Recent Advances in the Photochemistry of Cyanine Dyes

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Abstract

In this presentation I intend to cover some of the highlights of the research carried out in our group since the last meeting in this series, in Victoria, BC, in 1997. Three topics of interest to us have been:

(a) relaxation dynamics of photoexcited cyanine dyes;
(b) characterization of the cyanine chromophore using hyper-Rayleigh scattering spectroscopy; and
(c) formation of complexes in solution between cyanine dyes and other compounds of photographic interest.

Our studies have focused on the homologous series of symmetrical N,N'-diethyl-2,2'-dithiacyanine dyes, as representative of dyes of photographic utility.

Relaxation dynamics

For most of the past decade, the paradigm for discussing relaxation dynamics of photoexcited cyanine chromophores has been that provided by the computational studies of Mommichioli, Ponterini and co-workers[1]. They described the potential surface for relaxation in terms of computational studies on simple streptocyanine cations, which were chosen as a model system in order to reduce the high level calculations to feasible size. We have studied more realistic systems, primarily the N,N'-diethyl-2,2'-dithiacarbocyanine cation at the AM1 level of semi-empirical modeling. Among our results, we found a dramatic difference between the HOMO electron density surface for the dithiacarbocyanine and for the streeptocyanine of the same chain length. In the former case, there are two degenerate HOMO's localized on each fused heterocyclic ring system of the molecule; in the latter case there is a single HOMO delocalized over the entire chromophore. As a result we counsel caution in extrapolating from the results on streptocyanines to more complex, more realistic systems.

Our initial experimental probes of the N,N'-diethyl-2,2'-dithiacyanine dye series involved laser flash photolysis followed by time-resolved absorption spectroscopy[2,3]. One of our first results was that in methanol solution, fluorescence decays for the dyes of the series were singly exponential, but ground state recovery was bi-exponential[2]. The shorter recovery time was the same as the fluorescence decay time. Owing to operation of the longer component,

significant transient bleaching could be observed up to 10 ns after excitation with a 30 ps pulse. Since absorption of ground state photoisomer is close to congruent with that of the starting isomer, we could not assign the bleaching to known isomerization processes, and instead chose to assign it to intervention of (mostly isomerized) triplet states. This assignment was confirmed by detection of the known[4] absorption of the *cis*-triplet derived from the dithiacarbocyanine dye.

Recently reported results[5] have implicated bond alternation, as well as torsional relaxation in the deactivation of photoexcited cyanine dyes. Accordingly, establishment of the bond-alternant structure should become increasingly rate-determining for internal conversion from S_1 to S_o with increasing polymethine chain length. Like the work of Mommichioli, these *ab initio* studies were carried out with streptocyanine models. Experimental support for the extension of this idea to, e.g., the more complex dithiacyanine dyes, comes from studies on the solvent dependence of internal conversion dynamics[3]. We found that solvent coupling to internal conversion decreases with increasing chain length. Thus for short chain-length dyes, the torsional relaxation which effects massive disruption of the dye's solvation shell is rate-determining (as envisioned by Mommichioli), but as the chain length becomes greater, coupled carbon-carbon stretching modes, which have little impact on solvation, become more important.

Why should we expect symmetrical cyanine chromophores to undergo molecular distortions leading to bond alternation? One reason can be seen in the nature of the dye HOMO; bond alternation is a form of Jahn-Teller distortion, breaking the degeneracy of the two HOMO levels. Coherent stretching along the polymethine chain thus causes the dye to oscillate between bond-alternant *extrema*, each of which takes on the character of one of the monopolar contributing resonance structures for the dye.

The geometry of the excited dye molecule at the bottom of the relaxation funnel, i.e., in the fully relaxed S_1 state, must be the same as for the ground state molecule at the top of the activation barrier for ground state *cis-trans* isomerization[1]. So in calculations at the AM1 level of theory, we estimated the energy barriers associated with ground state isomerization about a low order bond (bond order ca. 1.2) and about a high order bond (bond order ca. 1.8), in the bond alternant extreme geometry for the

dithiacarbocyanine cation. The enthalpy barrier for isomerization about the low order bond was ca. 13 kcal/mol, while the barrier was about 54 kcal/mol for isomerization about the high order bond. The former estimate is in good agreement with experimental measurements[6] for the activation energy for *cis-trans* isomerization of this dye in the ground state.

Hyper-Rayleigh scattering spectroscopy

It is thus plausible that bond alternation, as proposed by Schlegel and co-workers[5] for simple streptocyanine dyes, may be involved in the relaxation processes of both ground state and excited dyes of photographic interest. Crystal structure determinations do not support the idea for, e.g., the dithiacarbocyanine dye[7], in the solid state. To test the idea, we needed a probe which would detect distortion away from C_{2v} symmetry in solution. Hyper-Rayleigh scattering (HRS) is such a probe. It involves incoherent generation of second harmonic radiation under not very intense optical fields, and is extremely sensitive to transient deviations from symmetry, which enhance the dipole moment difference between ground and excited states[8]. Experimental work[9] revealed that large HRS signals could be detected from methanol solutions of the symmetrical dithiacyanine, dithiacarbocyanine and dithiadicarbocyanine dyes (but not the dithiatricarbocyanine analog). These results were indicative of molecular hyperpolarizabilities comparable to those of the commonly used standards[10], *m*- and *p*-nitroaniline, and, in turn, implicated significant transient deformation from C_{2v} symmetry in these dye molecules.

However, the cyanine cations are monopolar; how could they exhibit differences in dipole moment between ground and excited state, as required by the two-level model of hyperpolarizability[10]? We hypothesized that ground and excited state dipole moments were properties of the cyanine cation-solvation shell system, rather than just the dye molecule. Accordingly, the HRS signal should exhibit a substantial solvent effect. In fact, the HRS signal from the dithiacarbocyanine cation, unlike that of the standards, disappears entirely, when it is probed in non-polar toluene, instead of polar methanol.

From these results we infer the importance of strategies to inhibit deformation leading to bond alternation as critical to avoiding energy wasting in cyanine dye sensitized photosystems. Incorporation of the individual dye molecules into supramolecular architectures, e.g. J-aggregates, in which the coherent carbon-carbon stretches of the polymethine chain are damped out, may be principal among such strategies. We are also undertaking preliminary work to see if HRS is a useful analytical tool for monitoring adsorption of dyes to silver halide nanoparticles and emulsion grains.

Complex formation

The initial step in establishing such a sensitizing supramolecular architecture comprising cyanine dyes may be the formation of 1:1 and 1:2 complexes in solution with other dyes, supersensitizers, or other photographic addenda, prior to adsorption of the dyes onto the silver halide grain. In particular the supersensitizing interactions between dyes and a number of stabilizers have been reported[11,12], though explanations have usually been couched in terms of effects of the stabilizers on the solid state physics of the silver halide[11]. These interpretations are sometimes inconsistent, and do not readily explain order of addition effects[13]. Alternative mechanisms involving incorporation of the stabilizers into dye aggregates have, however, been proposed[12].

We have found[14] that a variety of heterocycles form 1:1 and, in some cases, 1:2 complexes in solution with representative cyanine dyes, including the symmetrical dithiacarbocyanine and dithiadicarbocyanine cations. These results have been extended[15] to include the supersensitizing stabilizers, 2-methylbenzimidazole (**MeBI**), 2-mercaptobenzoxazole (**MBO**) and tetraazaindene (**TAI**). These complexes can be detected fluorimetrically, and usually correspond to an enhancement of the dye fluorescence. This enhancement can be elucidated by time-resolved laser flash spectroscopy, where a bi-exponential decay of the emissive state is observed; the shorter decay time corresponds to the fluorescence decay of the free dye. Extended radiative lifetime, such as we observe on complex formation, has been shown in numerous studies to correlate with enhanced efficiency of spectral sensitization in silver halide systems.

Computational studies at the AM1 level of theory coupled with MMFF (or SIBYL) molecular mechanics have suggested that such complexes embody a sandwich geometry, with (primarily) electrostatic pattern recognition and (secondarily) charge transfer providing the driving forces for complexation[14,15]. Similarly, electrostatic pattern recognition can drive the adsorption of the complexes, epitaxially to the silver halide surface. We propose, based on our hypothetical structures for complexes of photographic interest, their preferential adsorption to the silver bromide (111) surface.

The work suggests that the supersensitizing role of stabilizer molecules can be discussed in terms of dye-stabilizer complex formation with: (a) preferential adsorption of complexes to the silver halide surface; (b) nucleation of dye aggregates[13]; (c) concomitant incorporation of the complex in a J-aggregate, leading to disruption of the J-aggregate structure[12]; and/or (d) perturbation of dye energy levels owing to the charge-transfer character of the complexes.

Acknowledgment

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Biography

Prof. M. R. V. Sahyun received his Ph.D. in chemistry from the University of California at Los Angeles in 1963. He spent an NIH postdoctoral fellowship at California Institute of Technology to learn photochemistry, and also had a short assignment with the United States Public Health Service in its environmental science program. He joined 3M in 1966, where he worked in various aspects of imaging science, including silver halide, photothermographic, electro-photographic, and photopolymer technologies. During the course of his 30 year career there, he was awarded Fellowship and Senior Membership in IS&T, having served the Society in various, primarily conference organizing, capacities. Since 1996, he has been Adjunct Professor of Chemistry at University of Wisconsin—Eau Claire and Editor of the *Journal of Imaging Science and Technology*.