

Energy gap dependence of electron transfer rates in porphyrin–imide supramolecular assemblies

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The energy gap dependence of the rate of electron transfer has been revealed for donor–acceptor supramolecular assemblies composed of zinc–tetraphenylporphyrin and a series of spacer–acceptor conjugate molecules which are structurally similar but with varying redox potentials.

Artificial photosynthetic devices rely on spatially organised units with suitable photochemical and electrochemical properties.¹ An increasing number of reports use non-covalent interactions, such as metal–ligand coordinate bonds, hydrogen bonding and so on, to construct a donor–acceptor supramolecular architecture.² We noticed, however, that there have been very few cases dealing with systematic variations in supramolecular donor–acceptor assemblies. As such little is known about the energy gap dependence of electron transfer rates through non-covalent interactions in well defined synthetic systems, while several systematic studies have been conducted for covalent donor–acceptor conjugates.^{3–7}

Hunter and coworkers reported on a very simple way to assemble donor–[spacer–acceptor] supermolecules, *i.e.* to use axial ligation of pyridine ligands to zinc–porphyrin (*e.g.* Fig. 1 with **1**).⁸ We reasoned that systematic variations on the redox potential of the imide unit would be made possible by this strategy and synthesised a series of pyridine–imide conjugates, **2–7**, which were structurally similar but with varying redox potentials (Table 1). Two ethoxy groups were introduced in the pyridine spacer to impart enough solubility to be used in excess, in order to ensure nearly complete complexation of Zn–tetraphenylporphyrin (ZnTPP). The key intermediate, 3,5-diethoxy-4-aminomethylpyridine, was prepared according to a literature method.⁹ Once this material was obtained in a fair amount, a variety of commercially available phthalic anhydride derivatives were reacted with it to prepare **2–7**.[‡]

Upon addition of pyridine–imide conjugates to a solution of ZnTPP in CH₂Cl₂, the Q bands exhibit a red-shift of *ca.* 15 nm, which is characteristic of the axial coordination to the metal centre of ZnTPP. From the change in the electronic spectra, binding constants were determined, as shown in Table 1, which

are virtually constant (log *K* 4.0 ± 0.2, 25 °C, CH₂Cl₂) for the whole series of pyridine–imide conjugates employed. § Owing to the intense ring-current effect of the porphyrin macrocycle, ¹H NMR spectroscopy is a powerful tool to probe the complexation.^{11,12} For example, in the limit of complete complexation, protons at pyridine-H2, pyridine-H3, and methylene of **1** experience upfield shifts of 6.29, 1.91 and 1.25 ppm, respectively, which are in accord with the axial coordination of the pyridine ligand. The minimum energy conformation of pyridine–imide conjugates was systematically searched with a molecular mechanics calculation by incrementally rotating C(pyridine)–CH₂ and CH₂–N bonds. The result suggests that, in the most stable conformation, the imide ring lies more or less in a face-to-face orientation with the porphyrin plane, assuming that the pyridine moiety coordinates perpendicular to the porphyrin plane.¹³ All this evidence indicates that a supermolecule as depicted schematically in Fig. 1 is formed exclusively.

Fluorescence from the singlet excited state of ZnTPP is quenched upon addition of pyridine–imide conjugates due to electron transfer to the imide^{14,15} as shown in Fig. 2. The degree of quenching is in proportion to the amount of complex formed and in quantitative accordance with the curve obtained from the binding constant determined as above. A slight increase in fluorescence intensity (5%) is noted upon complexation with 4-picoline which is used to serve as a model compound to differentiate the effect of axial coordination from that of electron transfer. Quenching by dihexylpyromellitic diimide, which is a model compound for **1** and **7** and lacks coordination capability, is also noted. However, this collisional quenching rate is more than two orders of magnitude smaller than that of **1** or **7** in the concentration range studied and can be safely neglected. Thus the collisional quenching is assumed negligible also for the other acceptors.

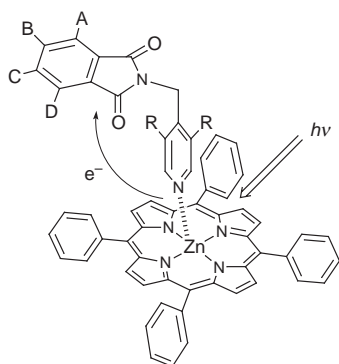


Fig. 1 A supramolecular assembly from ZnTPP and [spacer–acceptor] conjugates with various redox potentials

Table 1 Structures and properties of imides and porphyrin–imide assemblies

R	A	B	C	D	<i>E</i> ^a /V vs. Fc/Fc ⁺	log <i>K</i> ^b /M ⁻¹	φ _{et} ^c	log <i>k</i> _{et} ^d /s ⁻¹
1	H	H	(CO) ₂ NC ₆ H ₁₃	H	-1.34	3.8	0.91	9.7
2	OEt	H	H	H	-2.06	4.1	0.11	7.8
3	OEt	F	H	F	-1.81	4.1	0.13	7.9
4	OEt	F	F	F	-1.68	4.2	0.24	8.2
5	OEt	NO ₂	H	H	-1.44	4.1	0.55	8.8
6	OEt	H	NO ₂	H	-1.26	4.1	0.83	9.4
7	OEt	H	(CO) ₂ NC ₆ H ₁₃	H	-1.37	4.0	0.85	9.5

^a One-electron reduction potentials. The cyclic voltammetry was conducted with glassy C, Pt and Ag/Ag⁺ as working, counter and reference electrodes, respectively, under a N₂ atmosphere. Millimolar amount of samples were used in CH₂Cl₂ containing 0.1 M Bu₄NClO₄. ^b Binding constants in CH₂Cl₂ at 25 °C. ^c The quantum yields of intrasupramolecular electron transfer. Repeated runs agreed within ±2% with respect to the initial fluorescent intensity. ^d See footnote ¶. The propagated errors are indicated in Fig. 3.

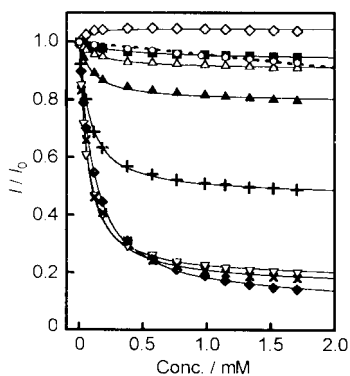


Fig. 2 Quenching of ZnTPP fluorescence upon addition of coordinating acceptors and model compounds (ZnTPP 10 μM in CH_2Cl_2 at 25 $^\circ\text{C}$ in air). 4-Picoline (\diamond), **2** (\blacksquare), **3** (\triangle), **4** (\blacktriangle), **5** (+), **6** (∇), **7** (\times), **1** (\blacklozenge) and dihexylpyromellitic diimide (dotted line).

In the limit of complexation, the quantum yields of the intrasupramolecular electron transfer, ϕ_{eT} , are obtained and listed in Table 1. For the studied acceptors with redox potentials varying in the range of 0.8 V, the electron transfer yield varies from 0.11 for **2** to as high as 0.91 for **1**. The rates of electron transfer obtained from these data \ddagger are plotted against the free energy gap (ΔG°) \parallel between the singlet excited state of ZnTPP and acceptors. Increasing energy gap results in increasing electron transfer rate, which is apparently 'normal' behaviour.

In the classical Marcus theory for nonadiabatic electron transfer for the case of weak coupling, the rate of electron transfer, k_{eT} , is given by

$$k_{\text{eT}} = (\pi/\hbar^2\lambda k_{\text{B}}T)^{1/2}|V|^2\exp[-(\Delta G^\circ + \lambda)^2/4\lambda k_{\text{B}}T]$$

where \hbar is Planck's constant divided by 2π , λ is the reorganisation energy, k_{B} is the Boltzmann constant, T is the temperature (298 K), and V is the coupling matrix element. 3,16 Here the two parameters, λ and V , are to be determined by experiment. Assuming that these parameters are constant throughout the series of acceptors, which may be justified on account of their chemical and structural similarity, possible curves from some combinations of these parameters are shown in Fig. 3. It is impossible to single out parameter values to fit all the observed data, especially when the data point for **2** is included. This system awaits further detailed photophysical scrutiny, including transient absorption measurements, to reveal the nature of electron transfer through space or intermolecular bonds.

We have shown that the supramolecular approach is powerful in constructing donor-acceptor architecture with relative ease that can be systematically addressed. In addition, the data presented herein may provide a guide to acceptors to be used in more elaborate donor-acceptor assemblies to obtain desired

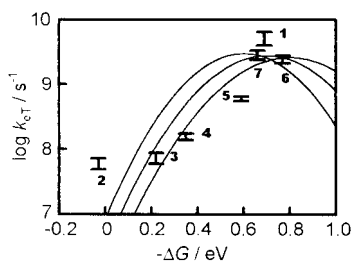


Fig. 3 The dependence of intrasupramolecular electron transfer rate on the energy gap. Curves are also shown according to the Marcus equation with $V = 3 \text{ cm}^{-1}$ and $\lambda = 0.6, 0.7, 0.8 \text{ eV}$ from left to right.

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Notes and References

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\ddagger Typically, separate solutions of 3,5-diethoxy-4-aminomethylpyridine and substituted phthalic anhydride in MeOH were mixed and heated on a hot plate, letting MeOH evaporate. The reaction mixture was purified by PLC. All compounds obtained had the expected ^1H NMR, IR spectra, and HRMS or elemental analyses and purity checked by TLC.

\S The Q bands obey Beer's Law around the concentration (10 μM) used in the absorption and fluorescence measurements and no broadening or splitting of the Soret band 10 is observed, indicating that ZnTPP exists as monomers before complexation. Clear isosbestic points upon addition of the pyridine-containing compounds indicate that only the 1 : 1 complex forms.

\parallel The electron transfer rates were determined from $k_{\text{eT}} = k_{\text{P}}\Phi_{\text{eT}}/(1 - \Phi_{\text{eT}})$, where k_{P} is the decay rate constant of ZnTPP in the absence of quenching ligand, which is $4.9 \times 10^8 \text{ s}^{-1}$. Some of the values (due to our instrumental limit) were independently confirmed by measurement of fluorescence decays, which were single exponential.

\parallel The redox potential of the lowest excited state of ZnTPP (E_{P}°) was estimated to be $-1.84 \text{ V vs. Fc/Fc}^+$ from the ground state redox potential (0.22 V) and the energy of the Q(0,0) band (2.06 eV) of pyridine-complexed ZnTPP. The energy gap, ΔG° , was obtained according to the equation $\Delta G^\circ = E^\circ - E_{\text{P}}^\circ + e^2/\epsilon r$

where the last term is the Coulomb correction in which ϵ is the relative permittivity of CH_2Cl_2 and r is the donor-acceptor distance. This term was set to be 0.20 eV based upon the estimated value of r (9.5 \AA) from the molecular mechanics calculation described in the text and the known geometry of a pyridine-porphyrin complex. 13

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