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Factoring the Contribution of Through-Space and Through-Bond Interactions to Rates of Photoinduced Electron Transfer in Donor-Spacer-Acceptor Molecules using Ultrafast Transient Absorption Spectroscopy

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Contributions from through-space and through-bond interactions to the electronic coupling matrix elements for photoinduced charge separation and recombination in linked donor-spacer-acceptor molecules were studied.

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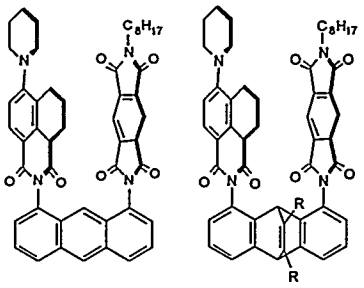
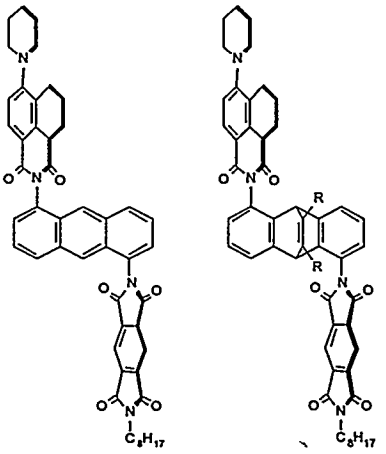
It is well known that the rate of intramolecular electron transfer in linked donor-acceptor molecules is not only dependent upon the distance and orientation between the donor (D) and acceptor (A), but is also dependent upon the electronic properties of the intervening spacer (S) molecules between the redox centers[1]. If the distance between D and A is small enough to allow for direct overlap between the frontier orbitals of the donor and acceptor, electron transfer may occur by means of a through-space mechanism. When the D and A centers are too far apart for direct orbital overlap to be important, electron transfer may occur via a superexchange or through bond interaction. Both contributions to the total electronic coupling matrix element for electron transfer between the donor and acceptor depend on the distance and the orientation of the various molecular components. Thus, it is important to hold both the distance and geometry of the donor and acceptor fixed as the properties of the covalent spacer between them are varied. Achieving this degree of structural control in a D-S-A molecule is often a difficult task.

We present here a study of a series of linked D-S-A molecules. The molecules consisted of a 4-piperidinyl-naphthalene-1,8-dicarboximide (ANI) electron donor and a N-(n-octyl)pyromellitimide (PI) electron acceptor attached to the 1,5- and 1,8-positions of either anthracene (ANC) or dibenzobicyclo(2.2.2)octatriene (DBO) spacers. For the 1,8-disubstituted compounds (**5A** and **6A**), ANI and PI are held approximately cofacial with a center-to-center distance of 5.3 Å, whereas for the 1,5-disubstituted compounds (**5B** and **6B**), the center-to-center distance increases to 13.5 Å. These spacers position the ANI donor and PI acceptor at fixed distances relative to one another, provide the desired rigidity, and strongly limit through-bond electron transfer.



5A **6A**



5B **6B**

Fluorescence quantum yields (Φ_f), charge separation lifetimes (τ_{cs}) and charge recombination lifetimes (τ_{cr}) determined in toluene and THF are listed in the table below for the various compounds (compound **7** is simply the ANI chromophore with no electron acceptor). The fluorescence arises from the excited CT state of the ANI chromophore, which has a fluorescence quantum yield of 0.91 in toluene[2]. The fluorescence emission from **5a** and **6a** is strongly quenched in both toluene and THF, whereas **5b** and **6b** exhibit very little quenching in either solvent. The lifetimes were measured by monitoring the formation and decay kinetics of PI^- at 715 nm following 412 nm, 140 fs laser excitation. Figure 1 shows the transient absorption spectra for the four molecules 20 ps after excitation. The 715 nm PI^- band is present only in the top spectra proving that only in compounds **5a** and **6a** is electron transfer competitive with spontaneous decay of the ANI excited state.

A detailed analysis of the electronic coupling matrix element, *V*, using the data from the table as well as electrochemically determined redox potentials and reference compounds shows that charge separation in **5a** and **6a** in both toluene and THF occurs via a through-space mechanism[3]. Charge recombination in **5a** in toluene and **6a** in both toluene and THF is shown to also occur via a through-space mechanism. Charge recombination in **5a** in toluene however occurs via a mixture of through-space and through-bond mechanisms. The through-bond mechanism is thought to involve the intermediate ANI-ANC^{+}-PI^{-}.

Cmpd	Solvent	Φ_f	τ_{cs} (ps)	τ_{cr} (ps)
7	Tol	0.91	--	8500
5a	Tol	<0.001	2.4	70, 250
5b	Tol	0.90	>8500	--
6a	Tol	.007	2.4	450
6b	Tol	0.90	>8500	--
7	THF	0.72	--	8500
5a	THF	<0.001	1.6	39
5b	THF	0.70	>8500	--
6a	THF	<0.001	1.8	43
6b	THF	0.70	>8500	--

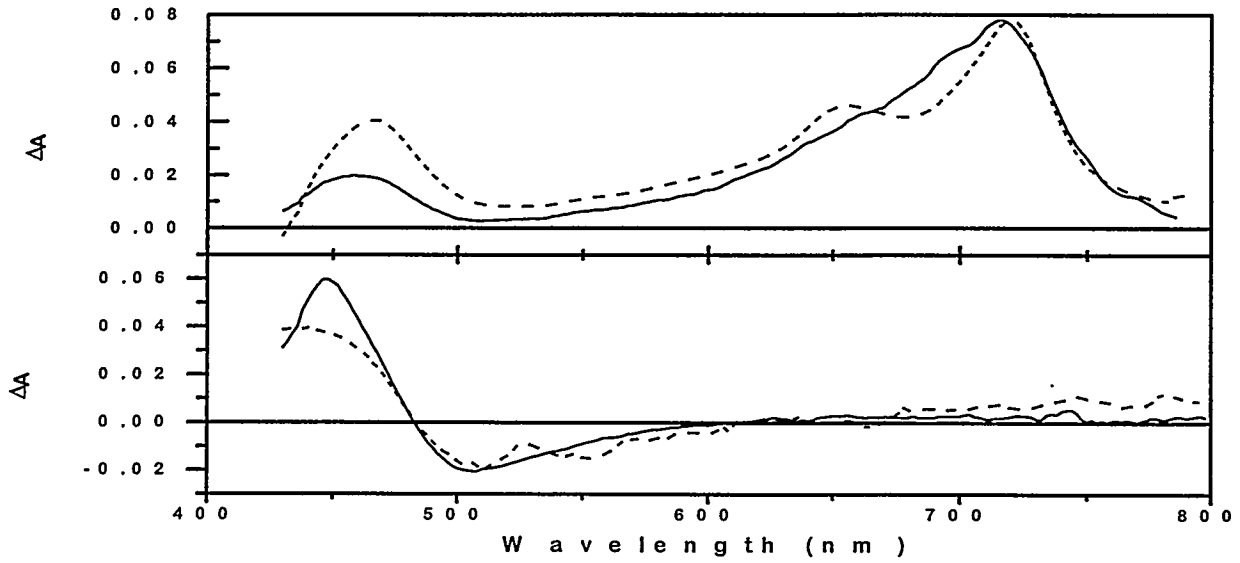


Figure 1: Top: Transient absorption spectra of 5a(——) and 6a(------) in toluene. Bottom: Transient absorption spectra of 5b(——) and 6b(------) in toluene. All spectra were recorded 20 ps after excitation with a 140 fs pulse at 412 nm.

References

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