in the presence of DMA $(1.0 \times 10^{-2} \text{ M})$ in deaerated PhCN at 298 K taken at 48 µs after nanosecond laser excitation at 440 nm. b) Time profiles at 620 nm obtained at 13 (•) and 9 ($_{\odot}$) mJ per pulse in the 40 ms range. Inset: Second-order plots.

The driving-force dependence of $\log k_{bet}$ is shown in Figure 2, which reveals a clear parabolic dependence including the Marcus inverted region, that is, a decrease in the k_{bet} value with increasing the BET driving force. This is the first definitive confirmation of the existence of the Marcus inverted region in a truly intermolecular BET reactions. The data in Figure 2 are well fitted by the Marcus equation for

intermolecular BET reactions [Eq. (6)] to afford the reorganization energy of BET ($\lambda = 0.68 \text{ eV}$) in PhCN. The λ value of the BET reactions is larger than the λ value (0.59 eV) of the photoinduced ET reactions in the Marcus normal region. The solvent reorganization energy of BET (λ_s) is expected to increase with an increase in the distance (R_{DA}) between D and A as given by Equation (7), where *e* is the electric charge, ε_0 is the dielectric constant in a vacuum, r_D and r_A are the ionic radii of D and A, and ε_{op} and ε_s are the optical and static dielectric constants of the solvent, respectively.^[18a,20c] Equation (7) suggests that BET reactions occur at the longer distance from MeFI⁻ to D⁺⁺ as compared with the photoinduced ET reactions in the Marcus normal region.

$$\lambda_{\rm S} = \frac{e^2}{4\pi\varepsilon_0} \left(\frac{1}{2r_{\rm D}} + \frac{1}{2r_{\rm A}} - \frac{1}{R_{\rm DA}}\right) \left(\frac{1}{\varepsilon_{\rm op}} - \frac{1}{\varepsilon_{\rm s}}\right) \tag{7}$$

The small difference in the λ values between the two cases cannot account for the absence of the Marcus inverted region for photoinduced ET in Figure 2. However, it should be noted that there is a fundamental difference between the two types of ET, that is, photoinduced ET produces radical ions, whereas BET does not produce radical anions. It is well known that radical ions particularly for those of delocalized π radical ions have much lower lying excited states compared with the corresponding neutral comas pounds.^[37-40] Invoking the formation of excited-state products has frequently been suggested to explain the absence of the Marcus inverted region as pointed out by Gray and coworkers.^[41,42] Thus, it is likely that photoinduced ET from D (14-17) to MeFl with large ET driving forces results in formation of the doublet excited state of D'+*. In such a case, the actual ET driving force is not in the Marcus inverted region to afford the diffusion-limited ET rate. The driving force $[-\Delta G_{et}(S)]$ of photoinduced ET from D (14-17) to MeFl to produce D⁺⁺ and MeFl⁻ is obtained by subtracting the energy of the low-lying excited state of $D^{\cdot+}$ (²E*),^[31] as given by Equation (8).

$$-\Delta G_{\rm et}(\mathbf{S}) = {}^{1}E^{*} - e \ (E_{\rm ox} - E_{\rm red}) - {}^{2}E^{*}$$
(8)

The first low-lying excited state of PTZ and TMPD radical cations were reported by photoelectron spectra (PES) as to be 1.09 and 1.52 eV, respectively.^[31] Absorption bands at NIR of BEDT-TTF and TMBZ are shown at Table 2 as to be 1.24 and 1.15 eV, respectively. Only the vertical ${}^{2}E^{*}$ values are available because of the lack of the fluorescence data of D⁺⁺.^[37] In such a case, the actual deriving forces of photoinduced ET from D (14–17) to MeFl to produce D^{++*} and MeFl⁻⁻ are larger than the estimated value using the vertical ${}^{2}E^{*}$ values. By taking this into account, the k_{et} values of photoinduced ET from D (14–17: closed circles) to 1 MeFl^{*} producing the excited state (D^{*} and MeFl⁻⁻ agree reasonably well with the Marcus curve (broken line in Figure 2) is satisfactory. In contrast to photoinduced ET in Figure 2, BET is not intercepted by the excited states of

BET products because of the higher energies than the BET driving force to the ground state, exhibiting the Marcus inverted region in Figure 2 (broken line).

The Marcus inverted region for intermolecular BET is further confirmed by the temperature dependence of k_{bet} as shown in Figure 4. The temperature dependence of k_{bet} is analyzed using Equation (9):



Figure 4. Plot of $\ln[\{k_{diff}k_{bel}/(k_{diff} - k_{bel})\}T^{-1}]$ versus T^{-1} for the intermolecular BET from MeFI⁻ to D⁺ (DMA⁺⁺ (\bullet), PTZ⁺⁺ (\circ), BEDT-TTF⁺⁺ (\bullet), and TMBZ⁺⁺ (\Box) in deaerated PhCN determined by nanosecond laser flash photolysis measurements.

$$\ln\left[\left(\frac{k_{\text{diff}}k_{\text{bet}}}{k_{\text{diff}}-k_{\text{bet}}}\right)\frac{1}{T}\right] = \ln\left(\frac{k_{\text{B}}}{h}\right) + \frac{\Delta S}{k_{\text{B}}} - \frac{\Delta H_{\text{obs}}^*}{k_{\text{B}}T}$$
(9)

which is derived from Equation (6). The observed ΔH^{\pm}_{obs} corresponds to the sum of the heat of formation of the complex (D⁺⁺ MeFl⁻⁻) in Scheme 1 (ln $K = (\Delta H - T\Delta S)/(k_{\rm B}T)$; $K = k_{\rm diff}/k_{-\rm diff}$) and the activation enthalpy of BET ($\Delta H^{\pm}_{\rm bet}$) as given by Equation (10).

$$\Delta H_{\rm obs}^{\pm} = \Delta H + \Delta H_{\rm bet}^{\pm} \tag{10}$$

The temperature dependence of k_{diff} is evaluated using Stokes–Einstein–Smoluchowski equation [Eq. (11)],

$$k_{\rm diff} = 8k_{\rm B}N_{\rm A}T/(3\eta) \tag{11}$$

where $N_{\rm A}$ is Avogadro constant and η is viscosity of PhCN which is taken as 1.17 mPas at 298 K.^[43,44] Plots of ln[{ $k_{\rm diff}k_{\rm bet}/(k_{\rm diff}-k_{\rm bet})$ } T^{-1}] and T^{-1} give good linear correlations as shown in Figure 4 in agreement with Equation (9). The $\Delta H^{+}_{\rm obs}$ values are determined from the slopes of the linear correlations in Figure 4 and the resulting values are listed in Table 3 together with the calculated ΔH^{+} values based on the Marcus equation, $\Delta G^{+}_{\rm bet} = (\lambda + \Delta G_{\rm bet})^{2}/4\lambda$, assuming that $\Delta H^{+}_{\rm bet} = \Delta G^{+}_{\rm bet}$. The $\Delta H^{+}_{\rm obs}$ values increases with increasing the BET driving force in accordance with the Marcus inverted region. The ΔH values are evaluated using Equation (10). The evaluated ΔH values are in the Table 3. Observed activation enthalpies (ΔH^{+}_{obs}) , heats of formation of CS complexes (ΔH) , activation enthalpies of BET in CS complexes (ΔH^{+}) .

Entry	Electron donor	$\Delta H^{\pm}_{ m obs}$ [kcal mol ⁻¹]	$\Delta H^{[a]}$ [kcalmol ⁻¹]	$\Delta H^{\pm[b]}$ [kcal mol ⁻¹]
13	DMA	2.63	3.21	5.84
14	PTZ	2.58	1.00	3.58
15	BEDT-TTF	1.90	0.67	2.57
16	TMBZ	0.63	0.87	1.50
[a] Dete	armined from AF	$I^{\dagger} = \Lambda H$	ΛH^{\ddagger} [b] Dete	rmined from

[a] Determined from $\Delta H^{-}_{obs} = \Delta H^{+} + \Delta H^{-}$. [b] Determined from $\Delta H^{+}_{bet} = \Delta G^{+}_{bet} = (\lambda + \Delta G_{bet})^2 / 4 \lambda$.

range of reported values of radical ion pair (ca. 2 kcal mol^{-1}).^[45,46]

A donor-substituted flavin affording the long-lived chargeseparated state: The result of Marcus inverted region in an intermolecular BET reveals that the smallest k_{bet} is obtained for electron transfer from MeFl⁻ to DMA⁺⁺. Thus, we synthesized a donor-acceptor linked dyad composed of DMA and a flavin analogue (10-[4'-(N,N-dimethylamino)phenyl]isoalloxazine: DMA-Fl) to achieve a long-lived charge-separated (CS) state. The synthesis of DMA-Fl was carried out according to the literature.^[47-49] The structure of DMA-Fl, which is optimized by DFT calculation with Gaussian 03 at B3LYP/6-31G(d) level (see Experimental Section), is shown in Supporting Information S13a. The dihedral angle made by aromatic ring planes was found to be approximately perpendicular (89.8°). The HOMO (the highest occupied molecular orbital) and LUMO (the lowest unoccupied molecular orbital) of DMA-Fl are localized on the DMA and the Fl moieties, as shown in Supporting Information S13b and 13c, respectively. This indicates that there is no π -conjugation between D and A moieties (see Supporting Information S1). Indeed, the absorption and fluorescence spectra of DMA-Fl are super-positions of the spectra of each component, that is, DMA and unlinked reference compounds (MeFl).

The singlet excited state energy of the Fl moiety (DMA–¹Fl*) is determined as 2.55 eV from the absorption $(\lambda_{max} = 440 \text{ nm})$ and fluorescence $(\lambda_{max} = 540 \text{ nm})$ spectra (see Supporting Information S1). The one-electron oxidation and reduction potentials of DMA–Fl in PhCN were determined by cyclic voltammetry (CV) to be 0.94 and -0.83 V versus SCE, respectively (see Supporting Information S14). The reversible CV waves were observed for the one-electron oxidation and reduction of the Fl moiety at fast scan (50 V s⁻¹) and low scan rate (0.1 V s⁻¹), respectively.

The energy of the CS state of DMA–Fl is determined from the difference in the one-electron oxidation and reduction potentials of DMA–Fl to be 1.77 eV, which is significantly lower than those of DMA–¹Fl* and DMA–³Fl*. Thus, photoinduced ET from the DMA moiety to both the singlet and triplet excited states of the Fl moiety is energetically feasible. The fluorescence intensity of DMA–Fl was too small to determine the quantum yield ($\Phi_{\rm fl}$), which is much smaller than the fluorescence from the MeFl reference ($\Phi_{\rm fl}$ =0.24; see Supporting Information S15).^[50]

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Time-resolved transient absorption spectra of DMA-Fl were measured by femtosecond laser photolysis in PhCN. The transient absorption spectra observed at 11 and 300 ps after the laser pulse excitation of a PhCN solution of DMA-Fl are shown in Figure 5a. The transient absorption band at 520 nm is assigned to the singlet excited state of the Fl moiety (DMA-¹Fl*) by comparison with that of ¹MeFl* (see Supporting Information S16). The transient absorption band of DMA-1Fl* disappears, accompanied by the appearance of a new band at 520 and 680 nm, which is ascribed to the CS state (DMA⁺-Fl⁻)^[51] by comparison with UV-visible spectra of DMA-Fl⁻ and DMA⁺-Fl (see Supporting Information S17 and S18),^[52] produced by the ET oxidation of DMA-Fl with $[Ru(bpy)_3]^{3+}$ and reduction with NA⁻⁻, respectively. The bleaching band at 470 nm is due to the DMA-Fl (see Supporting Information S17). Thus, the most of the absorption of DMA⁺-Fl at around visible region was bleached by the DMA-Fl. According to the transient spectrum in Figure 5a, the absorbance due to DMA⁺-Fl is obviously smaller than that due to DMA-1Fl* because of the small molar absorption coefficient of DMA+-Fl.[53] Photoinduced ET from the DMA moiety to the singlet excited state of the Fl moiety (1Fl*) occurs to produce the CS state, DMA⁺-Fl⁻, in competition with the intersystem crossing (ISC) to ${}^{3}Fl^{*}$. The rate constant of ET (k_{ET}) is determined as $1.2 \times 10^{10} \, \text{s}^{-1}$ by single exponential fitting for the rise and decay at 450 and 520 nm, respectively.

The charge-recombination process from Fl⁻⁻ to DMA⁺⁺ in the dyad was confirmed by nanosecond laser flash photolysis. Figure 6a shows the transient absorption spectrum in a PhCN solution containing Fl⁻⁻ and DMA⁺⁺ observed upon laser excitation at 440 nm. The transient absorption bands at 370 and 680 nm taken at 30 µs after laser excitation are assigned to Fl⁻⁻ and DMA⁺⁺, respectively. The bleaching band at 470 nm in Figure 6a is ascribed to the DMA-FI⁻⁻ and consistent with Figure 5 a. The decay time profile at 680 nm due to the CS state is shown in Figure 6b. The first-order decay was confirmed by single-exponential fitting for different laser power (30 and 10 mJ per pulse). The decay rate constants were determined as $4.7 \times 10^2 \, \text{s}^{-1}$ from the slope of the first-order plots for both of different laser power. The lifetime of CS state is determined as 2.1 ms in PhCN at 298 K. The quantum yield of CS state is determined by using the comparative method^[53,54] to be 31%. According to the comparison between $k_{\rm IC}$ and $k_{\rm ET}$, the rest of CS state could be considered as lost in internal conversion. The energy diagram of intramolecular photoinduced ET and BET in the dyad is summarized in Figure 7.

Temperature dependence of the CS lifetime of DMA⁺**–FI**⁻: The k_{BET} value of the CS state of DMA–Fl in PhCN exhibited significant temperature dependence: $4.7 \times 10^2 - 8.7 \times 10^3 \text{ s}^{-1}$ between 298–363 K (Figure 8). Such large temperature dependence of k_{BET} is predicted by the Marcus equation [Eq. (12)] for nonadiabatic electron transfer.^[18] Equation (13) is written by Equation (12):



Figure 5. a) Transient absorption spectra of DMA–Fl $(3.0 \times 10^{-4} \text{ M})$ in deaerated PhCN at 298 K taken 11 ps (•) and 300 ps (\odot) after femtosecond laser excitation at 440 nm. b) The decay and rise profiles at 450 nm (•) and 520 nm (\odot).

$$k_{\rm BET} = (\frac{4\pi^3}{h^2 \lambda k_{\rm B} T})^{1/2} V^2 \exp[-\frac{(\Delta G_{\rm BET} + \lambda)^2}{4\lambda k_{\rm B} T}]$$
(12)

$$\ln(k_{\rm BET}T^{1/2}) = \ln(\frac{2\pi^{3/2}V^2}{h(\lambda k_{\rm B})^{1/2}}) - \frac{(\Delta G_{\rm BET} + \lambda)^2}{4\lambda k_{\rm B}T}$$
(13)

which predicts a linear correlation between ln $(k_{\text{BET}}T^{1/2})$ and T^{-1} . The plot of $\ln(k_{\text{BET}}T^{1/2})$ versus T^{-1} for the intramolecular BET in DMA⁺⁺-Fl⁻⁻ in the temperature range from 298 to 363 K gives a linear correlation as shown in Figure 8. The activation enthalpy for the intramolecular BET was determined as $9.7(\pm 0.2)$ kcalmol⁻¹ from the slope of Figure 8. According to the line slope, the values of λ and V are determined to be $0.69(\pm 0.01)$ eV and $V=4.5(\pm 0.7)$ cm⁻¹,^[55] respectively.

The clear observation of the Marcus inverted region that exhibits significant temperature dependence in accordance with the Marcus theory of electron transfer [Eq. (12)] in this study is contrasted to some previous reports on no temperature dependence of intramolecular ET rate constants with the large ET driving force.^[56-58] On the other hand, there are a number of reports on temperature dependence of intramolecular ET in accordance with the Marcus inverted region including our results in Figure 8.^[16,17,59,60] It should be noted that there are two types of ET, one is charge-separation and

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Figure 6. a) Transient absorption spectrum of DMA–Fl $(6.0 \times 10^{-5} \text{ M})$ in deaerated PhCN at 298 K taken at 30 µs after nanosecond laser excitation at 440 nm. b) Decay time profile at 680 nm with different laser powers (30 (\bullet) and 10 (\odot) mJ per pulse) Inset: First-order plots.



Figure 7. Intramolecular photoinduced ET and BET in the dyad.

charge-shift types of ET, which produces radical ions, and the other is charge-recombination type ET, which does not produce radical ions. No temperature dependence of ET rate constants was reported for the former type of ET, whereas temperature dependence of ET in accordance with the Marcus inverted region was reported for the latter type of ET. As discussed in the intermolecular photoinduced ET versus the intermolecular BET (see above), the lack of temperature dependence of the intramolecular charge-separation and charge-shift types of ET reactions with large ET driving forces may be well interpreted by ET to produce the low lying excited states of product radial ions, when the ET driving force would never be in the Marcus inverted region.

The driving force dependence of $\log k_{\text{ET}}$ and k_{BET} is shown in Supporting Information S19, where the bell-shaped curve



Figure 8. Plot of ln $(k_{BET}T^{1/2})$ versus T^{-1} for the *intra*molecular BET in DMA–Fl $(6.0 \times 10^{-5} \text{M})$ in deaerated PhCN determined by laser flash photolysis measurements.

is obtained for the photoinduced ET processes.^[18] To quantify the driving force dependence of $\log k_{\rm ET}$, the Marcus semiclassical formulation [Eq. (12)] is employed.^[18] The best fit of Equation (12) (the solid line in Supporting Information S19) provides the values of $\lambda = 0.68(\pm 0.01)$ eV and V = $6.2(\pm 1.2)$ cm⁻¹. These values are well accorded with above values derived from the temperature dependence. Such a small λ value is the key factor to attain the long-lived CS state. According to the Marcus theory of electron transfer,^[18] the λ value of electron transfer from D to A is the average of the λ values of electron self-exchange of D⁺/D and A/ A⁺⁻. The small λ value of photoinduced ET and BET of DMA–Fl may result from the small λ value for electron selfexchange of DMA–Fl/DMA–Fl⁺⁻. This is confirmed in the next section.

Electron self-exchange between DMA–Fl and DMA–Fl⁻: A reversible CV wave was observed for the one-electron reduction of the Fl moiety of DMA–Fl in deaerated PhCN. Thus, the one-electron reduced species of DMA–Fl (DMA–Fl⁻) is stable in deaerated PhCN. DMA–Fl⁻ was produced by the photoinduced ET reduction of DMA–Fl with dimeric 1-benzyl-1,4-dihydronicotinamide (BNA)₂^[35] in PhCN as shown in Equation (14).



The ESR spectrum of DMA–Fl⁻ with the hyperfine coupling structure is shown in Supporting Information S20). The hyperfine coupling constant and the maximum slope line width (ΔH_{msl}) were determined from a computer simulation of the ESR spectra (see Supporting Information S20). The spin distribution of unpaired electrons was mainly localized on the Fl moiety. The ΔH_{msl} value thus determined increases linearly with an increase in the concentration of DMA–Fl (Figure 9). The rate constants of the ET self-ex-



Figure 9. Plot of ΔH_{msl} of DMA–Fl⁻ versus concentration of DMA–Fl.

change reaction (k_{ex}) were determined using Equation (15):

$$k_{\rm ex} = \frac{1.57 \times 10^7 (\Delta H_{\rm msl} - \Delta H_{\rm msl}^0)}{(1 - P_{\rm i})[{\rm DMA} - {\rm Fl}]}$$
(15)

where $\Delta H_{\rm msl}^0$ (in Gauss) is the $\Delta H_{\rm msl}$ of the ESR spectrum in the absence of unreduced DMA–Fl and P_i is a statistical factor, which can be taken as nearly zero.^[61] The $k_{\rm ex}$ value is determined from the slope of the linear correlation between $\Delta H_{\rm msl}$ and [DMA–Fl] to be $3.2 \times 10^9 \,{\rm m}^{-1} {\rm s}^{-1}$ within experimental error $\pm 5 \,\%$. The $\lambda_{\rm ex}$ value of the ET exchange reaction is determined from the $k_{\rm ex}$ values using Equation (16) to be 0.26 eV:

$$[(k_{\rm ex})^{-1} - (k_{\rm diff})^{-1}] = Z^{-1} \exp(\lambda/4k_{\rm B}T)$$
(16)

which is significantly smaller than the λ value of photoinduced ET and BET of DMA–Fl. Thus, the small λ value mainly results from the extremely small λ_{ex} value of the flavin moiety. The small λ_{ex} value may be ascribed to the cancellation of solvent reorganization energy of the polarized flavin molecule before and after the electron transfer.

Intermolecular electron-transfer reactions with the CS State of DMA-FI: The CS state of DMA-FI should have both the oxidizing and reducing ability, because the DMA⁺⁺ and FI⁻⁻ moieties can act as a strong electron acceptor and an electron donor, respectively. This is confirmed by examining the intermolecular ET reduction and oxidation of appropriate aromatic compounds by the Fl⁻ moiety and the DMA⁺⁺ moiety, respectively. Since the one-electron oxidation potential of the Fl⁻ moiety (E_{ox} =-0.83 V vs. SCE) is more negative than that of the one-electron reduction potential of *p*dinitrobenzene (*p*-C₆H₄(NO₂)₂) (E_{red} =-0.71 V vs. SCE), ET from the Fl⁻ moiety to the *p*-C₆H₄(NO₂)₂ is energetically feasible. Thus, nanosecond laser excitation of a deaerated PhCN solution of DMA-Fl containing *p*-C₆H₄(NO₂)₂ at 440 nm results in formation of *p*-C₆H₄(NO₂)₂ radical anion (*p*-C₆H₄(NO₂)₂^{--)[⁶²] at 920 nm shown in Figure 10a. Accord-}



Figure 10. a) Transient absorption spectra of DMA–FI $(4.7 \times 10^{-5} \text{ M})$ in deaerated PhCN containing *p*-dinitrobenzene $(p-C_6H_4(\text{NO}_2)_2)$ $(1.0 \times 10^{-4} \text{ M})$ taken at 10 µs after laser excitation at 440 nm at 298 K, showing formation of $p-C_6H_4(\text{NO}_2)_2$ ($E_{red} = -0.71 \text{ V}$ vs. SCE; $\lambda_{max} = 920 \text{ nm}$): the transient absorption due to DMA⁺⁺–FI ($\lambda_{max} = 370 \text{ nm}$) remains the same. b) Rise time profiles at 920 nm of DMA–FI ($4.7 \times 10^{-5} \text{ M}$) in deaerated PhCN containing various concentration of $p-C_6H_4(\text{NO}_2)_2$ ($2.0 \times 10^{-6}-1.0 \times 10^{-4} \text{ M}$). Inset: Plot of the pseudo-first-order rate constant versus [$p-C_6H_4$ -($\text{NO}_2)_2$].

ing to the time profiles at 920 nm, the rate of rise in absorbance obeys pseudo-first-order kinetics. The observed pseudo-first-order rate constant (k_{obs}) increases linearly with increasing concentration of $p-C_6H_4(NO_2)_2$. The rate constant (k_{et}) of ET from DMA⁺-Fl⁻ to $p-C_6H_4(NO_2)_2$ is determined from the slope of a linear plot of k_{obs} versus concentration of $p-C_6H_4(NO_2)_2$ (Figure 10b) to be $4.9 \times 10^9 \text{ m}^{-1} \text{ s}^{-1}$. This value is close to the diffusion rate constant in PhCN

$(k_{\text{diff}}=5.6\times10^9 \,\text{M}^{-1} \,\text{s}^{-1}).^{[34]}$ The transient absorption spectrum of the radical cation of bis(ethylenedithiol)tetrathiafulvalene (BEDT-TTF) ($E_{\text{ox}}=0.40 \,\text{V}$ vs. SCE; $\lambda_{\text{max}}=1000 \,\text{nm}$) is also observed by the one-electron oxidation of BEDT-TTF with the DMA⁺⁺ moiety of DMA⁺⁺-Fl⁻⁻ in PhCN (see Supporting Information S21), when ET is thermodynamically feasible. In contrast, no ET from the Fl⁻⁻ moiety to nitrobenzene ($E_{\text{red}}=-1.17 \,\text{V}$) occurred, when the laser excitation of DMA-Fl with nitrobenzene results in the same transient absorption spectra as the CS state of DMA-Fl (see Supporting Information S22). Similarly, the one-electron reduction was not observed from DMA⁺⁺ moiety to 1,4-dimethoxybenzene ($E_{\text{ox}}=1.21 \,\text{V}$) (see Supporting Information S23). Thus, the Fl⁻⁻ and DMA⁺⁺ moieties of the CS state act as a strong reductant and an oxidant, respectively.

Conclusion

We have discovered that the rate constants of intermolecular back electron-transfer (BET) reactions from the radical anion of a flavin analogue (MeFl⁻) to the radical cations of electron donors (D'+) following intermolecular photoinduced electron transfer (ET) from D to MeFl decrease remarkably with increasing the driving force of BET. Among examined electron donors N,N-dimethylaniline (DMA), which afforded the slowest rate of BET, was selected to be linked at the 10-position of flavin to synthesize N,N-dimethylaniline-flavin (DMA-Fl). DMA-Fl undergoes efficient intramolecular photoinduced ET to afford the charge-separated (CS) state that has the longest CS state lifetime (2.1 ms) ever reported for electron donor-acceptor linked molecules by preventing the intermolecular charge recombination in solution at 298 K. Such a long CS lifetime results from an extremely small reorganization energy for electron self-exchange between DMA-Fl/DMA-Fl⁻⁻ (0.26 eV),which was determined by the ESR line width alternation. The long-lived CS state acts as both a strong electron donor and an acceptor, not only reducing electron acceptors with $E_{\rm red}$ < -0.83 V versus SCE but also oxidizing electron donors with $E_{\rm ox} < 0.94$ V versus SCE.

Experimental Section

General procedures: ¹H NMR spectra were measured on a JEOL JNM-AL300 using tetramethylsilane as an internal standard. Fast atom bombardment (FAB) mass spectra were obtained on a JEOL EX-270. Matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF) mass spectra were measured on a Kratos Compace MALDI I (Shimazu). Steady-state absorption spectra were measured on a Shimadzu UV3100 spectrometer. Fluorescence and phosphorescence spectra were taken using a Shimadzu RF5300PC fluorospectrophotometer.

Materials: All commercially available solvents and chemicals were of reagent grade quality and used without further purification unless otherwise noted. Tetra-*n*-butylammonium perchlorate (TBAP) used as a supporting electrolyte for electrochemical measurements was purchased from Tokyo Chemical Industry Co., Ltd. and recrystallized from EtOH/ water, and dried in vacuo according to the standard procedure.^[63] 10-

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Methylisoalloxazine (MeFl) was purchased from Aurora Fine Chemicals, Ltd. and used without further purification. Benzonitrile and butyronitrile were distilled from P_2O_5 in vacuo.^[63] Tris(2,2'-bipyridine)iron(III) hexafluorophosphate [Fe(bpy)₃](PF₆)₃, was prepared from a reaction between iron(II) sulfate heptahydrate and 2,2'-bipyridine followed by oxidation of the resulting iron(II) complex by ceric sulfate in aqueous H₂SO₄.^[64] Tris(2,2'-bipyridine)ruthenium(III) hexafluorophosphate [Ru(bpy)₃(PF₆)₃] was prepared by oxidizing Ru(bpy)₃²⁺ with lead dioxide in aqueous H₂SO₄ followed by the addition of KPF₆.^[65] Thin-layer chromatography (TLC) and column chromatography were performed with silicagel 60 F₂₅₄ (Merck) and silica gel 60, respectively.

Synthesis of DMA-Fl

4'-(N,N-Dimethylamino)-2-nitrodiphenylamine (1): A mixture of 2-chloronitrobenzene (8.1 g, 52 mmol), the *N,N*-dimethyl-*p*-phenylenediamine (7.0 g, 52 mmol) and DBU (7.88 g, 52 mmol) were heated at 140 °C for 10 h. The reaction mixture was allowed to cool to room temperature and partitioned between dichloromethane and water. The organic layer was dried over anhydrous sodium sulfate and the residue was purified via silica gel column chromatography with chloroform/hexane 2:1 as an eluent (R_f =0.4) to afford dark red color solid (2.3 g, 8.8 mmol, 17%). ¹H NMR (300 MHz, CD₃CN): δ =9.27 (s, 1H), 8.13 (d, 1H, *J*=9.0 Hz), 7.37 (t, 1H, *J*=7.7 Hz), 7.14 (d, 2H, *J*=8.7 Hz), 6.95 (d, 1H, *J*=8.4 Hz), 6.80 (d, 1H, *J*=8.7 Hz), 6.71 (t, 3H, *J*=8.0 Hz), 2.90 ppm (s, 6H); elemental analysis calcd (%) for C₁₄H₁₅N₃O₂ + 1/5 H₂O: C 64.45, H 5.95, N 16.11; found: C 64.52, H 5.79, N 16.00; MS (FAB): *m/z*: 257.2 [*M*]⁺.

4'-(N,N-Dimethylamino)-2-diphenyldiamine (2): A propanol solution (100 mL) of **1** (2.3 g, 8.8 mmol) was added to a well stirred refluxing aqueous solution (200 mL) containing ammonium chloride (1.5 g, 27 mmol) and reduced iron (1.5 g), and the reflux maintained for 3 h. The hot solution was filtered through celite and the residue was washed well with chloroform. The filtrate was extracted with chloroform and the combined extracts were washed with water, dried (MgSO₄), and evaporated. The brown oil was distilled to afford 4'-(N,N-dimethylamino)-2-nitrodiphenylamine (1.9 g, 8.5 mmol, 96 %). ¹H NMR (300 MHz, CD₃CN): δ =7.09 (s, 1H), 6.93 (d, 1H, J=7.8 Hz), 6.84 (t, 1H, J=7.5 Hz), 6.65–6.74 (m, 6H), 4.95 (s, 1H, NH), 3.55 (s, 1H, NH₂), 2.81 ppm (s, 6H).

10-[4'-(N,N-Dimethylamino)phenyl]-isoalloxazine (DMA-FI): Alloxane tetrahydrate (1.8 g, 8.5 mmol) and boric acid (0.56 g, 9.0 mmol) were added to an acetic acid solution (75 mL) of **2** (1.9 g, 8.5 mmol) and the mixture was heated at 60 °C for 1 h under a nitrogen atmosphere. After evaporation to dryness the residue was washed with a small volume of water and ether and recrystallized from MeOH to give **DMA-FI** (0.63 g, 22%). ¹H NMR (300 MHz, [D₆]DMSO): δ =11.37 (s, 1H, NH), 8.16 (d, 1H, J=8.4 Hz), 7.75 (t, 1H, J=7.2 Hz), 7.60 (t, 1H, J=7.2 Hz), 7.18 (d, 2H, J=9.0 Hz), 6.92 (d, d, 3H, J=12.0 Hz, 11.4 Hz), 3.02 ppm (s, 6H, NMe_2); HRMS (FAB⁺): *m*/z: calcd for: 333.1226; found: 333.1233 [*M*]⁺; elemental analysis calcd (%) for C₁₈H₁₅N₅O₂·0.17 H₂O: C 64.28, H 4.59, N 20.82; found: C 64.55, H 4.47, N 20.60.

Laser flash photolysis: For nanosecond laser flash photolysis experiments, deaerated PhCN solutions of DMA-Fl or MeFl and electron donors were excited by a Panther OPO pumped by Nd/YAG laser (Continuum, SLII-10, 4–6 ns fwhm) at λ = 440 nm. The photodynamics was monitored by continuous exposure to a xenon lamp (150 W) as a probe light and a photomultiplier tube (Hamamatsu 2949) as a detector. The transient absorption spectra were recorded using fresh solutions in each laser excitation. The solution was deoxygenated by argon purging for 15 min prior to measurements. The experiments at various temperatures were performed using a Unisoku thermostated cell holder. Femtosecond transient absorption spectroscopy experiments were conducted using an ultrafast source: Integra-C (Quantronix Corp.), an optical parametric amplifier: TOPAS (Light Conversion Ltd.) and a commercially available optical detection system: Helios provided by Ultrafast Systems LLC. The instrumental details are described in Supporting Information S24.

Fluorescence lifetime measurements: Fluorescence decays were measured by a Photon Technology International GL-3300 with a Photon Technology International GL-302 and a nitrogen laser/pumped dye laser system equipped with a four-channel digital delay/pulse generator (Standard Research System Inc. DG535) and a motor driver (Photon Technol-

ogy International MD-5020). The excitation wavelength was 440 nm with use of 1,4-bis(4-methyl-5-phenyl-2-oxazolyl)benzene (Dojindo Molecular Technologies, Inc.).

Fluorescence and phosphorescence measurements: Fluorescence and phosphorescence spectral measurements of MeFl were performed on a Shimadzu RF-5300PC fluorescence spectrophotometer. Fluorescence quenching experiments of MeFl by electron donors carried out as follows. The solutions were deoxygenated by argon purging for 15 min prior to the measurements. Typically, the relative emission intensities were measured for PhCN solution containing MeFl $(1.3 \times 10^{-5} \text{ M})$ with electron donors at various concentrations $(4.0 \times 10^{-4} - 5.0 \times 10^{-2} \text{ M})$. There was no change in the shape but there was a change in the intensity of the fluorescence spectrum by the addition of an electron donor. The Stern–Volmer relationship [Eq. (17)] was obtained for the ratio of the emission intensities in the absence and presence of electron donors (I_0/I) and concentrations of electron donors [D]. The observed quenching rate constants of photoinduced ET [k_{et} ($=K_{sv}\tau_0^{-1}$)] were obtained from the Stern–Volmer constants K_{sv} and the emission lifetime τ_0 .

$$I_0/I = 1 + K_{\rm sv} [D]$$
 (17)

Stopped-flow measurements: The transient absorption spectra of the radical cation of *N*,*N*-dimethylaniline (DMA) was measured in the electrontransfer oxidation of *N*,*N*-dimethylaniline with $[Ru(bpy)_3]^{3+}$ (bpy=2,2'bipyridine) using a UNISOKU RSP-601 stopped-flow rapid scan spectrophotometer equipped with the MOS-type high sensitive photodiode array under deaerated conditions. Gate time for the measurement was set at 2 ms. Typically, deaerated MeCN solutions of $[Ru(bpy)_3]^{3+}$ and DMA were transferred to a spectrophotometric cell by means of a glass syringe that had earlier been purged with a stream of argon.

Electrochemical measurements: Measurements of cyclic voltammetry (CV) were performed at 298 K using a BAS 630B electrochemical analyzer in a deaerated solvent containing 0.10 M TBAP as a supporting electrolyte at 298 K. A conventional three-electrode cell was used with a platinum working electrode and a platinum wire as a counter electrode. The measured potentials were recorded with respect to the Ag/AgNO₃ $(1.0 \times 10^{-2} \text{ M})$. The E_{ox} and E_{red} values (vs. Ag/AgNO₃) are converted to those versus SCE by adding 0.29 V, respectively.[66] All electrochemical measurements were carried out under an atmospheric pressure of argon. ESR measurements: ESR spectra were taken on a JEOL X-band spectrometer (JES-RE1XE) at various temperatures. ESR spectra of the CS state of DMA-Fl (DMA'+-Fl'-) in frozen PhCN and the one-electron reduced DMA-Fl (DMA-Fl-) in PhCN were measured under photoirradiation with a high-pressure mercury lamp (USH-1005D) through a water filter focusing at the sample cell in the ESR cavity at 243-203 K. The g value was calibrated using an Mn²⁺ marker. DMA-Fl^{-−} was generated by the photoinduced ET reduction of DMA-Fl $(2.8 \times 10^{-3} \text{ M})$ with dimeric 1-benzyl-1,4-dihydronicotinamide $[(BNA)_2]^{[67]}$ $(1.0 \times 10^{-3} - 2.5 \times 10^{-3} - 2$ 10⁻⁴ M). The resulting solution was transferred to a quartz ESR tube under an atmospheric pressure of Ar. The hyperfine coupling constants were determined using the Win-Sim program of the NIEHS public EPR software tools package, which is available on the Internet (http://EPR. niehs.nih.gov/).[68] This program was allowed to systematically vary the hydrogen and nitrogen hyperfine coupling constants and the relative concentrations of each species to achieve the best fit to the experimental spectra. 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. Theoretical calculations: Density-functional theory (DFT) calculations

were performed on an 8CPU workstation (PQS, Quantum Cube QS8-2400C-064). Geometry optimizations were achieved using the Becke3 LYP functional and 6-31G(d) basis set,^[69,70] with the restricted Hartree– Fock (RHF) formalism for neutral compounds and unrestricted Hartree– Fock (UHF) formalism for radical anion and radical cation species as implemented in the Gaussian 03 program Revision C.02.^[71] Graphical outputs of the computational results were generated with the Gauss View software program (ver. 3.09) developed by Semichem, Inc.^[72]

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- a) The Photosynthetic Reaction Center (Eds.: J. Deisenhofer, J. R. Norris), Academic Press, San Diego, 1993; b) Anoxygenic Photosynthetic Bacteria (Eds.: R. E. Blankenship, M. T. Madigan, C. E. Bauer), Kluwer Academic, Dordrecht, 1995.
- M. R. Wasielewski in *Photoinduced Electron Transfer, Part A* (Eds.: M. A. Fox, M. Chanon), Elsevier, Amsterdam, **1988**, pp. 161–206.
- [3] M. N. Paddon-Row in *Electron Transfer in Chemistry, Vol. 3* (Ed.: V. Balzani), Wiley-VCH, Weinheim, 2001, pp. 179–271.
- [4] a) D. Gust, T. A. Moore in *The Porphyrin Handbook, Vol. 8* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, **2000**, pp. 153–190; b) D. Gust, T. A. Moore, A. L. Moore in *Electron Transfer in Chemistry, Vol. 3* (Ed.: V. Balzani), Wiley-VCH, Weinheim, **2001**, pp. 272–336.
- [5] a) T. A. Moore, D. Gust, P. Mathis, J.-C. Mialocq, C. Chachaty, R. V. Bensasson, E. J. Land, D. Doizi, P. A. Liddell, W. R. Lehman, G. A. Nemeth, A. L. Moore, *Nature* 1984, 307, 630; b) D. Gust, T. A. Moore, *Science* 1989, 244, 35; c) D. Gust, T. A. Moore, A. L. Moore, S.-J. Lee, E. Bittersmann, D. K. Luttrull, A. A. Rehms, J. M. DeGraziano, X. C. Ma, F. Gao, R. E. Belford, T. T. Trier, *Science* 1990, 248, 199.
- [6] a) M. R. Wasielewski, *Chem. Rev.* 1992, *92*, 435; b) K. D. Jordan,
 M. N. Paddon-Row, *Chem. Rev.* 1992, *92*, 395; c) M. N. Paddon-Row,
 Acc. Chem. Res. 1994, *27*, 18; d) D. Gust, T. A. Moore, A. L. Moore,
 Acc. Chem. Res. 2001, *34*, 40.
- [7] a) T. J. Meyer, Acc. Chem. Res. 1989, 22, 163; b) J. R. Winkler, H. B.
 Gray, Chem. Rev. 1992, 92, 369; c) G. McLendon, Acc. Chem. Res.
 1988, 21, 160; d) G. McLendon, R. Hake, Chem. Rev. 1992, 92, 481.
- [8] a) C. R. Bock, T. J. Meyer, D. G. Whitten, J. Am. Chem. Soc. 1975, 97, 2909; b) M. R. Wasielewski, M. P. Niemczyk, W. A. Svec, E. B. Pewitt, J. Am. Chem. Soc. 1985, 107, 1080; c) S. R. Greenfield, W. A. Svec, D. Gosztola, M. R. Wasielewski, J. Am. Chem. Soc. 1996, 118, 6767; d) B. Rybtchinski, L. E. Sinks, M. R. Wasielewski, J. Am. Chem. Soc. 2004, 126, 12268.
- [9] a) D. M. Guldi, M. Maggini, G. Scorrano, M. Prato, J. Am. Chem. Soc. 1997, 119, 974; b) L. Sánchez, I. Pérez, N. Martín, D. M. Guldi, Chem. Eur. J. 2003, 9, 2457; c) L. R. Sutton, M. Scheloske, K. S. Pirner, A. Hirsch, D. M. Guldi, J.-P. Gisselbrecht, J. Am. Chem. Soc. 2004, 126, 10370; d) D. I. Schuster, K. Li, D. M. Guldi, A. Palkar, L. Echegoyen, C. Stanisky, R. J. Cross, M. Niemi, N. V. Tkachenko, H. Lemmetyinen, J. Am. Chem. Soc. 2007, 129, 15973.
- [10] a) F. D'Souza, P. M. Smith, M. E. Zandler, A. L. McCarty, M. Itou, Y. Araki, O. Ito, *J. Am. Chem. Soc.* **2004**, *126*, 7898; b) F. D'Souza, R. Chitta, S. Gadde, M. E. Zandler, A. L. McCarty, A. S. D. Sandanayaka, Y. Araki, O. Ito, *Chem. Eur. J.* **2005**, *11*, 4416.
- [11] a) S. Fukuzumi, *Bull. Chem. Soc. Jpn.* 2006, 79, 177; b) K. Ohkubo,
 S. Fukuzumi, *Bull. Chem. Soc. Jpn.* 2009, 82, 303; c) K. Ohkubo, S.
 Fukuzumi, *J. Porphyrins Phthalocyanines* 2008, 12, 993.
- [12] a) S. Fukuzumi, K. Ohkubo, W. E, Z. Ou, J. Shao, K. M. Kadish, J. A. Hutchison, K. P. Ghiggino, P. J. Sintic, M. J. Crossley, *J. Am. Chem. Soc.* 2003, 125, 14984; b) Y. Kashiwagi, K. Ohkubo, J. A. McDonald, I. M. Blake, M. J. Crossley, Y. Araki, O. Ito, H. Imahori, S. Fukuzumi, *Org. Lett.* 2003, 5, 2719.
- [13] a) S. Fukuzumi, H. Imahori, H. Yamada, M. E. El-Khouly, M. Fujitsuka, O. Ito, D. M. Guldi, J. Am. Chem. Soc. 2001, 123, 2571; b) H. Imahori, K. Tamaki, D. M. Guldi, C. Luo, M. Fujitsuka, O. Ito, Y. Sakata, S. Fukuzumi, J. Am. Chem. Soc. 2001, 123, 2607.
- [14] H. Imahori, D. M. Guldi, K. Tamaki, Y. Yoshida, C. Luo, Y. Sakata, S. Fukuzumi, J. Am. Chem. Soc. 2001, 123, 6617.

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- [15] a) S. Fukuzumi, K. Ohkubo, H. Imahori, J. Shao, Z. Ou, G. Zheng, Y. Chen, R. K. Pandey, M. Fujitsuka, O. Ito, K. M. Kadish, *J. Am. Chem. Soc.* 2001, 123, 10676; b) R. Chita, K. Ohkubo, M. Tasior, N. K. Subbaiyan, M. E. Zandler, M. Rogacki, D. T. Gryko, S. Fukuzumi, F. D'Souza, *J. Am. Chem. Soc.* 2008, 130, 14263; c) A. Jimenez, F. Spanig, M. S. Rodriguez-Morgade, K. Ohkubo, S. Fukuzumi, D. M. Guldi, T. Torres, *Org. Lett.* 2007, *9*, 2481.
- [16] K. Ohkubo, H. Kotani, J. Shao, Z. Ou, K. M. Kadish, G. Li, R. K. Pandey, M. Fujitsuka, O. Ito, H. Imahori, S. Fukuzumi, *Angew. Chem.* **2004**, *116*, 871; *Angew. Chem. Int. Ed.* **2004**, *43*, 853.
- [17] a) S. Fukuzumi, H. Kotani, K. Ohkubo, S. Ogo, N. V. Tkachenko, H. Lemmetyinen, J. Am. Chem. Soc. 2004, 126, 1600; b) K. Ohkubo, H. Kotani, S. Fukuzumi, Chem. Commun. 2005, 4520.
- [18] a) R. A. Marcus, Annu. Rev. Phys. Chem. 1964, 15, 155; b) R. A. Marcus, N. Sutin, Biochim. Biophys. Acta Rev. Bioenerg. 1985, 811, 265; c) R. A. Marcus, Angew. Chem. 1993, 105, 1161; Angew. Chem. Int. Ed. Engl. 1993, 32, 1111.
- [19] a) D. Rehm, A. Weller, Ber. Bunsen-Ges. 1969, 73, 834; b) D. Rehm, A. Weller, Isr. J. Chem. 1970, 10, 259.
- [20] a) A. Weller, K. Zacharaasse, Chem. Phys. Lett. 1971, 10, 590; b) S. Efrima, M. Bixon, Chem. Phys. Lett. 1974, 25, 34; c) B. S. Brunschwig, S. Ehrenson, N. Sutin, J. Am. Chem. Soc. 1984, 106, 6858; d) A. V. Barzykin, P. A. Frantsuzov, K. Seki, M. Tachiya, Adv. Chem. Phys. 2002, 123, 511.
- [21] a) T. Ohno, A. Yoshimura, H. Shioyama, N. Mataga, J. Phys. Chem.
 1987, 91, 4365; b) A. Yoshimori, T. Kakitani, Y. Enomoto, N. Mataga, J. Phys. Chem. 1989, 93, 8316.
- [22] W. P. Todd, J. P. Dinnocenzo, S. Farid, J. L. Goodman, I. R. Gould, J. Am. Chem. Soc. 1991, 113, 3601.
- [23] a) J. Hong, O. A. Kharenko, J. Fan, F. Xie, A. K. Petros, B. R. Gibney, M. Y. Ogawa, Angew. Chem. 2006, 118, 6283; Angew. Chem. Int. Ed. 2006, 45, 6137; b) C. Turró, J. M. Zaleski, Y. M. Karabatsos, D. G. Nocera, J. Am. Chem. Soc. 1996, 118, 6060.
- [24] S. Fukuzumi, K. Ohkubo, H. Imahori, D. M. Guldi, *Chem. Eur. J.* 2003, 9, 1585.
- [25] a) A. Niemz, V. M. Rotello, Acc. Chem. Res. 1999, 32, 44; b) A. Niemz, J. Imbriglio, V. M. Rotello, J. Am. Chem. Soc. 1997, 119, 887; c) A. O. Cuello, C. M. McIntosh, V. M. Rotello, J. Am. Chem. Soc. 2000, 122, 3517; d) Y.-M. Legrand, M. Gray, C. Cooke, V. M. Rotello, J. Am. Chem. Soc. 2003, 125, 15789.
- [26] a) C. Walsh, Acc. Chem. Res. 1980, 13, 148; b) A. van der H. Michael; J. H. Klaas, Acc. Chem. Res. 2004, 37, 13; c) V. Massey, Biochem. Soc. Trans. 2000, 28, 283.
- [27] a) J. Cadet, P. Vigny in *Bioorganic Photochemistry, Vol. 1* (Ed.: H. Morrison), Wiley, New York, **1990**, pp. 1–272; b) P. F. Heelis in *Chemistry and Biochemistry of Flavoenzymes, Vol. 1* (Ed.: F. Müller), CRC Press, Boca Raton, Fl, **1991**, pp. 171–193; c) G. R. Penzer, G. K. Radda in *Methods in Enzymology, Vol. XVIIIB* (Eds.: D. B. McCormick, L. D. Wright), Academic Press, New York, **1971**, p. 479; d) S. Fukuzumi, T. Tanaka in *Photoinduced Electron Transfer, Part C* (Eds.: M. A. Fox, M. Chanon), Elsevier, Amsterdam, **1988**, pp. 636–687.
- [28] a) M. Novak, A. Miller, T. C. Bruice, G. Tollin, J. Am. Chem. Soc. 1980, 102, 1465; b) C. Pac, K. Miyake, Y. Masaki, S. Yanagida, T. Ohno, A. Yoshimura, J. Am. Chem. Soc. 1992, 114, 10756; c) J. E. Hearst, Science 1995, 268, 1858; d) H. Kasai, Z. Yamaizumi, M. Berger, J. Cadet, J. Am. Chem. Soc. 1992, 114, 9692; e) R. Epple, E.-U. Wallenborn, T. Carell, J. Am. Chem. Soc. 1997, 119, 7440.
- [29] a) R. Traber, T. Werner, S. Schreiner, H. E. A. Kramer, W.-R. Knappe, P. Hemmerich in *Flavins and Flavoproteins* (Eds.: K. Yagi, T. Yamano) Japan Scientific Society Press, Tokyo, **1980**, p. 431;
 b) P. F. Heelis, *Chem. Soc. Rev.* **1982**, *11*, 15; c) F. Müller, *Photochem. Photobiol.* **1981**, *34*, 753.
- [30] a) M. Sun, T. A. Moore, P.-S. Song, J. Am. Chem. Soc. 1972, 94, 1730; b) M. Murakami, K. Ohkubo, T. Hasobe, V. Sgobba, D. M. Guldi, F. Wessendorf, A. Hirsh, S. Fukuzumi, J. Mater. Chem. 2010, 20, 1457.

- [31] a) L. N. Domelsmith, L. L. Munchausen, K. N. Houk, J. Am. Chem. Soc. 1977, 99, 6506; b) R. Egdell, J. C. Green, C. N. R. Rao, Chem. Phys. Lett. 1975, 33, 600.
- [32] The triplet excited energy of flavin derivatives has been reported;
 a) G. R. Brunk, K. A. Martin, A. M. Nishimura, *Biophys. J.* 1976, 16, 1373;
 b) A. Gordon-Walker, G. K. Radda, *Biochem. J.* 1970, 120, 673;
 c) F. Bosca, L. Fernandez, P. F. Heelis, Y. Yano, *J. Photochem. Photobiol. B: Biol.* 2000, 55, 183.
- [33] K. Okamoto, K. Ohkubo, K. M. Kadish, S. Fukuzumi, J. Phys. Chem. A 2004, 108, 10405.
- [34] S. Fukuzumi, K. Ohkubo, T. Suenobu, K. Kato, M. Fujitsuka, O. Ito, J. Am. Chem. Soc. 2001, 123, 8459.
- [35] a) M. A. Cusanovich, G. Tollin, *Biochemistry* **1980**, *19*, 3343; b) M. Horiuchi, K. Maeda, A. Tatsuo, *Chem. Phys. Lett.* **2004**, *394*, 344.
- [36] Molar absorption coefficient of DMA⁺⁺ in PhCN at 620 nm was determined as 340 m⁻¹ cm⁻¹ by a stopped-flow technique (see Experimental Section). The DMA⁺⁺ was produced in the electron-transfer oxidation with [Ru(bpy)₃]³⁺ (see the Supporting Information S6). This value is corresponding well to the reported value, see: a) T. Shida, W. H. Hamill, *J. Chem. Phys.* **1966**, 44, 2369; b) I. Amada, M. Yamaji, S. Tsunoda, H. Shizuka, *J. Photochem. Photobiol. A* **1996**, 95, 27; c) T. Shida in *Electronic Absorption Spectra of Radical Ions*, Elsevier, Amsterdam, **1988**, p. 208.
- [37] a) X. Cai, M. Fujitsuka, T. Majima, J. Phys. Chem. A 2007, 111, 4743; b) X. Cai, M. Sakamoto, M. Fujitsuka, T. Majima, Chem. Phys. Lett. 2006, 432, 436; c) S. Pagès, B. Land, E. Vauthey, J. Phys. Chem. A 2006, 110, 7547; d) N. Ichinose, T. Tanaka, S. Kawanishi, T. Suzuki, K. Endo, J. Phys. Chem. A 1999, 103, 7923; e) A. R. Cook, L. A. Curtiss, J. R. Miller, J. Am. Chem. Soc. 1997, 119, 5729.
- [38] a) D. Gosztola, M. P. Niemczyk, W. Svec, A. S. Lukas, M. R. Wasielewski, *J. Phys. Chem. A* **2000**, *104*, 6545; b) J. E. Almlöf, M. W. Feyereisen, T. H. Jozefiak, L. L. Miller, *J. Am. Chem. Soc.* **1990**, *112*, 1206; c) J. Eriksen, K. A. Jørgensen, J. Linderberg, H. Lund, *J. Am. Chem. Soc.* **1984**, *106*, 5083.
- [39] a) Y. Honda, M. Hada, M. Ehara, H. Nakatsuji, J. Phys. Chem. A 2007, 111, 2634; b) Y. Honda, M. Hada, M. Ehara, H. Nakatsuji, J. Phys. Chem. A 2002, 106, 3838.
- [40] a) S. F. Nelsen, M. N. Weaver, D. Yamazaki, K. Komatsu, R. Rathore, T. Bally, *J. Phys. Chem. A* 2007, *111*, 1667; b) S. Hirata, M. Head-Gordon, J. Szczepanski, M. Vala, *J. Phys. Chem. A* 2003, *107*, 4940.
- [41] a) G. A. Mines, M. J. Bjerrum, M. G. Hill, D. R. Casimiro, I-J. Chang, J. R. Winkler, H. B. Gray, J. Am. Chem. Soc. 1996, 118, 1961;
 b) J. V. Beitz, J. R. Miller, J. Chem. Phys. 1979, 71, 4579.
- [42] a) H. B. Gray, J. R. Winkler, *Quart. Rev. Biophys.* 2003, *36*, 341;
 b) A. R. Dunn, I. J. Dmochowski, J. R. Winkler, H. B. Gray, *J. Am. Chem. Soc.* 2003, *125*, 12450;
 c) H. B. Gray, J. R. Winkler, *Annu. Rev. Biochem.* 1996, *65*, 537.
- [43] C. Wohlfarth, B. Wohlfarth in Viscosity of Pure Organic Liquids and Binary Liquid Mixtures, Landolt-Börnstein-Numerical Data and Function Relationships in Science and Technology, IV/18, Springer, Berlin, 2009.
- [44] The calculated $k_{\rm diff}$ value $(5.6 \times 10^9 \,{\rm M}^{-1} {\rm s}^{-1})$ agrees with the reported experimental value.^[24,67]
- [45] a) S. Fukuzumi, Koumitsu, K. Hironaka, T. Tanaka, J. Am. Chem. Soc. 1987, 109, 305; b) S. Fukuzumi, N. Nishizawa, T. Tanaka, J. Org. Chem. 1984, 49, 3571.
- [46] A relatively large ΔH value of (DMA⁺⁺ MeFI⁻⁻: 3.2 kcalmol⁻¹) as compared with the other values (0.7–1.0 kcalmol⁻¹) in Table 3 may result from more localized positive charge of DMA⁺⁺ as compared with more delocalized π -radical cations.
- [47] S. M. S. Chauhan, R. Singh, Geetanjali, Synth. Commun. 2003, 33, 2899.
- [48] W. B. Cowden, P. K. Halladay, R. B. Cunningham, N. H. Hunt, I. A. Clark, J. Med. Chem. 1991, 34, 1818.
- [49] D. Hawkins, J. M. Lindley, I. M. McRobbie, O. Meth-Cohn, J. Chem. Soc. Perkin Trans. 1 1980, 3, 2387.

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- [50] Fluorescence quantum yields were determined by fluorescein in 0.1 M NaOH aqueous solution as a reference ($\Phi_{\rm fl}$ =0.92). See: G. Weber, F. W. J. Teale, *Trans. Faraday Soc.* **1957**, *53*, 646.
- [51] No π-dimer between the DMA–Fl and the CS state was detected in the near-IR region because of the steric hindrance of DMA. For the formation of a π-dimer between 9-mesityl-10-methylacridinium ion and the electron-transfer state, see: S. Fukuzumi, H. Kotani, K. Ohkubo, *Phys. Chem. Chem. Phys.* **2008**, *10*, 5159.
- [52] The one-electron reduced species of DMA–Fl (DMA–Fl⁻) is stable in deaerated PhCN. DMA–Fl⁻ was produced by the thermal ET reduction of DMA–Fl with naphthalene radical anion (NA⁻⁻) (see the Supporting Information S18). In contrast, the CV of DMA–Fl in deaerated PhCN shows an irreversible oxidation wave at a low scan rate (0.1 Vs⁻¹), while above 50 Vs⁻¹, it exhibits a reversible oxidation-reduction couple. Thus, DMA⁺⁺–Fl was detected in the thermal electron-transfer oxidation of DMA–Fl with [Ru(bpy)₃]³⁺ by using a stopped-flow method in millisecond timescale (see the Supporting Information S19).
- [53] The quantum yield of the CS state was determined using the comparative method. In particular, the strong fullerene triplet-triplet absorption $(\varepsilon_{740 \text{ nm}} = 18\,800 \text{ M}^{-1} \text{ cm}^{-1}: \Phi_{\text{triplet}} = 0.98)^{[54]}$ served as probe to determine the quantum yield of the CS state, especially for DMA⁺⁺ -Fl $(\varepsilon_{700 \text{ nm}} = 220 \text{ M}^{-1} \text{ cm}^{-1})$. The molar absorption coefficient of DMA⁺⁺-Fl in PhCN at 700 nm was determined by a stopped-flow technique (see Experimental Section).^[52]
- [54] C. Luo, M. Fujitsuka, A. Watanabe, O. Ito, L. Gan, Y. Huang, C.-H. Haung, J. Chem. Soc. Faraday Trans. 1998, 94, 527.
- [55] Larger V values have been reported for photoinduced ET in electron donor-acceptor dyads. See: a) M. Bixon, J. Jortner, J. W. Verhoeven, J. Am. Chem. Soc. 1994, 116, 7349; b) R. M. Williams, M. Koeberg, J. M. Lawson, Y.-Z. An, Y. Rubin, M. N. Paddon-Row, J. W. Verhoeven, J. Org. Chem. 1996, 61, 5055; c) S. V. Rosokha, D.-L. Sun, J. K. Kochi, J. Phys. Chem. A 2002, 106, 2283; d) H. Imahori, N. V. Tkachenko, V. Vehmanen, K. Tamaki, H. Lemmetyinen, Y. Sakata, S. Fukuzumi, J. Phys. Chem. A 2001, 105, 1750.
- [56] a) N. Liang, J. R. Miller, G. L. Closs, J. Am. Chem. Soc. 1990, 112, 5353; b) N. Liang, J. R. Miller, G. L. Closs, J. Am. Chem. Soc. 1989, 111, 8740; c) G. L. Closs, L. T. Calcaterra, N. J. Green, K. W. Pen-field, J. R. Miller, J. Phys. Chem. 1986, 90, 3673.
- [57] a) M. A. Smitha, K. R. Gopidas, *Chem. Phys. Lett.* 2001, *350*, 86;
 b) J. Kroon, H. Oevering, J. W. Verhoeven, J. M. Warman, A. M. Oliver, M. N. Paddon-Row, *J. Phys. Chem.* 1993, *97*, 5065.
- [58] a) C. Serpa, P. J. S. Gomes, L. T. Arnaut, J. S. de Melo, S. J. Formosinho, *ChemPhysChem* **2006**, *7*, 2533; b) H. Lemmetyinen, N. V. Tkachenko, A. Efimov, M. Niemi, *J. Phys. Chem. C* **2009**, *113*, 11475.
- [59] a) H. Kawauchi, S. Suzuki, M. Kozaki, K. Okasa, D.-M. S. Islam, Y. Araki, O. Ito, K. Yamanaka, J. Phys. Chem. A 2008, 112, 5878; b) Y. Araki, O. Ito, J. Photochem. Photobiol. C 2008, 9, 93; c) A. S. D. Sandanayaka, Y. Araki, O. Ito, G. R. Deviprasad, P. M. Smith, L. M. Rogers, M. E. Zandler, F. D'Souza, Chem. Phys. 2006, 325, 452; d) G. A. Rajkumar, A. S. D. Sandanayaka, K. Ikeshita, M. Itou, Y. Araki, Y. Furusho, N. Kihara, O. Ito, T. Takata, J. Phys. Chem. A 2005, 109, 2428; e) A. S. Sandanayaka, N. Watanabe, K. Ikeshita, Y. Araki, N. Kihara, Y. Furusho, O. Ito, T. Takata, J. Phys. Chem. B

2005, *109*, 2516; f) K. Yamanaka, M. Fujitsuka, Y. Araki, O. Ito, T. Aoshima, T. Fukushima, T. Miyashi, *J. Phys. Chem. A* **2004**, *108*, 250; g) A. S. D. Sandanayaka, K. Matsukawa, T. Ishi-I, S. Mataka, Y. Araki, O. Ito, *J. Phys. Chem. B* **2004**, *108*, 19995.

- [60] a) M. Tanaka, K. Ohkubo, C. P. Gros, R. Guilard, S. Fukuzumi, J. Am. Chem. Soc. 2006, 128, 14625; b) D. Kuciauskas, P. A. Liddell, S. Lin, S. G. Stone, A. L. Moore, T. A. Moore, D. Gust, J. Phys. Chem. B 2000, 104, 4307; c) D. Wiedenfeld, M. Bachrach, T. M. McCleskey, M. G. Hill, H. B. Gray, J. R. Winkler, J. Phys. Chem. B 1997, 101, 8823.
- [61] a) R. Chang, J. Chem. Educ. 1970, 47, 563; b) K. S. Cheng, N. Hirota in Investigation of Rates and Mechanisms of Reactions, Vol. VI (Ed.: G. G. Hammes), Wiley, New York, 1974, p. 565.
- [62] A. Sauer, F. Wasgestian, U. Nickel, Bull. Chem. Soc. Jpn. 1989, 62, 2688.
- [63] W. L. F. Armarego, C. L. L. Chai in *Purification of Laboratory Chemicals*, 5th ed, Elsevier, London, 2003.
- [64] a) C. L. Wong, J. K. Kochi, J. Am. Chem. Soc. 1979, 101, 5593; b) S. Fukuzumi, C. L. Wong, J. K. Kochi, J. Am. Chem. Soc. 1980, 102, 2928.
- [65] R. E. DeSimone, R. S. Drago, J. Am. Chem. Soc. 1970, 92, 2343.
- [66] C. K. Mann, K. K. Barnes in *Electrochemical Reactions in Non-aqueous Systems*, Marcel Dekker, New York, **1970**.
- [67] S. Fukuzumi, T. Suenobu, M. Patz, T. Hirasaka, S. Itoh, M. Fujitsuka, O. Ito, J. Am. Chem. Soc. 1998, 120, 8060.
- [68] A. R. Murray, E. Kisin, V. Castranove, C. Komineni, M. R. Gunther, A. A. Shvedova, *Chem. Res. Toxicol.* 2007, 20, 1769.
- [69] a) A. D. Becke, J. Chem. Phys. 1993, 98, 5648; b) C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 1988, 37, 785.
- [70] W. J. Hehre, L. Radom, P. von R. Schleyer, J. A. Pople in *Ab Initio Molecular Orbital Theory*, Wiley, New York, **1986**.
- [71] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., J. T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Tovota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, F. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT. 2004.
- [72] R. Dennington II, T. Keith, J. Millam, K. Eppinnett, W. L. Hovell, R. Gilliland, Semichem, Inc., Shawnee Mission, KS, 2003.

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