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Synthesis and Cation-Mediated Electron Transfer in Fluorescence Quenching of Donor-Acceptor Podands

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Abstract: Reduced rate constants of photoinduced electron transfer in intramolecular fluorescence quenching of donor-acceptor podands induced by cation-complexation are observed in the highly exothermic reactions.

Keywords: Electron transfer, donor, acceptor, podands.

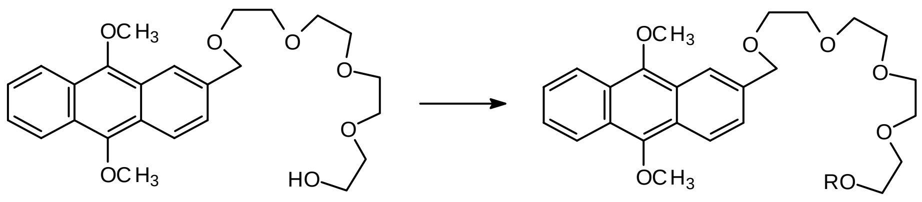
Covalently linked donor-acceptor (D-A) systems have been designed to study photoinduced electron transfer (PET) in a way that mimics the process occurring in natural photosynthesis[1]. For a given D-A system, the rate of PET depends on the D-A distance and relative orientation of the chromophores. For studies of this dependence, rigid dyads are generally used[2]. In contrast, if the spacer binding the chromophores is flexible, large conformational changes can occur following PET. Hence, the system usually exhibits more complicate behavior. Our interest in the development of supramolecular system based on host-guest complexation driven by non-covalent interaction brought us to prepare a series of long chain podands **2~7**. Despite the fact that the donor is not rigidly connected with the acceptors, the distance between the two chromophores is restricted by cations induced complexation.

In this paper, an attempt was made to examine the dependence of the rate of PET in intramolecular fluorescence quenching of the donor-acceptor podands induced by cation complexation.

The electron donor precursor **1** was synthesized by the reaction of 2-chloromethyl-9, 10-dimethoxy-anthracene[3] and tetraethylene glycol in THF, in the presence of NaH. The general procedures of the synthesis of **2~7** were as follows (**Scheme 1**): compound **1** and the corresponding substituted benzonic acid was mixed in anhydrous CH_2Cl_2 with DCC and DMAP as catalysts at room temperature. All compounds were purified by flash chromatography on silica gel using chloroform/methanol (100:0~3%) as eluant. All structures were characterised by IR, ^1H NMR , mass spectral data.

Addition of a small amount of CH_3COOK to solution of **2** in methol-d_4/acentonitrile-d_3 (1:9) produce downfield shift (up to 20Hz) in ^1H NMR shift of the oligooxaethylenic proton signals, which is consistent with that observed in the case of crown ethers and relative open-chain crown ethers[4]. Minor shifts were observed for **2** in the presence of $NaClO_4$.

Scheme 1



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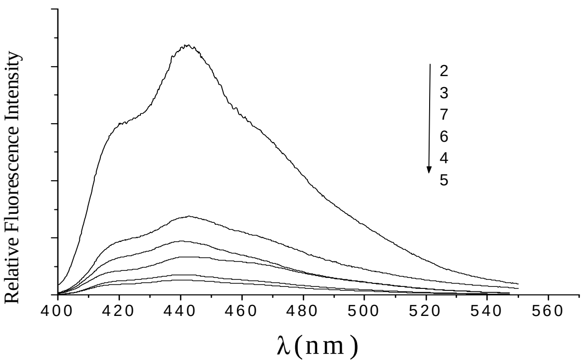
R : **2**. Benzoyl; **3**. 2,4-Dichlorobenzoyl;
4. 2-Chloro-5-nitrobenzoyl; **5**. 4-nitrobenzoyl;
6. 3, 5-Dinitrobenzoyl; **7**. 4-Chloro-3. 5-dinitrobenzovl

Reagents and condition: Benzoic acid or substituted benzoic acid, DCC,DMAP, in CH_2Cl_2, r. t.

Figure 1 Fluorescence spectra of **2~7** in the presence of K^+ at a molar ratio of (C_L=1×10^{-5}M C_L: C_M=1:20), λex=380nm



UV-vis studies of **2~7** and their cation-complexes show no ground state interaction between the donor and the acceptors. Fluorescence spectra of **3~7** demonstrate rapid and efficient quenching of the 9,10–dimethoxyanthracene S_1 excited state by the pending benzoate. The intensity of fluorescence decreases successively with increasing redox potential of the pending electron acceptor . The fluorescence spectra of **3~7** in the presence of K^+ also show pronounced quenching, Interestingly, the intensity of the fluorescence decreases in the order of **3** > **4** > **5**, and then increases in the order of **5**< **6** <**7** as the potential of the pending acceptor increases (**Figure 1**). The fluorescence spectra of the podands in the presence of Na^+ exhibit no difference compared with the free podands.

The intramolecular energy transfer in these systems can be ruled out because the overlap integral J may be assumed to be very small. The fluorescence quenching was mainly attributed to PET. The free energy change ΔG for each electron transfer reactions were obtained from the oxidation potential of the donor and the reduction potential of the acceptors (**Table 1**). The electron transfer rate can be estimated according to following equation[5]:

$$k_{ET} = (1/\tau_0)[(\Phi_0/\Phi)-1] \quad (1)$$

In this equation, Φ is the relative fluorescence quantum yield of **3~7** and their metal complexes (**Table2**). Φ_0 is the relative fluorescence quantum yield of model compound **2**, and τ_0 is the lifetime of **2**, which is 15.5 ns obtained by single-photon-counting.

Table 1. Redox potentials of substituted methyl benzoate in CH_3CN

Compounds	$E_R{}^a/V$	Compounds	$E_R{}^a/V$
Methyl-2,4-dichlorobenzoate	-1.2	Methyl-3,5-dinitrobenzoate	-0.76
Methyl-3-chloro,5-nitrobenzoate	-0.99	Methyl-4-chloro-3,5-dinitrobenzoate	-0.65
Methyl-4-nitrobenzoate	-0.90		

a Redox potentials were determined by cyclicvoltammetry with Pt electrode as working electrode using 0.1 M tetraethylammoniunperchlorate as supporting electrolyte in acetonitrile, Pt wire as counter electrode, and Ag/AgCl as reference electrode.

Table 2. Relative fluorescence quantum yields and PET rate constants for model compound **2**, **3~7** and their K^+ -complexes

Podand	$-\Delta G^a$/eV	$\Phi_1{}^b$	$\Phi_2{}^b$	k^c_{ET1}/s^{-1}	$k_{ET2}{}^c/s^{-1}$
2		1.00	1.00		
3	0.85	0.18	0.34	2.9×10^8	1.3×10^8
4	1.05	0.06	0.11	1.0×10^9	5.2×10^8
5	1.15	0.05	0.06	1.2×10^9	1.0×10^9
6	1.29	0.04	0.08	1.5×10^9	7.4×10^8
7	1.40	0.03	0.17	2.1×10^9	3.2×10^8

a.ΔG is calculated from the Weller equation[2]: $\Delta G=E_{O(D)}-E_{R(A)}-E_{S(D)}-C$, C is the coulombic energy term, which can be eliminated in this case. $E_{O(D)}$ and $E_{S(D)}$ were 0.90 and 2.95 V, respectively (see ref. 3). b. The value for **2** is arbitrarily taken as 1.00, Φ_1 are the relative quantum yield for **3~7**, Φ_2 are the relative quantum yield for K^+ complexes of **3~7**, c. k_{ET1} and k_{ET2} are calculted from Φ_1 and Φ_2, respectively. The uncertainty is less than ±15%.

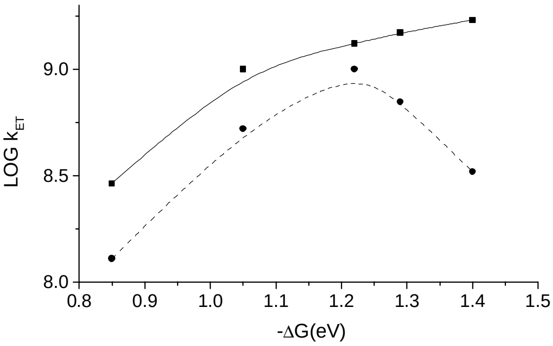
The Marcus express [6]of the form

$$k = A\exp[\frac{-(\Delta G+\lambda)^2}{4\lambda k_b T}] \qquad (2) \qquad \text{where} \quad A=\frac{2\pi}{\eta}\left|H_{DA}\right|^2\left(\frac{1}{\sqrt{4\pi k_b \lambda T}}\right)$$

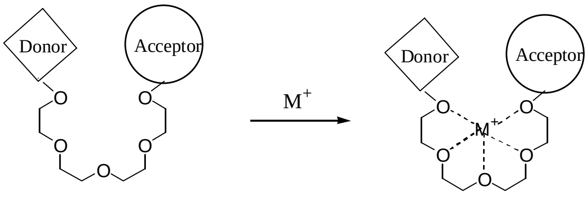
was used for a least-square analysis of the data (**Table 2**). The data for each system were fitted by two free parameters, the tunneling matrix element governing the electron transfer (H_{DA}) and the reorganization energy (λ) (**Figure 2**). The values obtained for **3~7** and their K^+ complexes were as follows: $H_{DA}=2.7cm^{-1}$, $\lambda=1.34eV$ and $H_{DA}=1.9cm^{-1}$, $\lambda=1.26eV$, respectively. The values obtained are larger than that ($H_{DA}=0.6cm^{-1}$, $\lambda=1.02eV$, unpublished results in our group) of long distance electron transfer between the same donor and acceptor system[3].

The findings suggest that the podand spacer has pseudo crown ether cavity. The binding of cations cause the change of topographic relationship of the donor and acceptor (**Scheme 2**). Computational studies using CPK model suggest a change in conformation of compounds induced by K^+, minor effect was observed in the presence of Na^+. We believe that the distance between the donor and the acceptor in the podands is restricted by K^+ binding, while Na^+ exerts negligible effect on the relative spatial disposition of the two chromophores in the system compared with the free podands. We can see that the dependence of rate of PET on ΔG in intramolecular fluorescence quenching of the present D-A podands induced by cation K^+-complexation present D-A podands induced

Figure 2 Plot of log k_{ET} against -ΔG/eV (**Table 2**). Solid line and dashed line are for **3~7** and their K^+-complexes, respectively.



Scheme 2



by cation K^+-complexation shows parabola shape (**Figure 2** dashed line), which indicate that the rate constants of PET in intramolecular fluorescence quenching of the present D-A podands were reduced in the highly exothermic reactions. We believe that this system is a promising one for demonstrating the existence of the Marcus "inverted region" in electron transfer fluorescence quenching process.

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