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First Unequivocal Observation of the Whole Bell-Shaped Energy Gap Law in Intramolecular Charge Separation from S_2 Excited State of Directly Linked Porphyrin−Imide Dyads and Its Solvent-Polarity Dependencies

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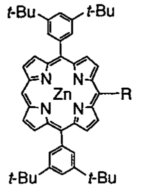
The photoinduced electron transfer (ET) reactions in solution are regulated by various factors including the magnitude of electronic interaction between donor (D) and acceptor (A), free energy gap, and solvation dynamics as well as intramolecular vibrations coupled with ET process.[1−7] When the nonadiabatic mechanism is applicable, the reaction can be well-understood on the basis of the conventional theories,[1−7] with an exception of the lack of unambiguous observation of the inverted region in the photoinduced charge separation (CS) reactions.[3−6,8] In the case of the reaction between D and A at diffusional encounter in polar solutions, a larger solvent reorganization energy λ_s is favorable to keep the rate constant k_{CS} large for larger energy gap $-\Delta G_{CS}$, and large λ_s means a large D−A encounter distance. This distance distribution effect makes the observation of the inverted region very difficult.[3−6] Accordingly, quite many studies on distance-fixed systems have been performed.[3,6,8−12] Nevertheless, it was difficult to synthesize such systems with various $-\Delta G_{CS}$ values including very large ones, and no unambiguous demonstration of the inverted or whole normal and inverted regions is available.

For the unequivocal observation of the inverted region, measurement of the ET from S_2 state of zinc (II)−porphyrin (D) to covalently linked acceptor is very fruitful, in view of the relatively long lifetime of the S_2 state (~2 ps measured in this work) as well as a wide range of the available $-\Delta G_{CS}$. Accordingly, we employed here a series of directly linked zinc (II)−porphyrin (ZP)−imide (I) dyads as shown in Chart 1. The direct linkage ensures the D−A electronic interaction strong enough to realize the rapid CS reaction in competition with the $S_2 \rightarrow S_1$ internal conversion. Nevertheless, we should note here that the Soret bands of these ZP−I dyads and the excitation energies $\Delta E(S_2) \approx 2.9$ eV are practically the same throughout the series, being close to that of ZP itself. The imide group shows no absorption band around the Soret band and longer wavelength side. Moreover, no extra-absorption band due to charge transfer (CT) as reported for the directly linked porphyrin−quinone systems[9,10] was observed in the neighborhood of S_2 and below it, and very weak S_2 fluorescence spectrum observed for the ZP−I series was in the same wavelength region as that of ZP itself. Somewhat reduced D−A electronic coupling may be ascribed to the nearly perpendicular conformation of the I moiety as revealed by X-ray crystallography (Supporting Information). Moreover, we have confirmed by MO calculation (PM3 INDO/S using WinMOPAC), that the LUMO of the attached I moieties commonly have a node at the connecting meso-positions, thereby minimizing the electronic interactions.

Chart 1



ZP-MePH (R=4-methylphthalimide)
ZP-PH (R=phthalimide)
ZP-ClPH (R=4-chlorophthalimide)
ZP-Cl$_2$PH (R=4,5-dichlorophthalimide)
ZP-Cl$_4$PH (R=tetrachlorophthalimide)
ZP-PI (R=pyromellitimide)
ZP-NI (R=1,8:4,5-naphthalenetetracarboximide)

We have measured one electron oxidation potential (E_{ox}) and reduction potential (E_{red}) of ZP−I in DMF (*N,N*-dimethylformamide) and have determined the free energy gaps ($-\Delta G_{CS}$) by using the equation, $-\Delta G_{CS} = \Delta E(S_2) - (E_{ox} - E_{red}) - \Delta G_S$, where ΔG_S is the correction term given by $\Delta G_S = (e^2/2)(r_D^{-1} + r_A^{-1})(\epsilon_s^{-1} - \epsilon_r^{-1}) - (e^2/\epsilon_s r)$ on the basis of the dielectric continuum model of the solvent.[1] Here, r_D and r_A are effective radii of ZP^+ and I^- ions, r is the center-to-center distance between the ions, and ϵ_r is the dielectric constant of DMF, and ϵ_s is that of the solvent used for the fluorescence measurements of the photoinduced CS reactions. This evaluation of ΔG_S in sufficiently polar solvents such as tetrahydrofuran (THF), acetonitrile (ACN), and GTA (glycerol triacetate) and using appropriate values for r_D, r_A, and r taken from our previous studies on similar porphyrin-acceptor linked compounds[11,12] seem to provide reasonable values for $-\Delta G_{CS}$. The values of $(E_{ox} - E_{red})$/eV determined by us are as follows: 1.322 (ZP−NI), 1.592 (ZP−PI), 1.836 (ZP−Cl$_4$PH), 2.034 (ZP−Cl$_2$PH), 2.080 (ZP−ClPH), 2.140 (ZP−PH), 2.152 (ZP-MePH).

Figure 1 shows fluorescence decay curves of ZP and seven ZP−I dyads in ACN solution measured by fs up-conversion technique similar to that described elsewhere.[13] All the decay curves can be reproduced satisfactorily with single-exponential functions. Quite similar decay curves have been observed also in other solvents examined. From the single-exponential decay, k_{CS} has been determined by $k_{CS} = \tau^{-1} - \tau_0^{-1}$, where τ_0 (~2 ps) is the lifetime of the S_2 state of ZP itself. Figure 2 shows obtained k_{CS} values plotted against $-\Delta G_{CS}$. The inverted, top and normal regions in the energy gap law for the photoinduced CS reaction have been unambiguously observed here.

We have examined the dynamics of the transient absorption spectra of $ZP^*(S_2) - I$ and $ZP^+ - I^-$ states with the fs−ps laser photolysis apparatus described elsewhere.[14] By analyzing time dependencies of absorbances, we have obtained k_{CS} values of ZP−NI, ZP−PI and ZP−MePH in THF solutions as 9.5×10^{11} s^{-1}, 5.1×10^{12} s^{-1} and 3.5×10^{12} s^{-1}, respectively, which agree

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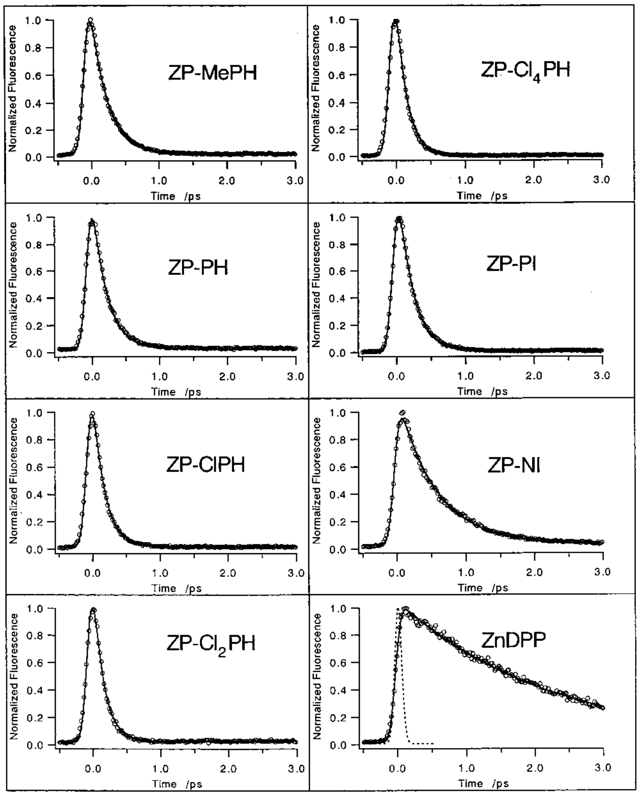

Figure 1. Normalized fluorescence decay curves of ZP and ZP−I excited at 405 nm and monitored at 430 nm at 20 °C in ACN. Observed fluorescence rise and decay (open circles), simulation with single-exponential function taking into account the apparatus response (solid lines), apparatus response function (dashed line).

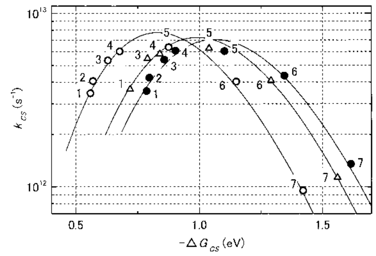

Figure 2. Energy gap dependencies of k_{CS} and simulation with eq 1 at 20 °C. Observed values in THF (○), GTA (△), ACN (●), and simulation (solid lines). ZP−I compounds: 1. ZP−MePH, 2. ZP−PH, 3. ZP−ClPH, 4. ZP−Cl_2PH, 5. ZP−Cl_4PH, 6. ZP−PI, 7. ZP−NI. Parameter values in the global fitting with eq 1: $V = 0.024$ eV, $\lambda_v = 0.3$ eV, $\hbar\langle\omega\rangle = 0.15$ eV throughout all three solvents, and λ_s for each solvent was determined so as to get the best fit between k_{CS} values calculated with eq 1 and the observed values. The determined values are: λ_s (ACN) = 0.76 eV, λ_s (GTA) = 0.69 eV, and λ_s (THF) = 0.54 eV.

exactly with those obtained by the fluorescence up-conversion studies. Moreover, our fs fluorescence studies on $S_2 \rightarrow S_1$ internal conversion of ZP in THF showed clearly the rise of rather strong S_1 fluorescence in accordance with the decay of the S_2 fluorescence.[15] But no such rise of S_1 fluorescence was recognized for ZP−I systems, which means that the $S_2 \rightarrow S_1$ internal conversion is strongly suppressed by competing CS.

It seems to be possible[16] that the photoinduced ET dynamics and its energy gap law depend on the excess vibrational energy of the initial state. Our measurements in THF, where the excitation wavelength was changed from 405 nm near the blue edge of the Soret band to 425 nm at the red edge of the Soret band showed the same CS rate constant in both cases, indicating that the excitation to the hot S_2 state is followed by ultrafast vibrational redistribution which gives the vibrational states near the bottom of S_2, from which the ultrafast CS reaction takes place. This result is compatible with the basic assumption for the conventional formula of eq 1, and we have used it to reproduce the observed results in Figure 2.

$$k_{CS} = (\pi/\hbar^2\lambda_s k_B T)^{1/2} V^2 \sum_n (e^{-S}(S^n/n!)) \times \exp\{-(\Delta G_{CS} + \lambda_s + n\hbar\langle\omega\rangle)^2/4\lambda_s k_B T\} \quad (1)$$

where V is the electronic coupling matrix element, $S = \lambda_v/\hbar\langle\omega\rangle$ is the electron-vibration coupling constant, λ_v is the reorganization energy associated with the averaged angular frequency $\langle\omega\rangle$ of *hfm* (intramolecular high-frequency modes) and λ_s is the solvent reorganization energy. The observed results in three polar solvents are reasonably well reproduced by using parameters which are close to those used in the related previous studies.[6,8,11,12]

In these polar solvents, the solvent reorganization in the course of CS plays important role of reaction coordinate and causes an activation barrier, giving rise to the normal region for ZP−MePH, ZP−PH, ZP−ClPH, and ZP−Cl_2PH with relatively small $-\Delta G_{CS}$ values in Figure 2. However, such normal region type energy gap dependence was not recognized, but only the top and inverted regions were detected in cyclohexane and toluene solutions, which can be ascribed to the much smaller solvent reorganization energies, leading to the negligibly small activation barrier at relatively small $-\Delta G_{CS}$ values. On the other hand, a very long solvent relaxation time ($\tau_L \approx 125$ ps at 20 °C) has been reported for GTA[17] in contrast to those of ACN (~0.1 ps) and THF (~0.5 ps).[18] Nevertheless, the fluorescence decay dynamics in GTA is unambiguously single exponential, decay times in 100 fs regime are very close to those observed in ACN and THF, and does not show multiexponential or nonexponential decays due to the CS at various solvation states along the slow solvation coordinate as indicated by the previous works.[2,7,17,20b,21]

Thus, the observation of the normal region and very fast single exponential decay dynamics caused by CS in highly viscous polar solvent GTA raises a question concerning the fundamental nature of the solvent reorganization coupled with photoinduced CS. It seems to be necessary to invoke the ultrafast solvation[2,19,20] coupled with CS reaction even in the viscous solvent GTA. We have examined the dynamic Stokes shift (DSS) of coumarin dye 153 fluorescence in GTA and clearly recognized ultrafast DSS in 100 fs regime in addition to main components with very long relaxation times. Moreover, there was a study on the fast response of GTA by using optical-heterodyne-detected Raman-induced Kerr-effect spectroscopy, which predicted that about 25% of the solvation dynamics will occur in 100 fs regime.[22] Therefore, the ultrafast solvent response in several 10 fs to 100 fs regime coupled with ultrafast photoinduced CS is possible not only in the case of such nonviscous polar solvents as ACN, THF, and so forth, but also in such "slowly relaxing" viscous polar solvents as GTA where the CS from S_2 state of ZP−I seems to be completed in 100 fs regime owing to the coupling with the ultrafast response component in the solvent reorganization dynamics.

Supporting Information Available: Molecular structure of ZP−Cl_2PH revealed by X-ray crystallography. Evidence for the formation of the ion-pair state from S_2 excited state of ZP−I by means of time-resolved transient absorption spectral measurements (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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