Fluorescence Systems

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Fully Reversible Interconversion between Locally Excited Fluorophore, Exciplex, and Radical Ion Pair Demonstrated by a New Magnetic Field Effect**

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Magnetic field effects (MFEs) on chemical reactions are well documented in the scientific literature.[1] Many of the recent studies rely on exciplex fluorescence as an easily detectable measure of the underlying (radical pair) dynamics.[2] MFEs on the locally excited (LE) fluorophore have, on the other hand, only been observed as a result of triplet–triplet annihilation[3] or in radiolysis[4,5] and electrochemiluminescence studies.[6]

Our experiments involve the photoexcitation of 9,10-dimethylanthracene (A) and its diffusion-controlled electron-transfer quenching by *N*,*N*-dimethylaniline (D). The resulting exciplex, $^1[D^{\delta+}A^{\delta-}]^*$, dissociates yielding a geminate radical ion pair (GRIP),[1,3] $[^2D^{\cdot+} + {}^2A^{\cdot-}]$, which diffusively separates and possibly reencounters (cf. Figure 1). The energetic scheme agrees in essence with that suggested by Gould and Farid for contact radical ion pairs.[7] At interradical separations for which the pertinent exchange interaction has decayed, the singlet (S) and triplet (T) states are no longer eigenstates of the spin Hamiltonian and are, hence, subject to coherent interconversion. For the system studied at moderate field strength the S–T mixing is induced by the hyperfine interaction. The effect of an external magnetic field is to lift the degeneracy of the three triplet levels giving rise to a reduced S–$T_\pm$ conversion.[1b,c,g] This enhances the singlet population of the GRIP and the delayed exciplex fluorescence.

Steady-state emission spectra were recorded in solvent mixtures of butyronitrile (BN) and propylacetate (PA) at the earth's magnetic field, B_0, and a field saturating the MFE, $B_{\text{sat}} = 150$ mT (see the Supporting Information). The fluorophore alone did not give rise to a MFE. Figure 2a shows the spectrally resolved MFE for a solvent permittivity $\varepsilon = 12.4$. Apparently the magnetic field response cannot be merely attributed to the exciplex, but extends to the fluorophore as well. In fact, it can be readily decomposed in terms of the individual emission spectra. Figure 2b gives the magnitude of the MFE, $\chi = I(B_{\text{sat}})/I(B_0) - 1$, where I denotes the emission intensity. We will henceforth denote this quantity as χ_E and χ_F when referring to the exciplex or unbound fluorophore, respectively. For the case depicted the MFEs on the exciplex and fluorophore amount to 5.7 % and 1.1 %, respectively.

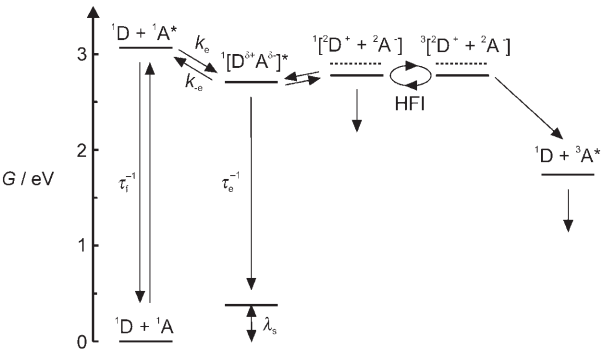

Figure 1. Species involved in the formation of the MFE on the fluorophore and their relative free energies. A and D denote 9,10-dimethylanthracene and *N*,*N*-dimethylaniline, respectively. For the radical pair states the dotted lines refer to the energy at infinite separation of the radicals, whereas the solid lines correspond to the ions at contact. Neither the T–T annihilation channel nor the intersystem crossing (ISC) in the fluorophore ($\Phi_{\text{ISC}} = 0.032$) and exciplex have been explicitly indicated. Only the outer-sphere reorganization energy has been considered in estimating the free energy of the exciplex, which hence corresponds to a lower bound. The reaction scheme has been augmented by a reversible quenching step in order to account for the experimental findings. HFI: Hyperfine interaction.

These findings pose the question of the origin of the MFE on the fluorophore. It can neither be attributed to T–T annihilation (P-type delayed fluorescence) nor thermal repopulation from the triplet state (E-type).[8] The latter can be safely excluded on the basis of the huge energy difference between T and S excited states ($\Delta G_{\text{ST}} = 1.3$ eV). The former is predicted to be proportional to the square of the excitation light intensity at low concentrations of triplets.[8] However, within experimental error no influence on the MFE was observed on varying the excitation intensity, hinting that the stationary triplet concentration remains insignificant. In addition, a significant contribution from both mechanisms can be excluded in view of the observation of a *positive* MFE on the fluorophore: Owing to the radical pair mechanism a negative MFE is expected for triplets originating from the radical ion pair triplet state by back electron transfer. In view of the small intersystem-crossing quantum yield of A ($\Phi_{\text{ISC}} = 0.032$)[9] this is the only relevant channel populating the triplet states. Moreover, the T–T annihilation channel is known to be magnetosensitive itself through the triplet pair mecha-

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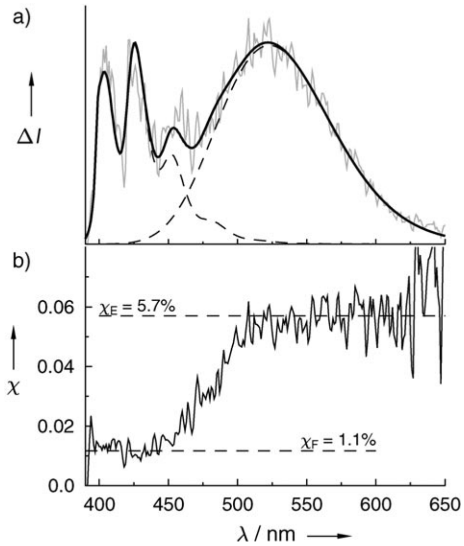

Figure 2. Spectrally resolved MFEs at $\varepsilon = 12.4$. a) Difference in fluorescence intensity, $\Delta I = I(B_{sat}) - I(B_0)$, in the presence of a saturating magnetic field, $I(B_{sat})$, and the earth's magnetic field, $I(B_0)$. The dashed lines correspond to the emitting species, the emitting fluorophore, and the exciplex, while the solid black line denotes their sum. The gray line is the difference of the experimental spectra at saturating and zero field. Five scans were accumulated in turns (sampling time: 1 s nm^{-1}, 1 point nm^{-1}). The spectral response has been decomposed in terms of the pure exciplex and LE fluorophore spectra. b) Wavelength dependence of the MFE, χ.

nism.[1b,3,10] In fluid solutions the effect is also negative for pairs encountering at random orientations and, additionally, does not level off at fields below the zero-field splitting (typically 1 T).[11] Analogous reasoning excludes the triplet–doublet pathway as well.[1b,12] Sensitized delayed fluorescence[8] involving intermolecular energy transfer from the exciplex to the fluorophore can be ruled out because of the lacking overlap of exciplex emission and fluorophore absorption spectra.

In view of this experimental evidence we propose that χ_F is due to the dissociation of the exciplex reestablishing the LE fluorophore. This supposition is closely linked to the energetic scheme and in particular to the relative energies of exciplex and fluorophore. Note that the 0–0 transition of the fluorophore ($E_{00} = 3.07$ eV) is virtually independent of the medium dielectric constant, ε, in the range of 6.0 to 24.8 for the solvent system used. The exciplex emission band, on the other hand, shifts to lower energies with increasing solvent polarity, in agreement with the model of self-consistent polarization of the medium.[13] In setting up the energetic scheme we followed Kuzmin's approach[14] and bore in mind that the exciplex emission proceeds vertically giving rise to the dissociative ground state in a nonequilibrium solvent environment. This fact is reflected by the inclusion of the solvent reorganization energy, λ_s, into the energy diagram. This gives rise to a reduction of the energetic gap between fluorophore and exciplex by $\lambda_s = (0.14 + 0.64(f(\varepsilon) - f(n^2)))$ eV, with $f(x)$ denoting the Lorentz–Debye solvent function. On this basis we predict that the free energy of exciplex formation, ΔG_{exc}, ranges from -0.30 eV for $\varepsilon = 6.0$ to -0.34 eV for $\varepsilon = 24.8$ at a distance of 4.0 Å. Small variations in the center-to-center distance of ±0.5 Å induce only minor changes in the energetics that do not lead to different conclusions. Thus, assuming detailed balance and a forward rate constant beyond the diffusion limit, a contribution of the backward reaction is still expected to be significant on a timescale of several tens to hundreds of nanoseconds, on which the MFE evolves. Note that the inner-sphere reorganization energy has not yet been included in the above treatment. Note furthermore that reversible exciplex formation is well established for systems with $\Delta G_{exc} \approx 0$ eV; its significance for the present energy gap has not been realized thus far.

Diffusive excursions and subsequent reencounters are essential for the generation of MFEs, since the exchange interaction blocks the S–T conversion at small interradical distances. As both particles in the GRIP are charged, the effect strongly depends on solvent polarity and is expected to go through a maximum at intermediate ε. We studied the polarity dependences of χ_E as well as χ_F (Figure 3) with the aim to test whether they can be reconciled with the presumption of a reversible exciplex formation. The solvent system BN/PA allows for systematic variation of ε at constant solvent viscosity and approximately constant Pekar factor, $n^{-2} - \varepsilon^{-1}$.

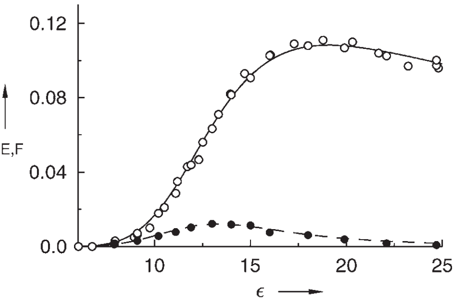

Figure 3. Dependence of the magnetic field effect on the fluorophore, χ_F (●), and the exciplex, χ_E (○), on the solvent dielectric constant, ε. The solid line represents the fit to χ_E in the low-viscosity approximation assuming the ion pair to be born at contact, with a mutual diffusion coefficient, $D = 250$ Å^2 ns^{-1}, and a radiative boundary characterized by a rate of $k = 1.3 \times 10^8$ M^{-1} s^{-1}. The dashed line was obtained on the basis of experimental values of the exciplex lifetime, an exponential dependence of k_{-e} on ΔG_{exc}, and the χ_Es.

We follow Nath's procedure to simulate the ε dependence in the low viscosity limit:[15] As opposed to this approach, we determine the singlet probability exactly from the corresponding Liouville–von Neumann equation taking into account all hyperfine coupling constants and degenerate electron exchange at a rate of $(2.4 \pm 0.4) \times 10^9$ M^{-1} s^{-1}.[2a,c] The simulated curve describes the experimental data exceptionally well, which we attribute to our attempts at keeping the viscosity constant.

The dependence of the MFE on solvent polarity differs for the two emissive species, that is, it peaks at $\varepsilon = 18 \pm 1$ for the exciplex and $\varepsilon = 13.0 \pm 0.5$ for the fluorophore. This can be rationalized by the suggested reaction scheme given in Figure 1. To properly account for the diffusion influence on the reactions we use Unified Theory[16] and extend the approach given in reference [17] by introducing a reversible quenching step and treating the spin evolution by the stochastic Liouville equation in the contact approximation.[18,19] Then a simple expression relating χ_F to χ_E results. For the system studied the lifetime of the fluorophore ($\tau_f = 14.8 \pm 0.1$ ns) and the quenching rate constant ($k_q = (8.2 \pm 0.1) \times 10^9\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ as obtained from the initial fluorophore decay) are virtually independent of solvent composition. Under these circumstances the MFE on the fluorophore relates to that on the exciplex, in first approximation, by Equation (1).

$$\chi_F \propto k_{-e}\,\tau_{exc}\,\chi_E \tag{1}$$

The effective lifetime of the exciplex, τ_{exc}, decays from 70 ns below $\varepsilon = 10.0$ to 14 ns at $\varepsilon = 21.7$, and the rate of reformation of the fluorophore, k_{-e}, depends exponentially on ΔG_{exc}. These two factors cause, in combination with the peaking behavior of the MFE on the exciplex, the characteristic dependence of χ_F on ε. It is convincing that a simple model for ΔG_{exc} and the reversibility are able to reconcile the MFEs on both exciplex and fluorophore as two manifestations of a common underlying mechanism.

Since all exciplex systems for which MFEs have so far been observed exhibit similar energetic characteristics, our findings are expected to reach far beyond the peculiarities of the system studied here. It appears that the irreversibility of the quenching step, which has apparently been assumed owing to its exergonicity, is illusive. In fact, a reconsideration of the approaches to model the MFE will be required.

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