A Donor–Crown–Acceptor Triad: the Effect of Cations Included into the Triad on the Photo-induced Electron-transfer Rate

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A donor–crown–acceptor triad, consisting of 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane as a spacer, is designed as a new approach to the elucidation of the electronic effect of a spacer on intramolecular electron transfer between bridgehead chromophores.

The electronic coupling element, the magnitude of the overlap between reactant and product wave functions, is regarded as an important factor to govern the rate of a long-distance electron transfer (ET).[1] Throughout numerous studies on ET either of donor–spacer–acceptor triads or in proteins, it has been accepted[2] that the element would be affected by the nature of the media lying between a donor and an acceptor. Recently, there have been several notable works[3] on the electronic effect of the spacer energetics on the element in ET rate by chemical modification of the spacer in the triads. A more systematic study is still required to understand the delicate role of the intervening medium on the ET rate.

Our approach is to design a triad consisting of an inclusion compound as a spacer and then to manipulate the electronic state of the spacer through inclusion of various guest molecules, in due consideration of both the included cations and their counter anions. Target molecules are donor–crown–acceptor triads† (Fig. 1) where 1-pyrenyl group (Py) as an electron donor, and 4-nitrobenzyl (NB) or 2,4-dinitrobenzyl (DNB) as an acceptor were arranged at bridgeheads of 1,7,10,16-tetraoxa-4,13-diazacylooctadecane through an amide bond. Py–phenyl is a reference triad without an acceptor.

Photo-induced intramolecular ET rate from the excited Py to NB or DNB was evaluated here by fluorescence lifetime measurement.‡ All the spectroscopic measurements were performed at 25 °C in acetonitrile solution (1.0×10^{-5} mol dm^{-3})§ deaerated by N_2 bubbling for 15 min. The absorption spectrum of every triad completely agreed with a simple sum of those of the relevant chromophores. The fluorescence spectra of Py–NB and Py–DNB coincided in shape with that of Py–phenyl, characteristic of an excited monomeric pyrene, although their intensities were very weak relative to Py–phenyl. This evidence showed no important interactions between chromophores in the ground and the excited states, *i.e.* neither charge-transfer interaction nor exciplex formation. Additionally, no shift on the absorption maxima of the triads was observed in the presence of salts used here.

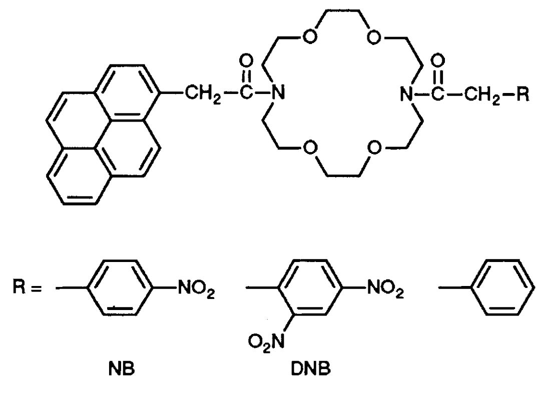

Fig. 1 Structures of donor–crown–acceptor triads

A fast (<2 ns) fluorescence decay (τ) at 400 nm was predominantly observed in both Py–NB and Py–DNB under excitation at 340 nm, while Py–phenyl had a single-exponential fluorescence decay with 150 ns of lifetime (τ_0). The fast decay component was interpreted as intramolecular ET from the excited Py to NB or DNB. The rate constants, $k_{ET} = (1/\tau) - (1/\tau_0)$, agreed with those obtained from steady-state fluorescence spectra by using $k_{ET} = \{(I_0/I) - 1\}/\tau_0$, where I and I_0 are fluorescence intensities with and without an acceptor, respectively. Table 1 summarizes the k_{ET} in the absence and the presence of $NaClO_4$, $LiClO_4$, or Bu_4NClO_4 (tetrabutylammonium perchlorate).

A substantial increase in k_{ET} of Py–NB and Py–DNB was realized by the addition of $NaClO_4$, while neither $LiClO_4$ nor Bu_4NClO_4 influenced their rates. The result on Bu_4NClO_4, not included to the crown, suggested the present ionic strength of the solution does not influence the rate. Two important factors must be considered on the Na^+ specificity: the electronic effect of the spacer and the conformational change of the triad. At present no significant conformational change was obtained by absorption and fluorescence spectra, and NMR study. The authors here tried to discuss this result from the viewpoint of the electronic effect. The superexchange mechanism,[2a] a well-accepted theory on long-distance ET, postulates that k_{ET} would increase with the magnitude [$\propto (1/\Delta E)^2$] of the contribution of the spacer LUMOs to the electronic coupling element, independent of acceptors, where ΔE is the energy difference between the donor LUMO and the spacer. The oxidation potential of the excited Py is estimated to be −2.14 V *vs.* SCE¶;[4] Li^+ and Na^+ have −3.23 and −2.87 V *vs.* SHE of the reduction potentials[5] in acetonitrile, respectively, corresponding to their LUMO. Although there is no reliable information on reduction potentials of aliphatic ethers and amides which the present crown consists of, it should be accepted that they would be more cathodic than Li^+ and Na^+. The above energetics leads us to the interpretation that superexchange interaction enhanced by Na^+ included to the crown would increase the rate.

Table 1 Intramolecular electron-transfer rate constants (k_{ET}) of the triads, Py–NB and Py–DNB, in the absence and the presence of salts (1.0×10^{-2} mol dm^{-3}) in acetonitrile

		k_{ET}/s^{-1}			
Triad	ΔG/eV	None	$NaClO_4$	$LiClO_4$	Bu_4NClO_4
Py–NB	−0.99	4.4×10^8	1.5×10^9	4.5×10^8	4.9×10^8
Py–DNB	−1.24	5.5×10^8	1.9×10^9	5.1×10^8	5.9×10^8

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† The synthetic procedure for the triads will be reported elsewhere. All the triads gave satisfactory elementary analyses and ^1H NMR spectra and their purities were checked by HPLC with a fluorescence detector.

‡ Fluorescence lifetime was measured by a single photon counting method and analysed by a deconvolution program.

§ At dilute concentrations the contribution of intermolecular ET was excluded.

¶ $\Delta G = \{E_{ox}(D) - E_{00}(D)\} - E_{red}(A)$ where $E_{ox}(D)$, $E_{red}(A)$, and $E_{00}(D)$ are the oxidation potential of a donor, the reduction potential of an acceptor, the excitation energy of the donor, respectively. $E_{ox}(Py) = 1.20$, $E_{red}(NB) = -1.15$, $E_{red}(DNB) = -0.90$ V *vs.* SCE and $E_{00}(Py) = 3.34$ eV.

The ratio increased by Na^+ was almost the same value (3.4) in both Py–NB and Py–DNB, regardless of their free energy changes ($\Delta G = -0.99$ and -1.24 eV, respectively).¶[4,6,7] Li^+ also has potential to increase k_{ET}, although a smaller magnitude due to larger ΔE than Na^+. However, little influence on the rate was observed because Li^+ is not well included to the crown.[8]

The preliminary result suggests that our approach is available for evaluation of the roles of the spacer on long-distance interaction as well as ET between bridgehead chromophores described here. A systematic study on the spacer energetics of a wide variety of guest molecules in this type of triad will provide quantitative elucidation of their electronic effect.

One of the authors (T.I.) is grateful to Dr John R. Miller, Argonne National Laboratory, USA, for his valuable suggestions. This work was partly supported by a Grant-in-Aid from the Ministry of Education of Japan and the financial support of the Toray Science Foundation.

Received, 10th July 1991; Com. 1/03473A

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