

Photoinduced Electron Transfer Between Fullerenes, Fullerene Clusters, and bis- triphenylamine Substituted Oligimers

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Intermolecular photoinduced electron transfer (PET) between fullerenes, fullerene clusters, and bis-triphenylamino polyenes that function as electron donors was measured in dilute solution. The temporal behavior of the system was followed by measuring transient absorption via step scan Fourier transform spectroscopy following a 5 ns, 2 mJ, 532 nm laser pulse (Figure 1).

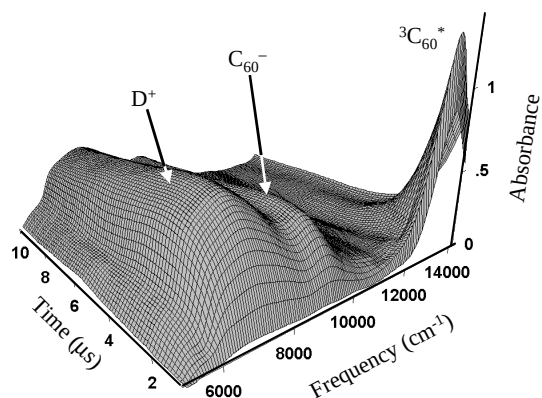
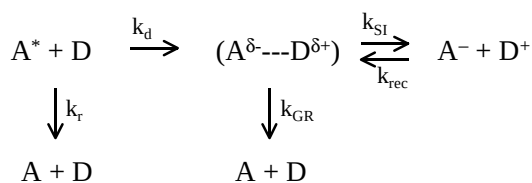


Figure 1. A time and frequency resolved photo-induced absorption (PIA) spectrum from the step-scan FT system for a solution of 0.25 mM C₆₀ and 0.25 mM bis-(triphenylamino) ethene (n=1) in a 1:1 o-dichlorobenzene / benzonitrile solvent mixture. The broad, near IR band which peaks at 6750 cm⁻¹ is the intervalence band of the singly charged donor cation.

For the ethene and butadiene, PET in the dilute solutions was diffusion limited and a kinetic treatment was developed that enables determination of the quantum efficiency for formation of solvated ions from the intermediate, Φ_{SI}. Because the system is diffusion limited, all intermediates in the actual reaction mechanism can reasonably be approximated with a single intermediate as in Scheme I and Φ_{SI} = k_{SI} / (k_{SI} + k_{GR}) where k_Q is the psuedo-first order quenching rate constant.



Scheme I. Simplified mechanism with a single intermediate for diffusion limited PET. A = acceptor (fullerene) and D = donor (bis-triphenylamino polyene).

Because of the high signal to noise and remarkably smooth temporal data in the transient absorption spectra generated via step-scan FT spectroscopy, this first derivative plot has a well determined slope and provides convenient method for extracting Φ_{SI} (Figure 2).

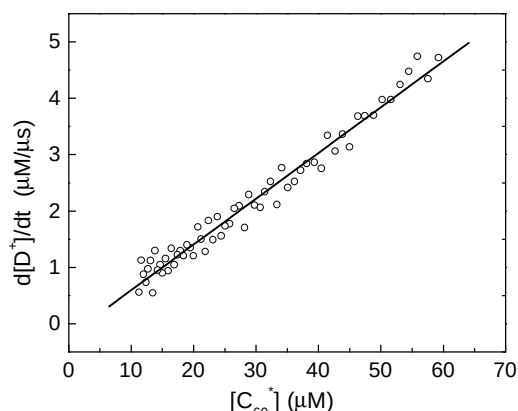


Figure2. A plot of d[D⁺]/dt vs. [³C₆₀*] using D⁺ data corrected for back electron transfer. The slope equals k_d Φ_{SI} [D] or k_Q Φ_{SI}.

For comparison purposes, data for triphenylamino triphenylphosphino substituted polyene donors was also acquired. The intermolecular PET between these donors and C₆₀ exhibits non-diffusion limited kinetics with a distinctly non-exponential decay of the ³C₆₀ absorption band (Figure 3).

Dynamic light scattering measurements indicate that this behavior correlates with the formation of large (diameter > 750 nm) aggregates in solution. Additionally, ion signal rise times are faster than the diffusion limit which indicates photoinduced electron transfer is taking place in aggregates containing both donor and C₆₀.

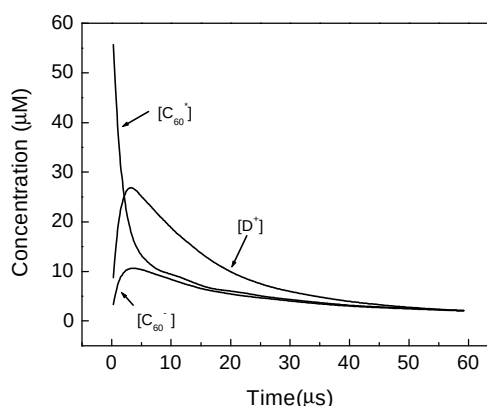


Figure 3. Transient absorption spectrum of triphenylamino triphenylphosphino ethene + C₆₀ in benzonitrile. The ³C₆₀* absorption band decay is distinctly non-exponential and exhibits kinetics that are very different than the equivalent non-phosphorous containing donor.