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DYNAMICS OF CHARGE-TRANSFER EXCITED STATES RELEVANT TO PHOTOCHEMICAL ENERGY CONVERSION

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We have initiated a systematic study of intramolecular photoassociation and photoinduced CT in bichromophoric systems of the general structure M–X–M, where two identical aromatic hydrocarbons (M) are joined to each other by a single bridging group (X=CH_2, O, NH, etc.). The results for the bridged dinaphthyl compounds indicate that the nature of the intermoiety interactions can vary very strongly with the nature of the bridging group, the position of linkage, as well as the solvent polarity. Thus, dinaphthylmethanes (1,1' and 2,2') and dinaphthylethers (1,1' and 2,2') exhibit intermoiety interactions in the lowest triplet state through weak vdW forces,[1,2] while in dinaphthylamines the interactions occur in the triplet state[3] as well as in the lowest excited singlet state,[4] with dynamics which greatly depend on the nature of the solvent and the position of the N-H linkage (1,1' or 2,2').[4] In non-polar solvents, 2,2'-dinaphthylamine (β–DNA) does not exhibit intramolecular photoassociation in the singlet manifold, and the observed fluorescence is similar to that of the β–naphthylamine, both in spectral shape and temporal decay profile. As in the case of the dinaphthylmethanes and dinaphthylethers, the dinaphthylamines in nonpolar solvents form triplet excimers, following intersystem crossing of "non-interesting" singlets to the triplet manifold. In strongly polar solvents, on the other hand, the molecule forms an intramolecular CT state, as evidenced by the appearance of new transient absorption and the strong solvent-polarity dependence of the Stokes shift of the fluorescence. The formation of the intramolecular CT exciplex occurs more efficiently in α–DNA (1,1'-di-α-naphthylamine) than in β–DNA.[4] Thus, α–DNA exhibits the CT exciplex formation even in low polarity solvents, and the time evolution of the fluorescence is too fast to follow, in fluid solution at room temperature, with our instrument response time of about 70 picoseconds. The increase in the dipole moment in going from the ground state to the lowest excited singlet state, as deduced from the solvatochromic shift of the fluorescence maximum, is also substantially greater ($\Delta\mu \approx 17D$) for α–DNA than for β–DNA ($\Delta\mu \approx 11D$). The study of the interchromophore interactions has been extended to N-phenyl-2-naphthylamine (NPNA), in which two different aromatic moieties (naphthalene and benzene) are joined to each other through an -NH- bridge. As in the dinaphthylamines, NPNA forms an intramolecular triplet exciplex in nonpolar solvents and an intramolecular (CT) singlet exciplex in polar solvents.[5]

The lowest excited singlet state of α-DNA and β-DNA have been investigated by semiempirical quantum chemical methods, for the purpose of gaining theoretical understanding of the intramolecular CT state experimentally observed in polar solvents. The CT state is found to correspond to a state of perpendicular geometry in which one naphthalene ring is in conjugation with the lone-pair electrons of the amino bridge, while the other ring is perpendicular to the first.[6] As one naphthalene ring is rotated from the nearly coplanar orientation (of the two moieties) to the perpendicular geometry, the dipole moment of the molecule increases substantially with only a small increase in energy.[6] In medium of high dielectric constant, the CT state with large dipole moment is therefore expected to be the lowest excited singlet state of the molecule, consistent with the experimental observation.[4]

We have also initiated a systematic study of exciplex formation in the excited states of jet-cooled van der Waals (vdW) complexes. Complexes formed between two similar molecules (case 1), as well as those formed between a molecule with low ionization potential and a molecule with a large electron affinity (case 2), are probed by laser-induced fluorescence. This study has shown that for the fluorene/substituted benzenes vdW complexes (case 1), the exciplex formation following the electronic excitation of fluorene (F) is observed only for substituted benzene (B) whose S_1 (lowest excited singlet state) electronic origin is similar in energy to that of the lower-lying S_1 fluorene.[7] The results suggest that the exciplex formation, as monitored by the appearance of a broad structureless fluorescence red shifted from the corresponding LE fluorescence, is driven largely by exciton resonance ($F^*B \leftrightarrow FB^*$) between the component molecules. This conjecture is supported by the observation that the efficiency of the exciplex formation is greater for fluorene-h_{10} than for fluorene-d_{10} with greater energy mismatch (due to smaller zero-point energy of fluorene-d_{10} relative to fluorene-h_{10}). The appearance of a long progression in the low-frequency (~5 cm^{-1}) intermoiety vibrations, both in the excitation spectra of the LE fluorescence and exciplex fluorescence, makes it possible to probe the efficiency of the exciplex formation as a function of the number of quanta of the intermolecular vibrations excited. It was observed that the ratio of the intensity of the exciplex fluorescence to that of the LE fluorescence increases with increasing quanta of the intermolecular vibrations initially deposited in the LE state of the fluorene/tetrachlorobenzene complex.[7] This observation, which is the first of its kind, suggest that the progression-forming intermolecular vibration observed in the fluorescence excitation spectra is the mode that is closely related to the reaction coordinates for the exciplex formation.

For the case of the vdW complexes of 1-cyanonaphthalene (CNN) with aliphatic amines, belonging to case 2, the efficiency of the exciplex formation was found to depend both on the ionization potential (IP) of the amine (electron donor) as well as on the excess vibrational energy of the electronically excited CNN (electron acceptor) moiety.[8] Thus, the complex involving the donor molecule with the highest IP (viz., ammonia) does not exhibit exciplex formation even at high excess energies, while that involving the donor molecule with the lowest IP (viz., tributylamine) forms an exciplex even at zero excess energy. For donors with intermediate IPs (dimethylamine, diethylamine, trimethylamine and tripropylamine), the exciplex formation from LE state (A*D) of the vdW complex requires excess energies above a certain threshold value, which decreases with increasing donor strength. These results indicate that the exciplex formation in these systems is driven primarily by CT forces, and that the energy of the CT state A^-D^+ relative to that of the initially excited LE state determines the efficiency of the exciplex formation (via their effects on the reaction barrier for the $A^*D \rightarrow A^-D^+$ transformation).

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