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Dipolar Excitonic States of Oligo-Anthrylenes[†]

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Photoexcitation of dimeric, trimeric, and tetrameric oligomers of anthracene in benzene results in the formation of relaxed S_1 excitonic states with dipole moments of 6.9, 8.0, and 9.1 D respectively. Dipole reversal occurs with a relaxation time in the range of 8 ± 2 ps and is driven by a combination of fluctuations in the solvent environment and torsional motion about the central sigma bonds. The excitonic interaction at any given moment in time involves mainly only two neighboring anthracene moieties rather than delocalization over all chromophoric units.

1. Introduction

The relaxed S_1 state of 9,9′-bianthryl has been the subject of a large body of experimental and theoretical research since the initial finding by Schneider and Lippert that the fluorescence of bianthryl was strongly solvent-dependent.[1,2] Despite the underlying D_2 symmetry, the fluorescence data clearly indicate an excited-state dipole moment close to 20 D in medium to high polarity solvents which corresponds to close to complete, center-to-center charge separation. The symmetry breaking required has been rationalized for polar solvents in terms of vectorial pinning and stabilization of a charge-separated state by the preferential orientation of the dipolar solvent molecules around the charged centers. The resulting charge-separated state is considered to have a minimum-energy configuration with an orthogonal (90°) relative orientation of the anthryl moieties.[3,4] To explain the fluorescence results, the persistence time of the charge separated state must be considerably longer than the dielectric relaxation times of the solvents used, i.e., tens of picoseconds.

Subsequent time-resolved microwave conductivity (TRMC)[5−7] and electrooptical emission (EOEM)[8] measurements have shown that the relaxed S_1 state of bianthryl has a net dipolar character even in weakly (quadru)polar solvents such as benzene and paradioxane and in nonpolar saturated hydrocarbons. In this case, it has been suggested that torsional relaxation after initial local excitation results in the formation of a delocalized excitonic state which may have a large polarizability because of the admixture of charge resonance states. Lifting of the degeneracy of the charge resonance states resulting in a net (transient) dipole moment has been attributed to local density and/or structural fluctuations in the solute environment.[7] In contrast to the charge separated state formed in polar solvents, the excitonic state of bianthryl is found to have a much lower dipole moment of ca. 8 D and undergoes rapid flip−flop dipole reversal on a time scale of a few picoseconds in saturated hydrocarbon solvents and close to 10 ps in benzene and dioxane.[6,7]

A study of the fluorescence of the longer oligomers of anthracene in Figure 1 has shown them to display properties qualitatively similar to those of bianthryl,[9] i.e., only a slight, if any, solvent dependence in weakly polar media but large bathochromic shifts in medium to high polarity solvents. On the basis of the bathochromic shifts, dipole moments of 20, 27, and 42 D have been estimated for the relaxed S_1 states of the dimer, trimer, and tetramer, respectively. The tetramer was found to display in general a much greater propensity toward charge separation than the trimer even in low-temperature polar glasses.

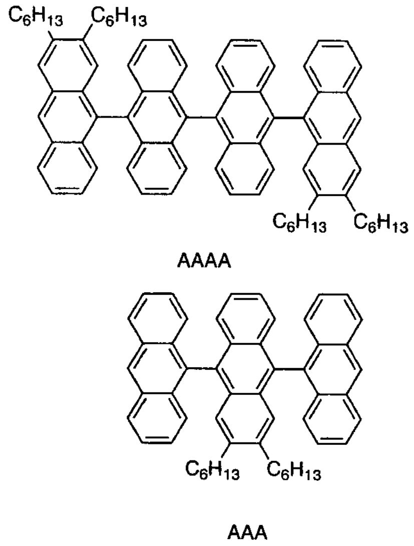

Figure 1. Molecular structures of the compounds studied together with the pseudonyms used in the text.

In the present work, we have carried out TRMC measurements on flash-photolyzed benzene solutions of the anthracene oligomers with the aim of seeing if the trend which is apparent from the optical properties mentioned above is paralleled in the properties of the excitonic states formed in a weakly polar solvent.

2. Experimental Section

The molecular structures of the solute molecules investigated are shown in Figure 1. Dilute solutions (ca. 10^{-4} M) in benzene

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TABLE 1: Lifetimes, τ, of the S_1 States of the Compound and the Parameters ΔIm and ΔRe Obtained from Fits to the TRMC Transients Shown in Figure 2 together with the Values of the Dipole Relaxation Times, Θ_*, and Dipole Moments, μ_*, Derived using Equations 3 and 4

compound[a]	τ (ns)	ΔIm (10^{-60} C^2 m^2)	ΔRe (10^{-60} C^2 m^2)	Θ^*[b] (ps)	μ^*[c] (D)
A	4.3	<20	52		0
AA	11.7	202	429	7.9	6.9
AAA	9.2	232	620	6.3	8.0
AAAA	9.8	395	704	9.4	9.1

[a] Benzene solutions at root temperature. [b] Absolute error ±2 ps. Relative error ±10%. [c] Absolute error ±1 D. Relative error ±5%.

(Fluka, UV spectroscopic grade) were deaerated by purging with CO_2. The optical absorption spectra were found to be identical to those reported previously[9] and displayed the well-defined vibrational structure characteristic of local excitation of anthracene moieties.

The lifetimes of the relaxed S_1 states were measured by time-resolved fluorescence measurements using a 0.8 ns pulse of 337 nm light from a PRA LN1000 N_2 laser. The fluorescence was detected using a Photek PMT-113-UHF channel-plate photomultiplier with a rise-time of 150 ps. The lifetimes obtained are given in Table 1.

For TRMC experiments the solutions were contained in a resonant cavity and irradiated with the 7 ns 308 nm pulse of a Lumonics HyperEx 400 laser. The power output of the laser was monitored routinely using a Scientec 365 power meter, and the fraction of photons entering the cell was determined using an actinometry solution of 4-(*N*,*N*-dimethylamino)-4′-nitrostilbene (DMANS) in benzene. A full description of the TRMC technique has been given elsewhere.[10,11] For a given solution, the transient change in microwave power reflected by the cavity on flash-photolysis, ΔR, was monitored at the half-power frequencies of the resonance, f_- and f_+. By addition and subtraction of the two transients, the sum and difference transients, $\Sigma_\pm$ and $\Delta_\pm$, are obtained which are separately related to changes in the imaginary (dielectric loss), ϵ'', and real (dielectric constant), ϵ', permittivity of the solution, respectively.[7,11] The oscillatory nature of the $\Delta\epsilon'$ transients results from the nondissipative nature of changes in dielectric constant.

3. Results and Discussion

TRMC transients resulting from changes in both the imaginary (dielectric loss), ϵ'', and real (dielectric constant), ϵ', components of the complex permittivity on flash photolysis of benzene solutions of anthracene and the oligomeric anthrylene compounds are shown in Figure 2. The dramatic difference between the monomer and the oligomers is immediately apparent and clearly demonstrates the occurrence of electronic coupling between anthracene moieties and the excitonic nature of the relaxed S_1 state of the multichromophoric compounds. The change in the dielectric loss is a definitive indication that the relaxed S_1 state has a net dipolar character with a dipole moment, μ_*, which has a persistence (or relaxation) time, θ_*, on the order of, or longer than, the reciprocal radian frequency of the microwaves used ($1/\omega = 17$ ps). For all oligomers, a large concomitant change in ϵ' is observed. This has been explained in the case of bianthryl by the occurrence of rapid, intramolecular dipole reversal on a time scale comparable with $1/\omega$ and much shorter than that expected for rotational diffusion.[6,7] The same explanation is considered to apply for the trimer and tetramer.

Quantitative convolution fits to the $\Delta\epsilon''$ and $\Delta\epsilon'$ transients, incorporating the S_1 lifetimes given in Table 1, yield values of the parameters ΔIm and ΔRe which are also listed in the Table. Taking the ground-state dipole moments of the present compounds to be zero and the changes in both ϵ'' and ϵ' to result from dipole relaxation, these parameters are related to μ_* and θ_* by[7]

$$\Delta\mathrm{Im} = \omega\theta_*\mu_*^2/[1 + (\omega\theta_*)^2] \quad (1)$$

$$\Delta\mathrm{Re} = \mu_*^2/[1 + (\omega\theta_*)^2] \quad (2)$$

The dipole relaxation time is seen to be given simply by

$$\theta_* = \Delta\mathrm{Im}/\omega\Delta\mathrm{Re} \quad (3)$$

and the values obtained are listed in Table 1.

Although the differences in θ_* for the three compounds are considered to be outside the relative error limits of ± 10%, the values all lie within the range of 6−10 ps. We conclude that the same mechanism for dipole relaxation is operative and that the solubilizing *n*-hexyl substituents in the trimer and tetramer have a negligible effect on the relaxation process. The mechanism of dipole relaxation will be discussed after first considering the processes leading to the formation of the excitonic state, *E*.

In the case of bianthryl, the two anthracene moieties are orthogonal in the ground state. Although electrostatic coupling may occur via the short-axis transition dipole moment of the individual anthryl moieties, electronic coupling should be negligible. Photoexcitation results therefore initially in the formation of the locally excited (LE) Franck−Condon state, in which the energy is localized on a single anthracene moiety. Subsequent torsional motion about the central sigma bond results in a deviation from the orthogonal orientation. Electronic coupling between the two anthracene units can then occur and results in the formation of a delocalized excitonic state, *E*. The combined effects of the electronic interaction and the steric repulsion between the hydrogen atoms at the 1,1′ and 8,8′ positions result in the excitonic state having shallow minima for relative angles of approximately 60 and 120°.[3,12−16] For angles other than 90°, charge resonance states, CR, can contribute to *E* and result in a large electronic polarizability. For the isolated molecule, the CR states are degenerate because of the D_2 symmetry, and no net dipole moment should result. The fact that a net dipole moment is observed for solutions of bianthryl, even in nonpolar or weakly polar solvents, is attributed to density and structural fluctuations in the environment of the solute molecules which break the symmetry of the overall solute−solvent system and lift the degeneracy of the CR states.[7,17]

In light of the above, dipole reversal can be ascribed to a combination of thermally induced density and structural fluctuations within the surrounding medium and torsional equilibration between the two *E* state minima. The latter process will occur via transient formation of the LE state for configurations close to 90°. The similarity in the dipole relaxation times found for the trimer and tetramer to that for bianthryl suggest that the relaxation processes are similar for all three compounds and that, most probably, the excitonic state of the longer oligomers involves interaction between two neighboring anthracene moieties at any given time rather than more extensive delocalization over all chromophoric units. This conclusion is substantiated by the values of the dipole moments of the S_1 states given below.

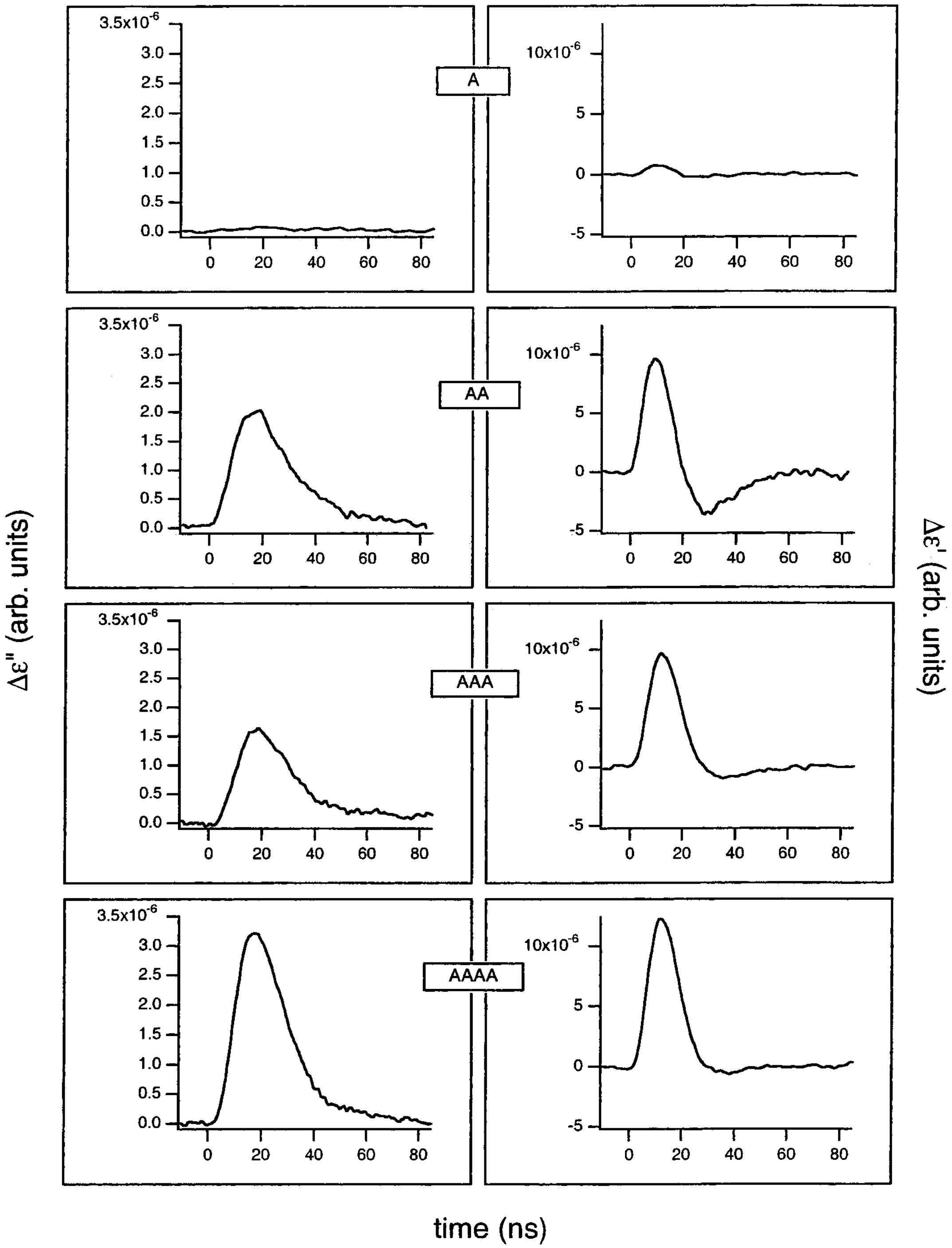

Figure 2. Sum (left) and difference (right) of the half-power transients observed on flash photolysis of benzene solutions of the compounds indicated in the center boxes. The transients are a measure of the change in the imaginary (dielectric loss), $\Delta\epsilon''$, and real (dielectric constant), $\Delta\epsilon'$, components of the permittivity of the solutions, respectively.

The dipole moments can be derived from the experimental ΔRe and ΔIm parameters using the relationship

$$\mu_*^2 = \Delta\mathrm{Re}[1 + (\Delta\mathrm{Im}/\Delta\mathrm{Re})^2] \quad (4)$$

The values obtained are listed in Table 1. As can be seen there is a tendency for the dipole moment to increase gradually in going from AA (6.9 D) to AAA (8.0 D) and AAAA (9.1 D). The overall change, however, is only approximately 30% which is much smaller than would have been expected if the *E* state involved delocalization over all anthracene moieties. It is also much smaller than the factor of 2 found for the charge separated state formed in polar solvents.[9]

The fluorescence spectra and relaxation kinetics of bianthryl in nonpolar and weakly polar solvents have been analyzed by some in terms of an equilibrium between a dipolar, charge transfer state, and a neutral, locally excited state, LE.[3,9,12,18–21] On the basis of this admittedly oversimplified model, the equilibrium ratio [CT]/([CT] + [LE]) has been estimated to be approximately 0.7 for biantryl in benzene (or toluene).[19,21,22] Correction of the value of μ_* found in the present work for this factor results in an estimate of closer to 8 D for the dipole moment of the CT state.

In terms of the present model of dipole relaxation, “CT” and “LE” states do not exist as specific entities in weakly polar solvents. Rather, there will be a distribution of torsional angles within an ensemble of excited solute molecules. Those with torsional angles closer to the 60 and 120° potential energy minima of the *E* state will have a relatively large dipolar character, and those closer to the orthogonal configuration will have a dipole moment close to zero. At least part of the gradual increase in μ_* with increasing length of the oligomers could therefore result from slightly deeper potential energy minima for the *E* states of the trimer and tetramer resulting in a larger fractional contribution from the dipolar configurations. Although we cannot completely exclude the possibility that the excitonic states in the longer oligomers may be slightly more delocalized than for bianthryl, we conclude, on the basis of the above and the similarity of the relaxation times, that excitonic interactions involve mainly only two neighboring anthracene units even for the tetramer.

An extensive study has been carried out of the optical absorption, emission, and photoinduced absorption of the present oligomers in a variety of solvents.[9] The photophysical properties are found to be qualitatively similar for all three compounds including relatively sharp, vibrationally structured absorption bands indicative of local excitation of individual chromophores and fluorescence spectra which display little solvent dependence in weakly polar solvents (including benzene) but marked bathochromic shifts in medium to high-polarity media. From these shifts, dipole moments of the emitting states have been estimated to be 20, 27, and 42 D for AA, AAA, and AAAA, respectively. Not only are these values much larger than those estimated for the excitonic states in the present work but, as mentioned above, they display a much greater increase with increasing length of the oligomers. In accordance with previous assignments, the S_1 states of the present compounds in polar solvents are considered to involve (close to) complete CS and an orthogonal relative orientation of the anthracene moieties. The increase in dipole moment with length is then attributed to an increasing contribution of those CS states in which the charge is separated over more than two anthracene moieties.

In conclusion, the present results show that, although the excitonic S_1 state of oligoanthrylenes has a net dipolar character in a weakly polar solvent such as benzene, the nature of the state is quite different to the CS state formed in more polar media. Thus, the dipole moment of the *E* state is much smaller than that of the CS state and is only slightly dependent on the length of the oligomer. This, together with the similarity of the dipole relaxation times, suggests that only two neighboring anthracene moieties interact at any moment in time even in the tetramer. In addition, the *E* state has a potential energy surface with minima at angles of approximately 60 and 120° compared with 90° for the CS state. Torsional motion about the central sigma bond in the *E* state results in an interchange between the two minimum energy configurations and an equilibrium contribution from the LE state.

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