SPECTROSCOPY, PHOTOPHYSICS AND PHOTOCHEMISTRY OF 1,3-DIKETOBORONATES
VI: THE EXCIPLEXES OF 2-NAPHTHYL-SUBSTITUTED 1,3-DIKETOBORONATES

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Summary

The fluorescence quenching of 2-naphthyl-substituted 1,3-diketoboronates (2-NDKB) by naphthalene in heptane is accompanied by exciplex emission. The exciplex formation occurs irreversibly because of the high electron affinity of 2-NDKB. In one case the exciplex fluorescence decay reveals the existence of ground state rotamers.

1. Introduction

In many cases the existence of ground state rotamers of 2-naphthyl-substituted compounds leads to multiple fluorescence behaviour (*cf.* ref. 1 and references cited therein). The rotamers do not equilibrate within the excited state (non-equilibration of excited rotamers (NEER) principle [2]).
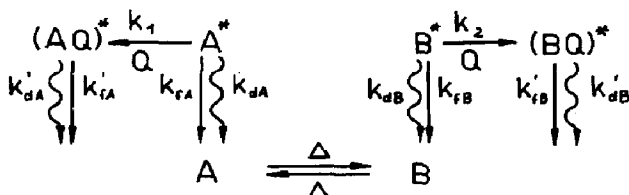
We have shown [3] that the 2-naphthyl-substituted 1,3-diketoboronates (2-NDKB) (Formula 1) form the rotamers A and B in polar solvents.
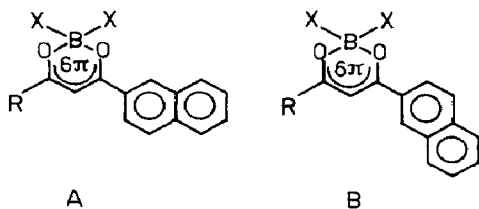
Formula 1.

However, the fluorescence of these molecules in non-polar solvents shows no evidence for the existence of rotamers. This paper is concerned with the exciplex formation and the fluorescence decay of compounds 1 ($R \equiv CH_3$, $X \equiv CH_3COO$, *cf.* Formula 1) and 2 ($R \equiv C_6H_5$, $X \equiv CH_3COO$) with the

donor naphthalene in heptane. Since the rotamers can possess different exciplex properties, as in the case of 2-naphthyl-substituted styrenes [4], we want to investigate the possibility of the simultaneous formation of different exciplexes according to Scheme 1.

$$(AQ)^* \xleftarrow[Q]{k_1} A^* \qquad B^* \xrightarrow[Q]{k_2} (BQ)^*$$

$$k'_{dA} \updownarrow \Big| k'_{fA} \qquad k_{fA} \Big| \updownarrow k_{dA} \qquad k_{dB} \updownarrow \Big| k_{fB} \qquad k'_{fB} \Big| \updownarrow k'_{dB}$$

$$A \underset{\Delta}{\overset{\Delta}{\rightleftharpoons}} B$$

Scheme 1.

2. Experimental details

Compounds 1 and 2 were prepared by refluxing naphthoylacetone and benzoylnaphthoylacetone respectively in $C_2H_4Cl_2$ in the presence of boron trioxide and acetic acid [5]. The compounds were recrystallized three times from acetic acid and then from heptane.

Heptane was first distilled over P_2O_5 under N_2 and then over K_2CO_3. Naphthalene was recrystallized four times from alcohol and finally from heptane.

The stationary fluorescence measurements were performed using a FICA 55 (ARL) automatically correcting spectrofluorometer−phosphorometer. The fluorescence quantum yields were determined relative to quinine sulphate ($\phi_F = 0.54$) as the standard. The fluorescence kinetics was measured by means of the nanosecond single-photon-counting technique [6]. The deconvolution of the fluorescence signals from the excitation pulse was performed using standard techniques (cf. ref 7). Both stationary and time-resolved fluorescence data were measured in non-degassed solutions unless stated otherwise. To degas solutions we used the simple technique of bubbling argon through them.

3. Results

3.1. Stationary absorption and fluorescence measurements

The absorption spectra of 1 and 2 do not show a marked change in the presence of naphthalene up to 0.1 mol l^{-1}. At higher concentrations ($c_N > 1$ mol l^{-1}) the formation of electron donor−acceptor complexes can be observed, but this concentration range is not of interest for our measurements.

Figure 1 shows the fluorescence spectra of 1 (Fig. 1(a)) and 2 (Fig. 1(b)) in non-degassed heptane at different naphthalene concentrations. In the low concentration range ($c_N < 0.04$ mol l^{-1}) isosstilbic points appear. At higher concentrations the exciplex fluorescence is quenched. The exciplex fluorescence bands (curve 9 in (a) and curve 7 in (b)) were calculated using
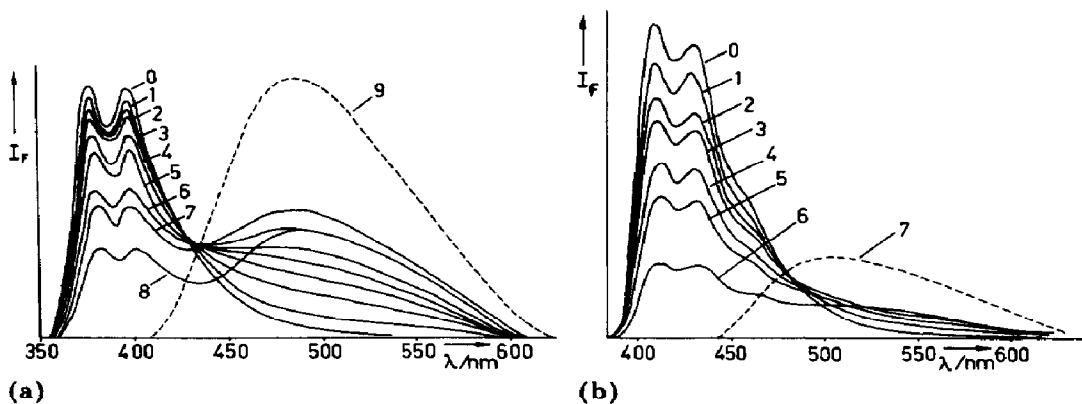
Fig. 1. Corrected fluorescence spectra of **1** (a) and **2** (b) in heptane as a function of naphthalene concentration (curves 0 - 8, 0 - 0.8 mol l^{-1}; curves 7 and 9, calculated exciplex spectra).
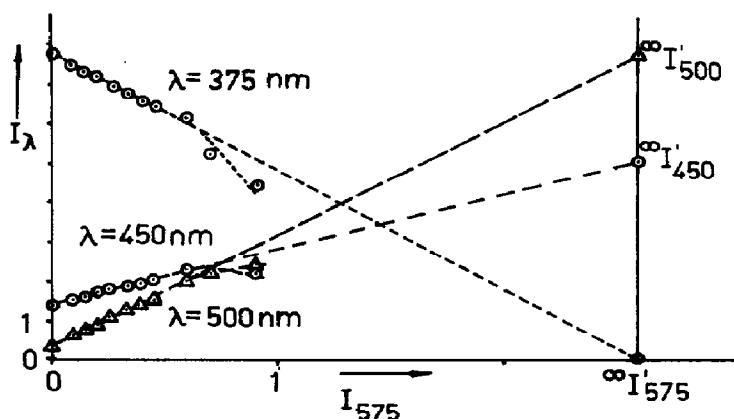

Fig. 2. Fluorescence intensity plots at selected wavelengths according to spectra 1 - 5 (Fig. 1(a)) for increasing naphthalene concentrations (concentration increments are smaller than in Fig. 1(a); I_λ and I_{575} are in identical arbitrary units, whilst the I_{575} are fivefold enlarged).

the intensity plots according to ref 8. These plots at selected fluorescence wavelengths are shown for **1** in Fig. 2 for the concentration range $c_N < 0.04$ mol l^{-1} (*cf.* selected spectra 0 - 5 in Fig. 1(a)).

The plots of the $I_\lambda(c_N)-I_{575}(c_N)$ pairs, with the two values at the same naphthalene concentration in each case, will give straight lines which increase with naphthalene concentration (up to $c_N < 0.03$ mol l^{-1} for compound **1**) if two fluorescent species only are present (*cf.* ref. 8 for more details of the formalism of the intensity plots). It can be concluded from the isosstilbic behaviour of the spectra of **1** in the low concentration range that the monomer and the exciplex are the two species. At 575 nm there is no monomer fluorescence, whilst at 375 nm there is no exciplex fluorescence. In order to determine the spectrum of the pure exciplex (*i.e.* $^\infty I_{375} = 0$) the straight lines $I_\lambda(c_N) = \text{f}\{I_{575}(c_N)\}$ are extrapolated in the direction of in-

creasing $I_{575}(c_N)$ beyond the measured points. The point at which the $I_{375}(c_N)-I_{575}(c_N)$ straight line crosses the abscissa gives the value of $^\infty I'_{575}$. The exciplex spectrum can now be derived from the intersections of the $I_\lambda(c_N)-I_{575}(c_N)$ straight lines with the perpendicular passing through $^\infty I'_{575}$. Thus, the $^\infty I'_\lambda$ determined in this way are not influenced by the effects resulting from exciplex quenching which occur in the concentration range $c_N > 0.03$ mol l^{-1} in the case of compound 1.
The plots

$$\frac{I(0)}{I} = f(c_N) \tag{Ia}$$

and

$$\frac{I'_\lambda}{I} = f\left\{\frac{^\infty I'_\lambda}{I(0)} c_N\right\} \tag{IIa}$$

($I(0)$ and I, fluorescence intensity of 2-NDKB in the absence of quencher and in the presence of quencher respectively; I'_λ, exciplex fluorescence intensity at the wavelength λ and at the same quencher concentration; $^\infty I'_\lambda$, calculated fluorescence intensity of the "pure" exciplex according to Fig. 1) yield straight lines up to quencher concentrations of 0.03 mol l^{-1} for 1 and 0.04 mol l^{-1} for 2. The slopes of these curves are independent of the fluorescence wavelengths in the case of both 1 and 2.

We did not detect any excitation-wavelength dependence of the exciplex bandshape or of the plots (Ia) and (IIa) in the case of compound 2. The excitation-wavelength dependence of the 1−naphthalene exciplex fluorescence cannot be investigated because of the overlapping absorption spectra of 1 and naphthalene at $\lambda < 360$ nm. The long wavelength edge of the absorption band of 1 is located at 380 nm.
The plots

$$\frac{\phi^0}{\phi} = f(c_N) = 1 + xc_N \tag{I}$$

and

$$\frac{\phi'}{\phi} = f(c_N) = \xi c_N \tag{II}$$

(ϕ^0, fluorescence quantum yield of pure 1 and 2; ϕ, fluorescence quantum yield in the presence of the quencher; ϕ', fluorescence quantum yield of the exciplex at the same quencher concentration; for the slopes κ and ξ cf. Table 1) are depicted in Fig. 3.

On degassing the solutions the fluorescence quantum yields of the exciplexes increase ($\phi'_{deg}/\phi' = 1.2$ for 1; $\phi'_{deg}/\phi' = 1.1$ for 2) but the shape of the exciplex fluorescence bands remains the same. The fluorescence quantum yield of the pure monomers is nearly independent of degassing because of the short fluorescence lifetimes τ^0 (cf. Table 2).
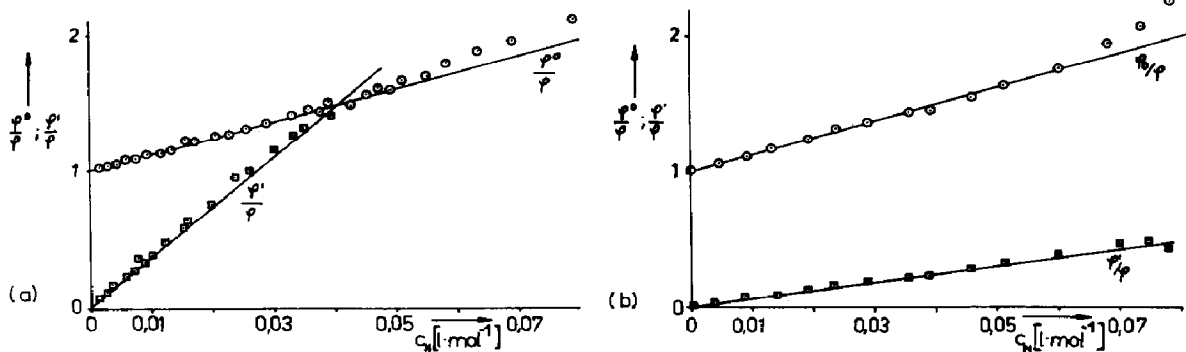
Fig. 3. Dependence of the fluorescence quantum yield ratios on the quencher concentration for 1–naphthalene (a) and 2–naphthalene (b) exciplex formation in non-degassed heptane at 293 K.

TABLE 1

Quantitative spectroscopic and kinetic data

Compound	λ_{abs}^{00} (nm)	λ_{f}^{00} (nm)	$\lambda_{f\,max}^{exiplex}$ (nm)	ϕ^0	$^\infty\phi'$ [a]	κ (l mol^{-1})	ξ (l mol^{-1})	κ' (l mol^{-1})	κ'' (l mol^{-1})
1	379	383	496	0.2_0	0.3_6	11.4	37.6	5.0	—
2	398	410	525	0.5_8	0.2_8	15.1	5.2	(0)	5.3

[a] $^\infty\phi'$, calculated fluorescence quantum yield of the "pure" exciplex.

TABLE 2

Quantitative kinetic and thermodynamic data

Compound	τ^0 (ns)	τ'_{max} (ns)	τ''_{max} (ns)	E_A^{red} [a] eV	ΔH_c^{exp} (kJ mol^{-1})	ΔH_c^{calc} [b] (kJ mol^{-1})	ΔG_c^{calc} [c] (kJ mol^{-1})
1	0.9_8 [d]	10.2 [e]	—	-1.0_6	-14.4	-48.9	-26.6
2	1.4_1 [d]	4.2 [f]	6.5 [f]	-0.8_9	-18.8	-44.8	-22.4

[a] In CH_3CN against Ag/AgCl [9].
[b] According to eqn. (2).
[c] According to eqn. (3); $T = 298$ K.
[d] Measured as described in ref. 3.
[e] $\lambda_{exc} = 366$ nm; $\lambda_f = 540$ nm.
[f] $\lambda_{exc} = 405$ nm; $\lambda_f = 560$ nm.

By varying the temperature and utilizing the plot

$$\ln\left(\frac{\phi'}{\phi}\right) = f\left(\frac{1}{T}\right) \tag{III}$$

the dissociation enthalpy ΔH_c of an exciplex can be determined [10]. For the case of a reversible exciplex formation and assuming the temperature independence of the ratio k'_f/k_f the following relationship holds:

$$\ln\left(\frac{\phi'}{\phi}\right) = \text{const} + \ln\left(\frac{k_1\tau'}{1 + k_{-1}\tau'}\right) \tag{1}$$

(k_1, formation rate constant; k_{-1}, dissociation rate constant; τ', fluorescence lifetime of the exciplex). Within the high temperature range ($k_{-1}\tau' \gg 1$)

$$\ln\left(\frac{\phi'}{\phi}\right) = \text{const} + \ln\left(\frac{k_1}{k_{-1}}\right) \tag{1a}$$

Therefore, in this temperature range the plots (III) give the temperature dependence of the equilibrium constant $K = k_1/k_{-1}$ and the value of ΔH_c can be calculated. Within the low temperature range ($k_{-1}\tau' \ll 1$) the temperature dependence of $k_1\tau'$ and consequently the activation energy for exciplex formation can be obtained, but this is not the aim of this work. In the cases of compounds 1 and 2 the plots (III) (cf. Fig. 4, 293 K < T < 343 K) fall in the non-linear region. This means that because of the low boiling point of the solvent we cannot reach the high temperature range necessary for a completely reversible exciplex formation. If solvents with higher boiling points (e.g. dodecane) were to be used at temperatures $T > 398$ K we would expect that the investigated 2-NDKB would not be completely stable. However, we have calculated the lower limits for the ΔH_c from the plots in Fig. 4 (cf. Table 2).

Assuming the formation of charge transfer exciplexes and utilizing the
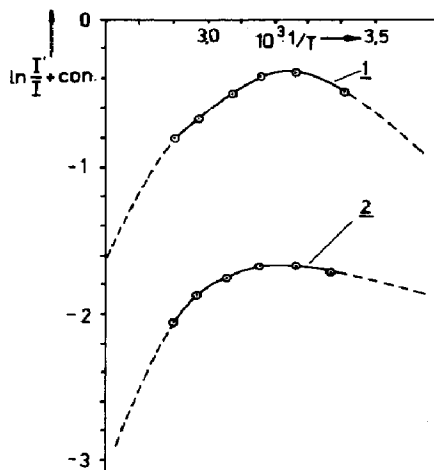

Fig. 4. Temperature dependence of the fluorescence intensity ratio of the 1–naphthalene and 2–naphthalene exciplexes.

semiempirical relation

$$-\Delta H_c \text{ (eV)} \approx E_{00} - (E_D^{ox} - E_A^{red}) - 0.15 \tag{2}$$

given by Weller *et al.* [10, 11] (E_{00}, molecular zero–zero fluorescence energy of the pure 2-NDKB) we can calculate approximately the real ΔH_c for the solvent heptane because the polarographic half-wave reduction potentials E_A^{red} are known (*cf.* Table 2; $E_D^{ox}{}_{naphthalene} = 1.52$ eV against Ag/AgCl).

For the exciplex formation free enthalpy in the excited state, taking into consideration the constant exciplex formation entropy for different exciplexes [10, 11]

$$\Delta G_c \text{ (kJ mol}^{-1}) \approx \Delta H_c + 0.075T \tag{3}$$

The calculated high negative exciplex formation free enthalpies ΔG_c (*cf.* Table 2) leading to the temperature dependence illustrated in Fig. 4 show that the formation of the exciplexes at room temperature occurs nearly irreversibly.

Fluorescence quenching and exciplex formation at higher temperatures have been investigated in the same manner as at room temperature. We did not observe any dependence of the exciplex bandshape on the temperature. Furthermore, the slopes of the plots (Ia) and (IIa) do not depend on the fluorescence wavelength at a fixed high temperature.

3.2. Fluorescence decay of the exciplexes

The fluorescence decay was measured at long wavelengths. For compound 1 within the limits of experimental error [6] the decay is monoexponential for all naphthalene concentrations. In the concentration range $0.01 \leqslant c_N \leqslant 0.03$ mol l^{-1} the decay time τ' remains nearly constant (τ'_{max}, *cf.* Table 2, see Fig. 5(a)). On increasing the naphthalene concentration τ' decreases and we can obtain κ' (see Table 1) by utilizing the equation

$$\frac{\tau'_{max}}{\tau'} = 1 + \kappa' c_N \tag{4}$$

In contrast with compound 1 the exciplex fluorescence of the 2–naphthalene exciplex decays biexponentially (again within the time resolu-
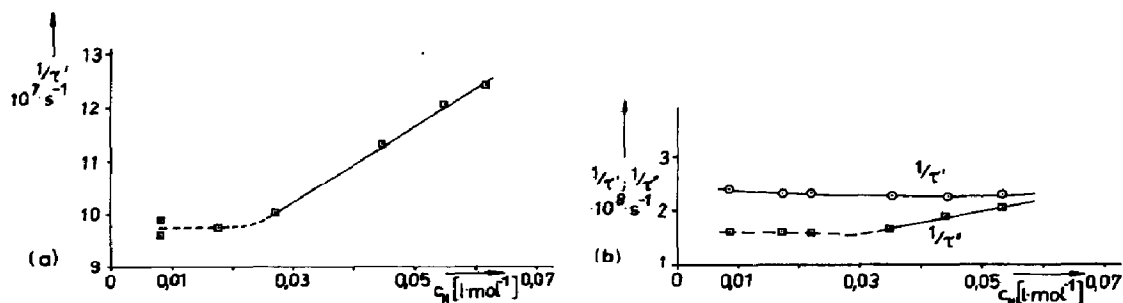

Fig. 5. Dependence of exciplex decay times on the naphthalene concentration in non-degassed heptane at 293 K: (a) compound 1; (b) compound 2.

tion and the limits of experimental error of our equipment) for all naphthalene concentrations and the decay times τ' and τ'' can be determined (*cf.* Table 2, Fig. 5(b)). Whereas τ' remains constant up to 0.06 mol l^{-1} the longer decay time τ'' is reduced on increasing the naphthalene concentration and with eqn. (4) we can obtain the value of the κ'' (see Table 1).

Furthermore, the values τ' and τ'' for both 1 and 2 are independent of the fluorescence wavelength.

4. Discussion

The rotamers A and B of 2-NDKB could be detected in polar solvents [3]. There may be two reasons why we cannot find any experimental evidence for the existence of rotamers in non-polar solvents from the fluorescence properties of the pure 2-NDKB. Firstly, the ground state equilibrium $A \rightleftarrows B$ may be shifted in non-polar solvents completely to one rotamer, or, secondly, the deactivation rate constants of the rotamers may be very similar to each other, *i.e.* $k_{fA} \approx k_{fB}$ and $k_{dA} \approx k_{dB}$ (*cf.* Scheme 1). In the second case there is the possibility of distinguishing the different properties of the rotamer exciplexes if at least two of the rate constants are not identical, *i.e.* $k_1 \neq k_2$ and/or $k'_{fA} \neq k'_{fB}$, and/or $k'_{dA} \neq k'_{dB}$ (*cf.* Scheme 1). The irreversibility of the exciplex formation at room temperature (see above) gives the advantage of a simplified reaction mechanism as indicated in Scheme 1 because the dissociation rate constant can be neglected. For the general case it can be shown easily that when there are two exciplexes simultaneously with different formation constants and spectral properties the plots (I) and (II) may be non-linear and a dependence of these plots on the fluorescence wavelength should be observed. Our stationary fluorescence investigations at different donor concentrations and at different temperatures give no hint of the existence of different exciplexes for either 1 or 2.

The time-resolved measurements, in contrast with stationary investigations, can be quite successful in searching for rotamers, but investigating both the monomer fluorescence decay and the exciplex rise time is not the proper way to distinguish between the rotamers. Therefore, we measured the exciplex fluorescence decay; according to Scheme 1 one obtains ($k_1 = k_2 = k_{diff}[Q]$)

$$I(t) = I_{(AQ)*}(t) + I_{(BQ)*}(t)$$

$$= c \exp\left(-\frac{t}{\tau'_A}\right) + d \exp\left(-\frac{t}{\tau'_B}\right) - (c + d) \exp\left(-\frac{t}{\tau}\right) \tag{5}$$

with

$$c = \frac{[A^*]_0 k'_{fA} k_{diff}[Q]}{k'_{fA} + k'_{dA} - k_{diff}[Q] - k_f - k_d}$$

$$d = \frac{[B^*]_0 k'_{fB} k_{diff}[Q]}{k'_{fB} + k'_{dB} - k_{diff}[Q] - k_f - k_d}$$

$$\frac{1}{\tau'_A} = k'_{fA} + k'_{dA}$$

$$\frac{1}{\tau'_B} = k'_{fB} + k'_{dB}$$

$$\frac{1}{\tau} = k_f + k_d + k_{diff}[Q]$$

The kinetics is triexponential. If we assume $\tau'_A \gg \tau$ and $\tau'_B \gg \tau$ (i.e. the growing component is very fast) we can observe, by nanosecond time resolution, a biexponential exciplex fluorescence decay for the case $[A^*]_0 \neq 0$ and $[B^*]_0 \neq 0$.

The decay of the exciplex fluorescence of 1 may be mono-exponential for the following reasons: (i) $[A^*]_0 \gg [B^*]_0$ or $[A^*]_0 \ll [B^*]_0$, i.e. we have only one rotamer; (ii) $[A^*]_0 \neq 0$, $[B^*]_0 \neq 0$ and $\tau'_A \approx \tau'_B$, i.e. the two exciplexes have very similar lifetimes (it ought to be mentioned that a lifetime difference of 10%, i.e. $\Delta\tau = \tau_1 - \tau_2 \geqslant \tau_1/10$ for $\tau_1 > \tau_2$, can be distinguished within two orders of magnitude in the dynamic range of the nanosecond single-photon-counting method); (iii) the exciplexes equilibrate according to Scheme 2.

Scheme 2.

We do not know anything about the electron distribution or the magnitude of the bond orders within the molecules of the exciplex. It may be that the NEER principle is not valid for the exciplexes. The kinetics for Scheme 2 can also lead to mono-exponential exciplex fluorescence decay.

At this time we cannot distinguish between cases (i) - (iii) for compound 1. The exciplex fluorescence of 2 decays biexponentially. Therefore, with respect to eqn. (5), $[A^*]_0 \neq 0$, $[B^*]_0 \neq 0$ and $\tau'_A \neq \tau'_B$. In addition, we must exclude the possibility of reversible formation of higher exciplexes according to Scheme 3.
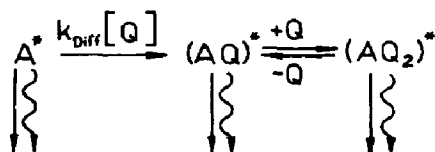
Scheme 3.

The processes in Scheme 3 give a biexponential decay in the case of the existence of one rotamer only:

$$I'(t) = g \exp\left(-\frac{t}{\tau_{(AQ)^*}}\right) + h \exp\left(-\frac{t}{\tau_{(AQ_2)^*}}\right) \tag{6}$$

For mechanism 3 the coefficients g and h must be related to the quencher concentration by the relation

$$\ln\left(\frac{g}{h} - 1\right) = f(c_N)$$

but we found the values $\ln(g/h - 1)$ to be independent of concentration and therefore the mechanism in Scheme 3 can be ruled out.

The exciplex fluorescence is quenched in the case of both 1 and 2 on increasing the naphthalene concentration, for instance by irreversible formation of terplexes or higher exciplexes with fluorescence quantum yields smaller than those of the 1:1 exciplexes, or by complete exciplex quenching [12]. Therefore, the intensity plots (cf. Fig. 2) and the plots (I), (Ia), (II) and (IIa) are non-linear at higher naphthalene concentrations. Furthermore, the exciplex decay times are reduced for this reason. Exciplex quenching at higher donor concentrations according to Scheme 4 gives further evidence for the existence of two exciplexes of compound 2.

$$(AQ)^* \xrightarrow[Q]{k_{q1}} A + Q$$

$$(BQ)^* \xrightarrow[Q]{k_{q2}} B + Q$$
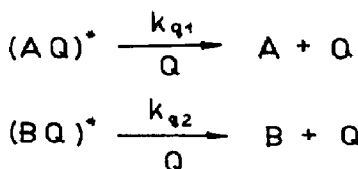
Scheme 4.

We found different κ' and κ'' (cf. Table 1) for the two fluorescence lifetime components and it may be understood that the longer living exciplex is more strongly quenched by the donor.

In summary, for compound 1 in heptane only one exciplex can be detected. For compound 2, nanosecond time-resolved measurements allow us to conclude that two different exciplexes with different lifetimes but identical fluorescence bands and formation rate constants exist. At this stage we cannot assign the conformational structure of either the rotamers A and B or the exciplexes (AQ)* and (BQ)*.

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