



Supporting Information

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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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Experimental

9,10-dimethylanthracene (Aldrich, 99%, $E^{\text{red}} = -1.96$ V vs. SCE [1], $E_{00} = 3.07$ eV) was sublimed and N,N-dimethylaniline (Aldrich, $\geq 99.5\%$, $E^{\text{ox}} = 0.81$ V vs. SCE [1]) was freshly distilled under reduced pressure. Solutions of the fluorophore were prepared in butyronitrile (Fluka, purum, $\geq 99.0\%$, distilled) and propylacetate (Aldrich, 99.5%, distilled or used as received, yielding identical results) in septa-sealed quartz cuvettes and subsequently deaerated by bubbling with argon. N,N-dimethylaniline was injected to the degassed solutions under anaerobic conditions. MFEs on emission spectra were recorded using a thermostated cell ((295.2 ± 0.2) K) coupled to a Jobin Yvon FluoroMax2 fluorescence spectrometer via liquid light guides (Lumatec). The magnetic flux in the sample compartment was measured using a F. W. Bell Model 9200 Gaussmeter. All spectra were obtained by exciting at 399 nm. The magnitude of the MFE was evaluated as $I(B_{\text{sat}})/I(B_0) - 1$ where B_{sat} amounted to 150 mT and B_0 was the earth magnetic field. Note that, that no contribution arising from the Δg mechanism has been detected up to 300 mT, i.e. the MFE saturates and does not go through a maximum. However, at fields weaker than the average hyperfine coupling the efficiency of S-T interconversion is

enhanced by the applied field due to a removal of nuclear spin state degeneracy and a change in selection rules (low- field feature).[2] For the quantification of the MFE three pairs of time scans (60 s each, 1 s integration time) were recorded at 425 nm (fluorophore) and 590 nm (exciplex) and corrected for background and residual fluorescence of the second species, i.e. exciplex and fluorophore, respectively. Scans in the presence and absence of the magnetic field were taken in turns, the three scans under field-on and field-off conditions in each case being indistinguishable with respect to a one-dimensional variance analysis using a confidence level of 95%. The fluorescence decays of the fluorophore and exciplex were monitored using a home-built time-correlated single-photon- counting apparatus as described in [3]. Appropriate interference (fluorophore) or longpass (exciplex) filters were used to separate the spectral components. The fluorophore traces exhibit delayed fluorescence components which, although contributing up to 20% of the integral steady-state spectrum remain low in amplitude due to the long effective lifetime. Both, the time traces of fluorophore and exciplex are essentially non-exponential (except for the fluorophore at high epsilon, where its quenching becomes irreversible. From the initial decay of the fluorophore we have extracted the quenching rate constants, $k_q = (8.2 \pm 0.1) 10^9 \text{ M}^{-1}\text{s}^{-1}$ for all solvent mixtures, and from the primary decay component of the exciplex we determine its effective lifetime. The latter was used in the simulations of the polarity dependence of the magnetic field effect on the LE fluorophore. Dynamic viscosities, $\eta(\text{at } 295.2 \text{ K}) = 0.58 \text{ cP}$, were obtained from $\eta = \nu\rho$, where ν is the kinematic viscosity, which was measured by means of a thermostated capillary Ubbelohde viscosimeter (Schott), and ρ is the density, which was measured using a pycnometer. The refractive indices, $n_D(\text{at } 295.2 \text{ K}) = 1.3845 \pm 5 \cdot 10^{-4}$, were determined using a temperature-controlled Abbé refractometer (1T model from Atago). Dielectric constants were obtained using a temperature-controlled home-built apparatus similar to the one described in reference [4].

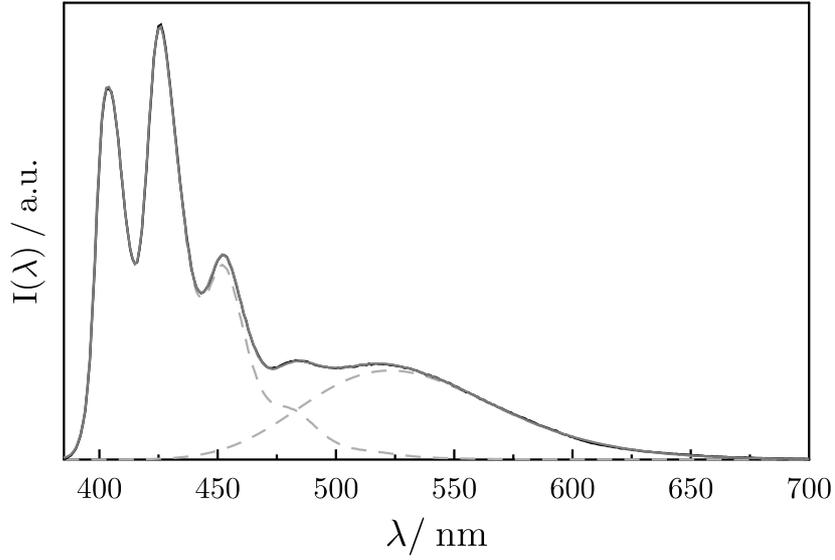


FIG. 1: Emission spectrum of the 9,10-dimethylanthracene / N,N-dimethylaniline system at $\epsilon = 12.4$. The dashed lines correspond to the pure fluorophore and exciplex spectra.

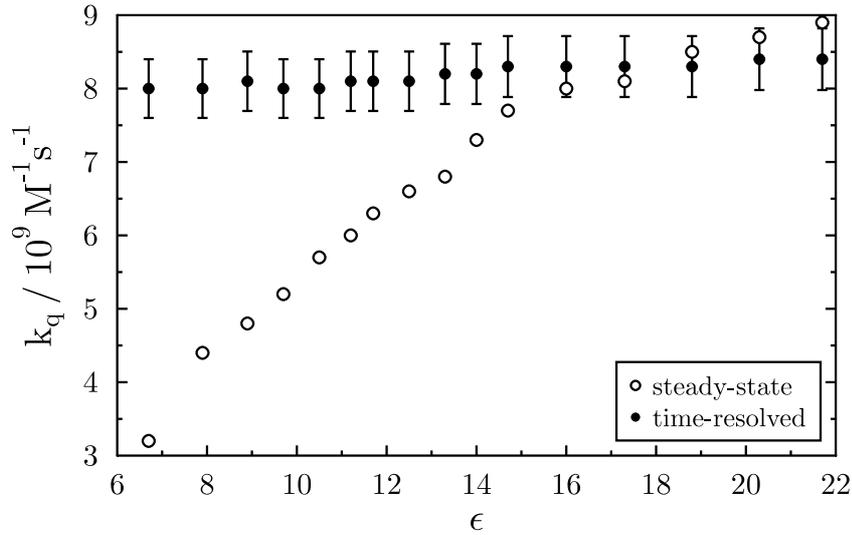


FIG. 2: Dependence of the quenching rates, k_q , on dielectric constant. The time-resolved data were obtained from a fit to the initial fluorophore decay. The reversibility of the fluorophore-exciplex system is relevant for $\epsilon < 20$, resulting in smaller steady-state quenching rate constants than those obtained from the time-resolved data.

Exciplex Energetics

In order to judge the reversibility of the fluorophore-exciplex equilibrium the relative position of the exciplex with respect to the fluorophore has to be determined accurately. We have, hence, analyzed the polarity dependence of the exciplex emission in the solvent mixture. The exciplex spectra were extracted from the fluorescence spectra by fitting the high frequency range (3.05 to 2.90 eV) with the pure fluorophore spectrum and subtracting the latter. Following Kuzmin's model of self-consistent polarization the emission lineshape is given as a sum of vibronic transitions with Gaussian bandsshape [5, 6]

$$\frac{I(\lambda)}{\nu^3} \propto \sum_m \frac{e^{-S} S^m}{m!} \times \exp\left(-\frac{(h\nu_0 - h\nu - mh\nu_v)^2}{2\sigma^2}\right), \quad (1)$$

where $S = \lambda_v/h\nu_v$ is the Huang-Rhys factor with λ_v denoting the internal reorganization energy associated with the average vibration mode of frequency ν_v . ν_0 is the frequency of the 0-0 transition and σ is the width of the vibronic transition. The latter accounts for medium reorganization and various kinds of molecular interactions. It thus usually exceeds the value of $(2\lambda k_B T)^{1/2}$. Note, that we use a spectral representation which yields direct proportionality to transition probabilities.[7] Equation (1) was fitted to the experimental exciplex spectra, with ν_0 and σ being optimized and S and ν_v set to 1 and 0.08 eV= 650 cm⁻¹, respectively. The latter two values represent the mean values when adjusting ν_0 , σ , S and ν_v simultaneously. An exemplary exciplex spectrum with the corresponding fit is shown in Figure 3.

In the framework of the self-consistent polarization model the 0-0 transition energies, $h\nu_0$, are expected to obey [8]

$$h\nu_0 = U_{CT}^0 - U_{GS}^0 - z \left(\underbrace{2 \frac{\epsilon - 1}{2\epsilon + 4}}_{f(\epsilon)} - z \underbrace{\frac{n_D^2 - 1}{2n_D^2 + 4}}_{f(n_D^2)} \right) \frac{e^2}{4\pi\epsilon_0} \frac{\mu_0^2}{\rho^3} - V_{12} \sqrt{\frac{1}{z} - 1}, \quad (2)$$

where U_{CT}^0 and U_{GS}^0 are the the energies of the charge transfer state (CT) and ground

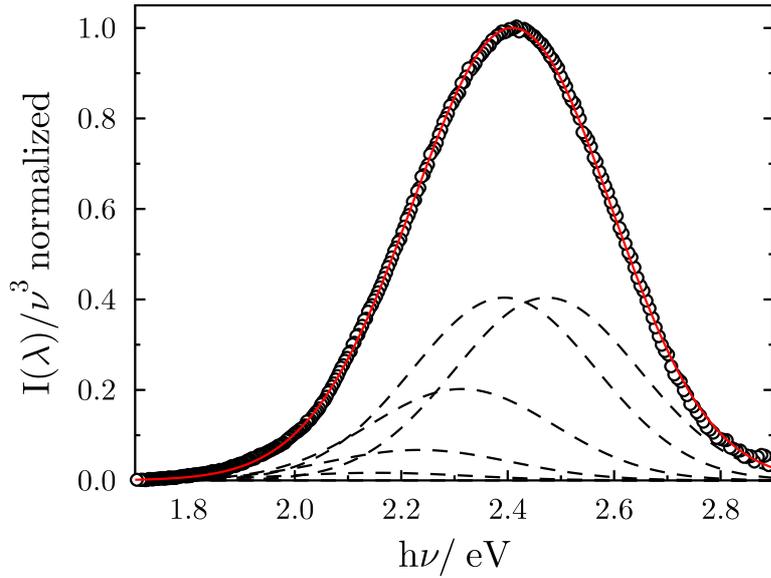


FIG. 3: Reduced emission spectrum [7] of the 9,10-dimethylantracene / N,N-dimethylaniline exciplex in neat propylacetate at 295.2 K and its fit by equation (1). The 0-0, 0-1, 0-2, 0-3, and 0-4 vibronic transitions are shown by dashed lines.

state (GS) of the reactant pair at contact in vacuum, respectively. z is the degree of charge transfer, μ_0 the dipole moment of the CT state, V_{12} the coupling matrix element and ρ the radius of the Onsager cavity.

The latter was estimated as the sum of the radii of N,N-dimethylaniline and 9,10-dimethylantracene. For N,N-dimethylaniline we obtained 3.11 Å on the basis of the molar volume using a packing factor of 1.725.[9] For 9,10-dimethylantracene we subscribed the ellipsoid of smallest surface about the van der Waals body of the molecule (from the B3LYP/6-31G(d,p) optimized geometry), which yielded an elliptical radius of 4.83 Å.[10] This value is large since the extent of the c-axis is overestimated due to significant deviations from the elliptical shape. We thus rescale this value by a factor chosen such that an analogous procedure for N,N-dimethylaniline yields the above radius (3.11 Å instead of 4.02 Å) and obtain 3.74 Å. We henceforth use $\rho = 6.85$ Å. Since $n_D = 1.3845 \pm 5 \cdot 10^{-4}$ is constant for the solvent mixtures used, a linear relation of $h\nu_0$ vs. $f(\epsilon)$ results for systems

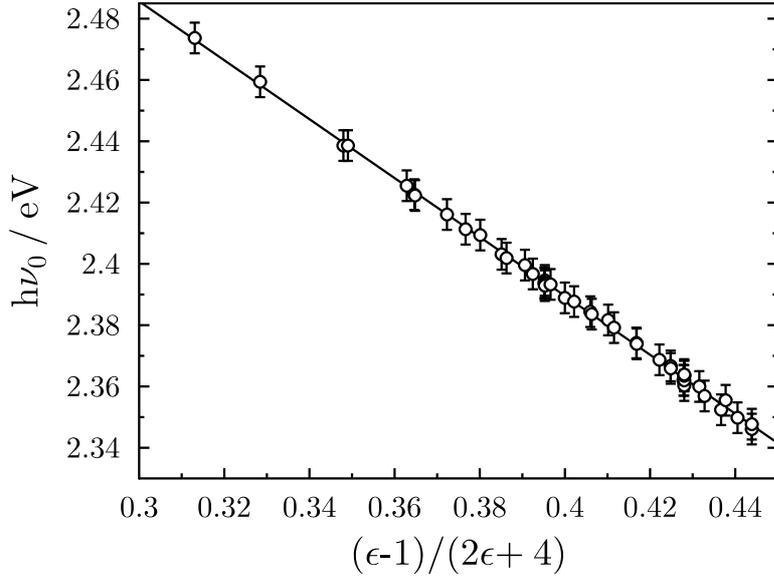


FIG. 4: Dependence of the N,N-dimethylaniline / 9,10-dimethylanthracene exciplex 0-0 transition energy on the Lorentz-Debye solvent function of ϵ in solvent mixtures of propylacetate / butyronitrile.

that do not exhibit a dependence of the degree of charge transfer, z , on solvent polarity. This is indeed the case as can be inferred from Figure 4. From the slope of this plot $\sqrt{z}\mu_0 = (15.73 \pm 0.06)$ D. If we assume a charge transfer distance of 4.0 ± 0.5 Å, which corresponds to a π - π stacked configuration in the exciplex, a partial charge transfer z of 0.67 ± 0.18 ensues. Although a large ambiguity in the values of z , due to the unknown interplanar distance is obvious, the effect on λ_s is comparably small and sufficient for the present purpose. Following Kuzmin's proposal [6] we estimate the solvent reorganization energy, λ_s from

$$\lambda_s = V_{12} \sqrt{\frac{1}{z} - 1} + \frac{e^2}{4\pi\epsilon_0} \frac{\mu_0^2}{\rho^3} z(2-z) (f(\epsilon) - f(n_D^2)). \quad (3)$$

For an $\epsilon = 18.8$ we thus obtain $\lambda_s = (0.38 \pm 0.08)$ eV. Note that interparticle distances larger than 4.5 Å give rise to a free energy of the exciplex larger than the free energy of the free ions at contact. Here we use a value of $V_{12} = 0.2$ eV, which was found for related

systems.[6] Despite the ambiguity of some parameters (μ_0 , V_{12}), a close energetic vicinity of the exciplex and the free ions at contact is characteristic for the system studied. It is important to note that a shift of the free energy of the exciplex independent of solvent composition does not change the conclusions obtained on the basis of the approximate expression (19) (the equation of the main document).

Simulations of the MFE on the exciplex

In the low-viscosity approximation the singlet yield reduces to the integral over the singlet probability, $p_S(B, t)$ weighted by a suitable recombination function, $f(t)$, the most popular being Noyes' random flight model [11] or the exponential model.[12]

$$I(B) \propto \int_0^\infty p_S(B, t) f(t) dt. \quad (4)$$

However, in order to accommodate the effect of solvent polarity, solutions of the diffusion equation in presence of a Coulomb potential are preferred. Here we follow Nath's proposal [13] and apply Hong and Noolandi's [14] long time asymptote for the reactivity. In the long-time limit ($t \gg r_0^2/D, r_c^2/D$) the recombination function (reactive flux through the central sphere of radius σ) assumes the simple form

$$f(t) = \frac{r_c}{\sqrt{4\pi Dt^3}} \frac{U(r_0)}{U(\infty)^2}, \quad (5)$$

where

$$U(r) = \exp(-r_c/r) + (4\pi Dr_c/k - 1) \exp(-r_c/\sigma), \quad (6)$$

with r_c denoting the Onsager radius, D the mutual diffusion coefficient and k the bimolecular rate constant for contact recombination.

Neglecting the exchange interaction, the singlet probability is related to the distance

independent spin density matrix of the GRIP, $\hat{\rho}$, by

$$p_S(t) = Tr(\hat{P}_S \hat{\rho}), \quad (7)$$

where Tr is the trace operation, \hat{P}_S is the singlet projector and $\hat{\rho}$ obeys the Liouville-von Neumann equation

$$\frac{d\hat{\rho}}{dt} = -i [\hat{H}, \hat{\rho}] + \hat{K}_{ex} \hat{\rho}. \quad (8)$$

The Hamiltonian, \hat{H} , comprises the hyperfine interaction with all coupled nuclei (confer to reference [49] of the main manuscript) and Zeeman interactions (we assumed $g_A = g_B = 2.0023$) and \hat{K}_{ex} accounts for degenerate electron exchange and is given by [15–17]

$$\hat{K}_{ex} \hat{\rho} = \frac{1}{\tau_{ex}} \left[Tr_n(\hat{\rho}) \otimes \frac{\hat{1}}{N} - \hat{\rho} \right], \quad (9)$$

where $1/\tau_{ex} = k_{ex}[D]$. Equations (7) to (9) can be reformulated in terms of spin correlation tensors, which allow an efficient solution by reducing the problem to subproblems in the Hilbert space of the individual radicals. The interested reader is referred to [16, 17] for a

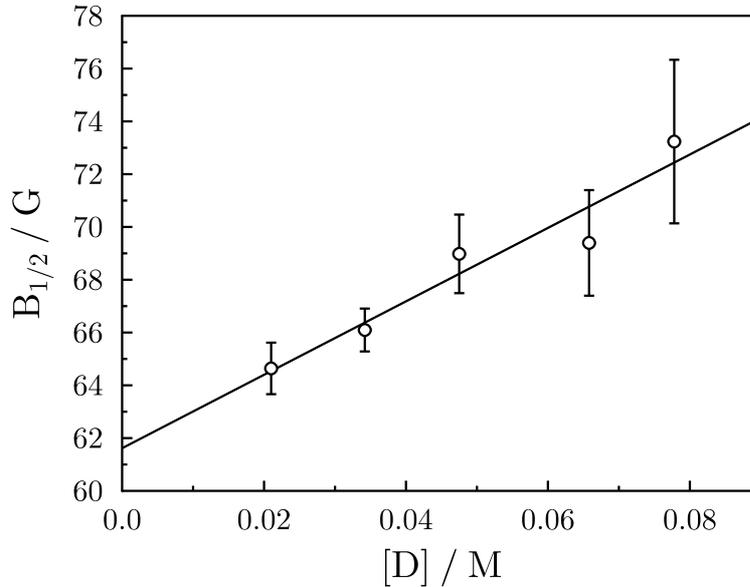


FIG. 5: Dependence of the $B_{1/2}$ value on the concentration of N,N- dimethylaniline, $[D]$, at $\epsilon = 13.1$ and $\eta = 0.58$ cP.

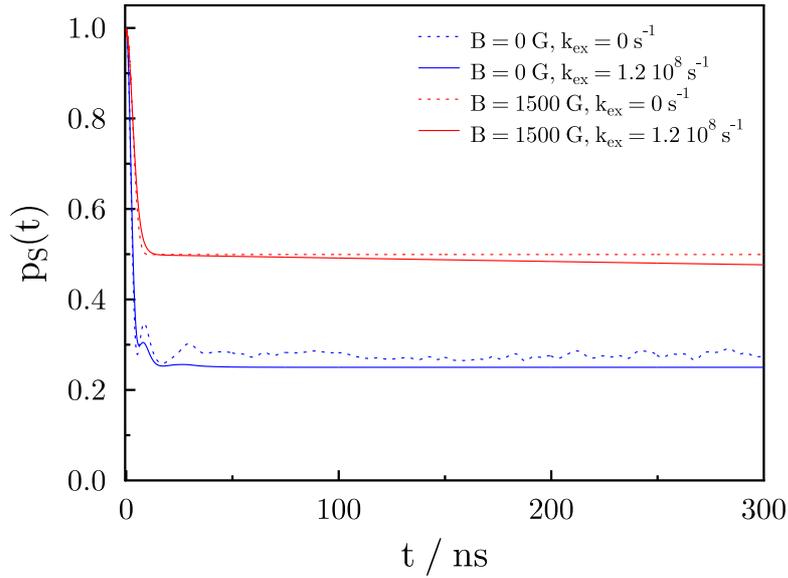


FIG. 6: Calculated singlet probabilities, $p_S(B, t)$, for the system 9,10-dimethylantracene / N,N-dimethylaniline taking into account all hyperfine coupling constants and optionally degenerate electron exchange.

detailed description of this approach. For A we used the coupling constants published by Bolton et al. [18] while for D we used values calculated using the UB3LYP/6-31+G(d,p) protocol, which for N,N-dimethyltoluidine reproduce the experimental coupling constants to within 15%. The values used for D are: 1.04 mT ($1 \times ^{14}\text{N}$), 1.22 mT ($6 \times ^1\text{H}$), -0.55 mT ($2 \times ^1\text{H}$), 0.20 mT ($2 \times ^1\text{H}$), -0.84 mT ($1 \times ^1\text{H}$). The values for A are: 0.388 mT ($6 \times ^1\text{H}$), -0.290 mT ($4 \times ^1\text{H}$), -0.152 mT ($4 \times ^1\text{H}$). Note that the experimental values published in [19] for D are incorrect. In fact we have repeated their experiments and conclude that the species erroneously taken to be the N,N-dimethylaniline cation is the cation of N,N,N',N'-tetramethyl-benzidine.

The rate of degenerate electron exchange, k_{ex} , was estimated from the concentration dependence of $B_{1/2}$, the magnetic induction at which half the saturation value of the MFE

is obtained (cf. figure 5), following Staerk et al. [20] from

$$B_{1/2}([D]) \approx B_{1/2}(0) + \frac{\hbar}{g_e \mu_B} k_{ex}[D]. \quad (10)$$

A rate $k_{ex} = (2.4 \pm 0.4)10^9 \text{ M}^{-1}\text{s}^{-1}$ was determined at $\epsilon = 13.1$ and subsequently used for all simulations irrespective of the sample polarity. Figure 6 shows the calculated singlet probabilities for the system 9,10-dimethylantracene / N,N-dimethylaniline taking into account all hyperfine coupling constants and optionally degenerate electron exchange.

Unified Theory Treatment of the Magnetic Field Effect

We shall make use of the reaction scheme depicted in figure 7. For simplicity all reactions are assumed to proceed at contact, which for the back electron transfer is a good approximation only at low viscosities. Following Burshtein's general exposition,[21–23] the locally excited state population is given by

$$\dot{N}_f(t) = - \left(n(\sigma, t)k_e c + \frac{1}{\tau_f} \right) N_f(t) + k_{-e}N_e(t) \quad (11)$$

where the back reaction from the exciplex was absent in previous treatments. The meaning of the different rate constants is obvious from Figure 7. $n(r, t)$ denotes the pair distribution function for the fluorophore quencher pair and obeys the auxiliary equation

$$\frac{\partial n(r, t)}{\partial t} = D_{DA} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} n(r, t) - \left(k_e n(r, t) - k_{-e} \frac{N_e(t)}{c} \right) \frac{\delta(r - \sigma)}{4\pi r^2}. \quad (12)$$

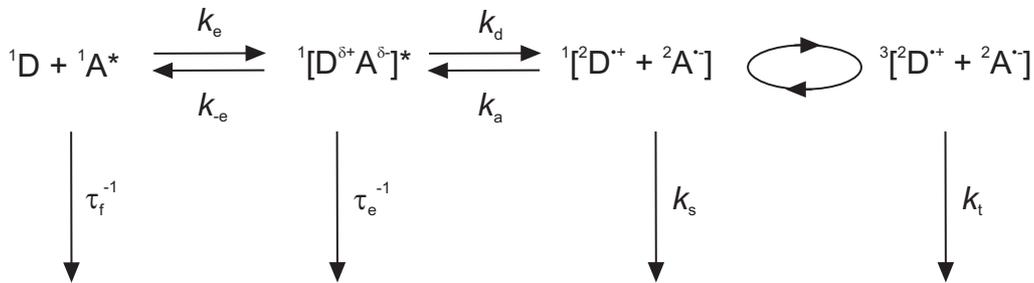


FIG. 7: Reaction scheme for the analysis of the magnetic field effects on exciplex and fluorophore in the framework of Unified theory.

The exciplex population, $N_e(t)$, on the other hand, is given by

$$\dot{N}_e(t) = n(\sigma, t)k_e c N_f(t) + k_a c \text{Tr}(\hat{P}_S \hat{\rho}(\sigma, t)) - \frac{1}{\tau_{\text{exc}}} N_e(t), \quad (13)$$

where $1/\tau_{\text{exc}} = 1/\tau_e + k_d + k_{-e}$. For the spin density matrix, $\hat{\rho}(r, t)$, the following equation of motion ensues

$$\begin{aligned} \frac{\partial \hat{\rho}(r, t)}{\partial t} = & -i\hat{L}\hat{\rho} + D_{D+A-} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 e^{-V(r)} \frac{\partial}{\partial r} e^{V(r)} \hat{\rho}(r, t) \\ & - \left((k_{-e} + k_a) [\hat{P}_e, \hat{\rho}(r, t)]_+ + k_t [\hat{P}_t, \hat{\rho}(r, t)]_+ - k_d \frac{N_e(t)}{c} \frac{P_e}{\text{Tr}(P_e)} \right) \frac{\delta(r - \sigma)}{4\pi r^2} \end{aligned} \quad (14)$$

Equations (11) to (14) are to be solved subject to reflective boundary conditions. Initially, all populations except $N_f(0)$ are zero and $n(r, 0) = 1$. Note that equations (11) to (14) define a set of coupled differential equations with $(12288 \cdot 32768)^2 + 3$ degrees of freedom (neglecting symmetry). Simultaneous time integration is thus hardly tractable and in fact no such attempt has appeared in the scientific literature. Still an expression relating the magnetic field effect on the fluorophore can be derived that does not require the evaluation of $N_e(t)$ and $N_f(t)$. To resolve this set of coupled differential equations we make use of an elegant Green function technique similar to that used in reference [24]. The details of the derivation are however beyond the scope of this publication and will be reported independently. Here, only the final result relating the MFE on the fluorophore to that on the exciplex will be reproduced

$$\chi_F = \frac{k_e c \tilde{\theta} k_{-e} \tau_{\text{exc}}}{1 + k_e c \tilde{\theta} (k_{-e} \tau_{\text{exc}} - 1) + (k_e c \tilde{\theta} - 1) k_a k_d \tau_{\text{exc}} \tilde{p}_S(B=0)} \chi_E, \quad (15)$$

where

$$\tilde{\theta} = \int_0^\infty \frac{n(\sigma, t) N_f(t)}{N_f(0)} dt \quad (16)$$

and \tilde{p}_S is the integral over the singlet probability at contact,

$$\tilde{p}_S = \int_0^\infty \text{Tr}(\hat{P}_S, \hat{\rho}(\sigma, t)) dt, \quad (17)$$

for a geminate radical ion pair born at contact and subjected to the singlet and triplet recombination processes according to Figure 7. This comprehensive approach is also applicable to the MFE on the exciplex beyond the low-viscosity approximation (though still in the contact approximation). In the low-viscosity limit the treatment given above for the exciplex preserves its validity and \tilde{p}_S can be approximated from equation (4). We thus use the UT approach only insofar as to predict the MFE on the fluorophore for an *a priori* given MFE on the exciplex. Under the experimental conditions employed throughout this work k_e and τ_f are virtually independent of the solvent composition and the quencher concentration, c , has been kept constant. Thus $\tilde{\theta}$, which characterizes the quenching behavior is constant. Furthermore $k_{-e} \ll \tau_{\text{exc}}^{-1}$ since the former corresponds to the endergonic dissociation of the exciplex reforming the unbound fluorophore. In first order, the denominator is therefore constant and equation (15) simplifies to

$$\chi_F \propto k_{-e} \cdot \tau_{\text{exc}} \cdot \chi_E \quad (18)$$

$$\propto \exp\left(\frac{\Delta G_{\text{exc}}}{k_B T}\right) \cdot \tau_{\text{exc}} \cdot \chi_E. \quad (19)$$

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