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Enhanced Energy Transfer between Aromatic Chromophores Bound to Hydrophobically Modified Layered Zirconium Phosphate Suspensions

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α-Zirconium phosphate intercalated with butylamine hydrochloride (BAZrP) was found to enhance singlet–singlet energy transfer between organic chromophores. Enhanced energy transfer among donor and acceptor pairs is of practical importance in solar energy harvesting, efficient degradation of pollutants, and supramolecular photochemistry.[1] Covalent linking of the donor–acceptor pairs can result in enhanced energy transfer.[1c] Alternatively, donors and acceptors can be assembled at macromolecular surfaces to achieve high local concentrations of these species for enhanced energy transfer.[1d] α-Zirconium phosphate (α-ZrP) is suitable for such an assembly of donors and acceptors. α-ZrP platelets are nearly 7 Å thick and carry negatively charged phosphate groups on the surface.[2] Adsorption of a cationic surfactant such as butylamine hydrochloride (BA) enhances the binding of hydrophobic chromophores to these anionic surfaces. Previous results from this laboratory[3] demonstrated the high-affinity binding of anthryl- and pyrenylalkylamine hydrochlorides (Chart 1) to BAZrP. At high surface coverages, both static and dynamic excimers were formed. At low coverages, only monomer emission was observed. Therefore, binding to BAZrP can result in high local concentrations which can be used to promote bimolecular photoprocesses. We now report the enhanced energy transfer among naphthyl, pyrenyl, and anthryl probes (Chart 1) bound to BAZrP. Without α-ZrP or BA, energy transfer was very weak or absent. No energy transfer was observed when these probes bind to DNA or to proteins.[4] The current method is an alternative to the covalent linking of donors and acceptors mentioned above.

1-Naphthalenemethylamine hydrochloride (NMAC) was used as the donor, and either 9-anthracenemethylamine hydrochloride (AMAC) or 3-(1-pyrenyl)butylamine hydrochloride (PBAC) served as the acceptor (Chart 1). The emission maxima of these probes in the presence of BAZrP (0.008% by weight[5]) are as follows: NMAC, 325 and 337 nm; PBAC, 376, 395, 418, and 440 nm; AMAC, 392, 416, and 465 nm.[6] Therefore, the donor and acceptor emission bands are well separated. Quenching of the donor emission and sensitization of the acceptor emission can be followed conveniently. Micromolar to submicromolar concentrations of the acceptor were enough to achieve efficient quenching of the donor emission and simultaneous sensitization of acceptor fluorescence. Several lines of evidence establish the enhanced energy transfer among these donor–acceptor pairs.

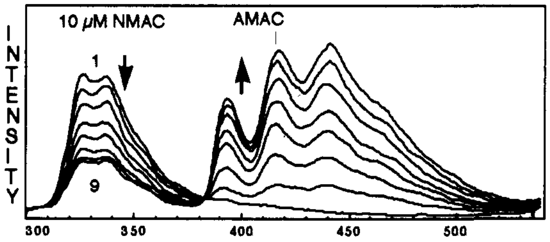
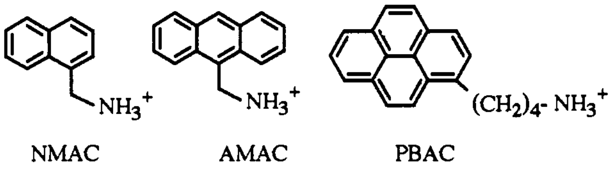


Figure 1. Fluorescence spectra of NMAC (10 μM) and AMAC (0–6.36 μM) in the presence of BAZrP (0.008% by weight). The spectra correspond to 0, 0.99, 1.87, 2.65, 3.35, 3.98, 4.54, 5.5, and 6.36 μM of AMAC.

Chart 1. Structures of the Donor and Acceptor Molecules Used for the Energy-Transfer Experiments



The gradual quenching of NMAC emission by AMAC and simultaneous sensitization of anthryl emission is shown in Figure 1. Aqueous NMAC solutions (10 μM) were excited at 280 nm in the presence of BAZrP (0.008% by weight). Concentration of the donor was kept constant, while that of the acceptor has been increased from 0 to 6.36 μM. Intensity of the naphthyl band at 337 nm decreases with increasing AMAC concentration. Concomitantly, the intensity of AMAC emission increases, and an isoemissive point at 385 nm is evident in the spectra. The isoemissive point is a clear indication of energy transfer from the donor to the acceptor. Without the donor, even at the highest concentration of the acceptor, direct emission from the acceptor was very weak,[7] indicating the efficient sensitization of acceptor emission by the donor. Energy transfer from NMAC to AMAC was also probed by recording the excitation spectra. The excitation spectra, obtained by monitoring the AMAC emission at 420 nm, showed intense bands at 270, 283, and 296 nm, corresponding to NMAC absorption bands (supplementary material, page 1). These bands were not detectable in AMAC excitation spectra when recorded in the presence or in the absence of BAZrP. Therefore, the excitation spectra clearly establish the initial light absorption by NMAC and subsequent emission by AMAC. Similar excitation spectra were observed with NMAC (50 μM) as the donor and PBAC (1 μM) as the acceptor in the presence of BAZrP (0.008%) (supplementary material, page 2). Thus, when PBAC was used as the acceptor instead of AMAC, NMAC emission was quenched by PBAC, which resulted in sensitized PBAC emission. No such energy transfer from NMAC to PBAC or from NMAC to AMAC was observed without BAZrP at these low acceptor concentrations.

A plot of I_0/I vs the acceptor concentration, where I and I_0 are the intensities of the donor emission at 337 nm with and without

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(1) (a) *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; VCH Publishers: New York, 1991. (b) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis Horwood: New York, 1991. (c) Gust, D.; Moore, T. A. In *Advances in Photochemistry*; Volman, D., Hammond, G., Neckers, D., Eds.; Wiley: New York, 1991, Vol. 16. (d) Baral, S.; Fendler, J. H. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part B, pp 541. Armitage, B.; Klekotka, P. A.; Oblinger, E.; O'Brien, D. F. *J. Am. Chem. Soc.* **1993**, *115*, 7920.

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(4) Kumar, C. V.; Asuncion, E. H. *J. Am. Chem. Soc.* **1993**, *115*, 8547. Kumar, C. V.; Tolosa, L. M. *J. Phys. Chem.*, in press.

(5) The estimated surface area of BAZrP is 100 m^2/g, and it is capable of exchanging 54 mM of cationic sites (ecg) per gram. The concentrations are expressed as % by weight or as mM ecg.

(6) These emission maxima are ~5 nm red-shifted with respect to the probe solutions in water.

(7) The direct emission from AMAC (6.4 μM) when bound to BAZrP (0.008%) was at least 1000 times weaker than the observed sensitized emission.

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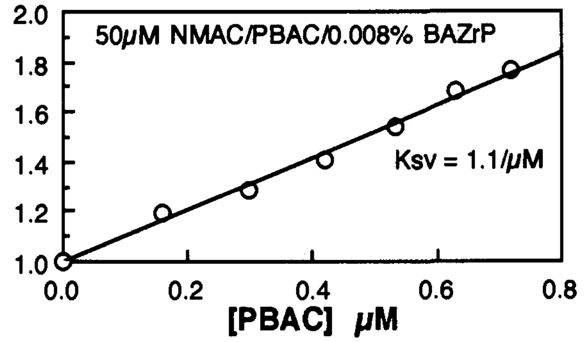

Figure 2. Stern–Volmer plot for the quenching of NMAC (50 μM) fluorescence intensity by PBAC in the presence of BAZrP (0.008%).

Table 1. K_{SV} Values for the Quenching of Donor Fluorescence in the Presence of BAZrP (0.008%)

donor	acceptor	[donor] (μM)	K_{SV} ($\times 10^6$ M^{-1})	K'_{SV} ($\times 10^6$ m^2/M)
NMAC	AMAC	20	0.1	0.8
NMAC	PBAC	20	0.7	5.6
NMAC	PBAC	50	1.1	8.8

the acceptor, resulted in linear plots (Figure 2). The quenching constant (K_{SV}) was evaluated using the Stern–Volmer equation.[8] NMAC fluorescence (50 μM) was quenched by PBAC in the presence of BAZrP (0.008%) with a high efficiency (Figure 2). It is noteworthy that only submicromolar concentrations of the acceptor were enough to quench nearly 50% of the donor emission. The Stern–Volmer quenching constants were calculated using the number of moles of acceptor adsorbed per square meter of BAZrP surface (100 m^2/g)[9] (Table 1) as well as bulk concentrations. Quenching constants shown in Table 1 are much larger than the values anticipated under diffusion-controlled energy-transfer conditions. The quenching constants depend upon the donor concentration, the nature of the donor–acceptor pair, and BAZrP concentration. For example, the K_{SV} value for the quenching of NMAC emission by PBAC was 7 times greater than that for quenching by AMAC at the same donor and BAZrP concentrations. Application of Forster's equation to the above data gave Forster radii in the range of 25–30Å.[10,11]

The effect of BAZrP on the energy transfer from NMAC to PBAC is illustrated in Figure 3. NMAC concentration was kept high (50 μM) with respect to PBAC concentration (0.5 μM). Samples were excited at 288 nm such that direct light absorption by PBAC was quite small. Addition of BAZrP quenches NMAC emission and simultaneously sensitizes PBAC emission. A plot of I_s/I_0 as a function of BAZrP concentration was linear (Figure 3), where I_s and I_0 are the acceptor fluorescence intensities at 376 nm in the presence and absence of BAZrP. Without BAZrP, only weak emission can be detected from PBAC. PBAC emission increased nearly 35-fold when BAZrP concentration was increased from 0 to 0.45 mM. The corresponding Stern–Volmer quenching plots, constructed by monitoring NMAC emission at 337 nm, indicate that nearly 80% of the donor emission was quenched, even though the donor concentration was 100 times that of the acceptor. Therefore, ground-state association between the donor and the acceptor cannot explain the enhanced energy transfer. It is very likely that donor-to-donor energy migration takes place and the excitation is transferred over a long distance to the acceptor.[11] Such migration is unusual in fluid solutions and has been observed in crystals, polymeric samples, and Langmuir–Blodgett films.[11] When the donor-to-acceptor ratio was further increased to 1000:1 (20 μM NMAC, 0.02 μM PBAC), nearly 56% of the donor emission was still quenched in the presence of BAZrP (0.004%). Therefore, donor-to-donor migration of excitation is perhaps a key feature in these systems. Ground-state association alone cannot explain the high quenching efficiencies when the donors are in large excess. Therefore, energy migration from donor to donor (antennae effect) is essential to explain the current data.[11] Acceptors and donors may form aggregates at the BAZrP surface, and energy transfer may occur in these aggregates. These results clearly highlight the utility of BAZrP in controlling the photoprocesses of organic molecules.

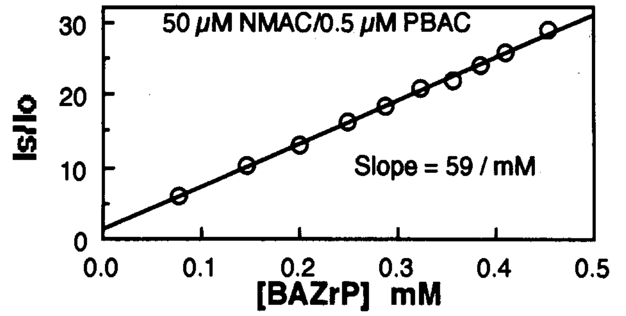

Figure 3. Plot of the ratio of the intensities of the sensitized (I_s) to direct (I_0) fluorescence from PBAC in the presence of NMAC as a function of BAZrP concentration, monitored at 420 nm.

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Supplementary Material Available: Excitation spectra of NMAC (20 μM) and AMAC (6 μM) with BAZrP (0.008%, dotted line) and without BAZrP (solid line); Excitation spectra of NMAC (50 μM) and PBAC (1 μM) with and without BAZrP (0.008%), as indicated (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(8) Steady-state data were plotted using the equation $I_0/I = 1 + K_{SV}[Q]$, where [Q] is the concentration of the acceptor and K_{SV} is the quenching constant. Only steady-state data are presented here due to the multicomponent decay of the donor and the acceptor excited states in the presence of BAZrP.

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(10) The modified Forster equation in two dimensions (2D) is $I/I_0 = 1 + (d_0/d)^4$, where d is the distance of separation between the donor and the acceptor. The constant d_0 is the Forster radius in 2D. We estimated d as one-half of the average distance of separation between the donors: Kuhn, H. ; Mobius, D. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 620.

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