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INTRODUCTION

In most polynuclear hydrocarbons such as anthracane and its derivatives e.g. CH_3, CN, Cl, OH compounds, photochemical reactivity is in direct competition with prompt fluorescence from the lowest singlet excited states. Accordingly, as reactivity proceeds the quantum yield of host emission decreases and products (guests) having different luminescence properties are formed. Thus the singlet exciton through its properties such as spectral distribution of emission, diffusion coefficient and lifetime may be considered an "active probe" for following such reactions. The triplet exciton on the other hand is not much involved in the reactivity of these systems and through its analogous properties is an efficient "passive probe" that allows us to study changes in the structure and chemical composition of the host–guest system as reactivity proceeds. The study of "dynamic" host–guest systems where the host : guest ratio is continually changing has its foundation in the vast literature available on similar "static" systems.[1] It does, however, possess the advantage that since the volume change following most of the topochemically controlled reactions is small the molecular "mismatch" in the dynamic systems is of the same order as in isotopically-substituted systems e.g. anthracene-d_{10} in anthracene-h_{10} and appreciably less than in several static systems e.g. tetracene in anthracene. This offers significant advantages in energy-transfer studies as indicated by Powell and co-workers.[2]

In this contribution attention will be focussed on the use of singlet and triplet excitons in following the photo-reactivity of anthracene crystals and prompt and delayed fluorescence spectra and lifetime studies will be described.

PROMPT FLUORESCENCE

The fluorescence spectra and lifetimes of ultra-pure anthracene crystals subjected to photodimerisation ($\lambda_{exc} = 365 \pm 10$ nm in N_2) are significantly different to those of freshly grown crystals whereas surface photo-oxidation ($\lambda_{exc} = 365 \pm 10$ nm in air or O_2) does not appreciably change the spectral characteristics in the low energy region 410 nm–500 nm). A broad unstructured *a* polarized emission with a maximum at 475 nm is observed in photodimerized samples; it is also present as a weak feature in the spectrum of the so-called "pure" parent crystal) together with the characteristic anthracene progression at 406, 421 and 444 nm that contains broad, vibronic maxima and is essentially unpolarized. These emissions are attributed, respectively, to traps which are interpreted as anthracene "incipient" dimers and single, displaced anthracene molecules in close proximity to the stable photodimer. The long and short components of the time dependent emission observed are consistent with such an assignment. For the singlet exciton, therefore, two trap depths may be assigned to ~ 4000 cm^{-1} and ~ 300 cm^{-1} respectively with a distribution for the latter extending to around ± 50 cm^{-1}. This shallow trap has been previously identified[3] and recently a detailed study of shallow traps generated and consumed during photodimerisation has been completed.[4] The broad unstructured emission observed in fresh crystals at ~ 475 nm may be enhanced by mechanical deformation in such a way as to introduce a concentration of the "new" polymorphic modification of anthracene.[5] Photodimerisation is enhanced in such crystals. The significance of these observations in the light of the possible configuration and conformation of "molecular pairs" will be considered.[6]

Photodimerisation in impure crystals e.g. containing 2-OH A forms the hetero-dimer and is in competition with the generation of the di-*p*-anthracene. The relative efficiency of dimer generation depends on the depth and concentration of the participating traps.

DELAYED FLUORESCENCE

Steady-state and temporal dependencies of delayed fluorescence as a function of temperature have been measured for a range of high purity anthracene crystals and crystals subjected to photodimerization following direct excitation of triplets with weakly absorbed red light of low and high intensity.[7] The highest technical lifetime measured from delayed fluorescence is ≈ 27 ms for sealed melt grown crystals; this value shows an appreciable reduction upon cleavage. Trap saturation is apparent over the entire temperature range, 350–4 K and the study indicates that even at high temperatures the triplet exciton is localised in deep structural traps of low concentration ($\approx 10^{-11}$ M/M). Even in the purest samples available the triplet exciton lifetimes reflect the fact that the routes controlling triplet exciton decay are extrinsic via trapping sites. During photodimerisation the deepest traps *ca.* 4,700 cm^{-1} deep are removed, whereupon other shallower traps appear.

PHOTOCHEMICAL "CYCLE"

It is apparent from the studies of both singlet and triplet excitons that there are (a) a range of shallow traps (b) a distribution of deeper traps present as a result of structural disorder in anthracene crystals. The ones of particular importance in the photodimerization of anthracenes are the deeper ones which correspond to various geometrical arrangements of anthracenic, molecular pairs (a) at dislocations (b) in the new polymorphic modification (c) at interfaces. The precise configurational and conformational properties of these are at present undetermined but useful analogies with other systems may be drawn.

By studying a range of anthracenic compounds and the changes brought about by irradiation in different environments we have established a photochemical cycle where the main reactions are topotactic and reversible.[8] The pivotal role of a green emitting transient species in this cycle has been established. Although its identity has not been conclusively proven, it is similar in its properties to the "incipient" dimer observed in our other studies.

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