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Fluorescence switching in 4-amino-1,8-naphthalimides: "on–off–on" operation controlled by solvent and cations

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Dedicated to Dr. A.T. Peters on the occasion of his retirement

Abstract

The fluorescence properties of 4-(2′-*N*,*N*-dimethylaminoethyl)amino-9-butyl-naphthalimide (**1**) are so strongly affected by the nature of the solvent medium in which the molecule is situated that the emission can be considered to be "switched off" when a certain solvent polarity is reached. The mechanism appears to involve the formation of an exciplex between the naphthalimide ring and the distal dimethylamino group which is stabilised by electron transfer. Kinetic parameters for the exciplex formation in **1** and its *N*,*N*-dimethylaminopropyl analogue are derived in a range of solvents. The fluorescence can be "switched on" again by metal ions and protons. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Fluorescence; Naphthalimide; PET; Solvent effects; Exciplex

1. Introduction

Solvent effects can play a significant role in the photophysics of excited states [1,2]. Polarity dependent shifts in absorption and fluorescence emission spectra are common and a few systems, such as Michler's ketone [3] and dansyl compounds [4], are known where the nature of the lowest excited singlet state changes on moving from non-polar to polar solvents. In addition, there can be very specific solvent effects due to e.g. hydrogen bonding which lead to processes such as proton transfer [5,6] or to phenomena such as specific solvation [7,8].

Additionally, there is now a considerable known range of compounds whose solution phase excited state properties, especially fluorescence, can be markedly altered by the addition of metal ions or protons [9,10]. Their application has been extended by de Silva and co-workers into the realms of molecular logic [11]. Many of these systems are considered to undergo photoinduced electron transfer (PET) and de Silva et al. have reported

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PET systems which can function as logical AND and OR gates [12] with the fluorescence emission being switched on and off by protons and/or metal ions such as Na^+ and K^+.

Many of the earliest reported fluorescent systems which involve PET are based on anthracene as the fluorophore bonded to one or more amine functions. Under appropriate solvent conditions, the anthracene emission is quenched by the amine group(s) with at least partial electron transfer from the amine group to the anthracene ring [13–16]. If the PET process is "switched off" by e.g. protonation of the amine group(s) [13,14] or by their complexation with a metal ion such as Zn^{2+} [13,14], the fluorescence of the anthracene is restored. This can be denoted using de Silva's fluorophore-spacer-receptor notation or as in Fig. 1 where the ionophore is the amine function. Such compounds act as fluorescent sensors for the proton or metal ion which switch off the PET and Czarnik has coined the phrase "chelation enhanced fluorescence" (CHEF) to describe the way that the complexed ion switches on the anthracene emission [16]. Elaboration of the receptor with azacrown ethers [17–19] shows the versatility of these systems in terms of the range of species which can be sensed.

Anthracene, as a UV-absorbing chromophore, is not the ideal choice for the fluorophore in a fluorescent sensor and a range of other fluorophores have also been employed [9,10]. In particular, there are a number of compounds, especially originating from de Silva's group, which employ an aminonaphthalimide as the fluorophore. Samanta and co-workers have pursued similar objectives utilising the 4-aminophthalimide system [20–22]. We have also been studying the properties of some 4-(dialkylaminoalkyl)amino-9-butyl-1,8-naphthalimides whose emission properties are sensitive to the presence of transition metal ions such as Cu^{2+} [23]. During the course of a study of the photophysics of some of these compounds as a function of solvent, we have discovered a notable switching effect of the solvent. In non-polar solvents the compounds are highly fluorescent, but in polar solvents the compounds show only weak fluorescence. In addition, the transition between these two states is very sharp; there is not a gradual decline in fluorescence efficiency with increasing polarity, rather the fluorescence is "switched off" when a certain solvent polarity is reached [14]. This switching appears to correlate with the formation of an intramolecular exciplex (stabilised by PET) as detailed below.

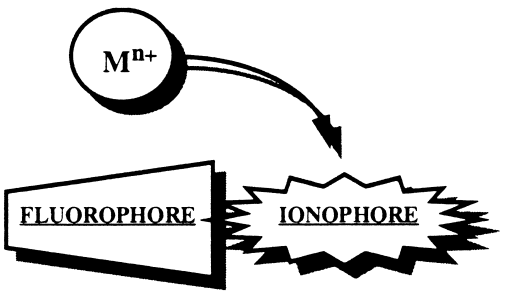
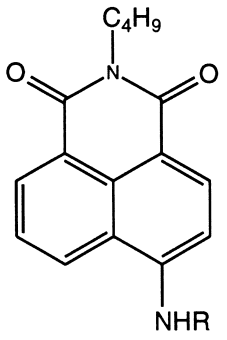


Fig. 1. Schematic representation of a fluorophore–ionophore combination.

2. Experimental

Naphthalimides **1**–**3** were prepared by standard methods [23–26] from 4-chloro- or 4-nitro-1,8-naphthalic anhydride by reaction with firstly butylamine and then *N*,*N*-dimethylethylenediamine (**1**), *N*,*N*-dimethylpropylenediamine (**2**) or propylamine (**3**). All three compounds were purified by recrystallisation and/or column chromatography and gave satisfactory NMR spectra and elemental analyses. All the solvents used were spectophotometric grade (Aldrich).

Absorption and fluorescence spectra were measured on a Hewlett-Packard 8452A diode array spectrometer and a SPEX Fluoromax spectrofluorimeter respectively. Fluorescence quantum yields were determined on optically dilute (absorbance < 0.05) samples by comparison with standards measured previously [24,27,28]. Fluorescence decay profiles were measured by the time-correlated, single photon counting technique [29] using the Daresbury Laboratory Synchrotron Radiation Source for excitation. The experimental set-up has been described elsewhere [30]. The decay profiles were analysed by computer convolution and the "goodness of fit" evaluated on the basis of the χ^2 value and the distribution of residuals.



1: R= $(CH_2)_2N(CH_3)_2$
2: R= $(CH_2)_3N(CH_3)_2$
3: R= C_3H_7

Scheme 1.

3. Results and discussion

The compounds considered here are structures **1**–**3**; 4-(2′-*N*,*N*-dimethylaminoethyl)-amino-9-butyl-1,8-naphthalimide (**1**), 4-(3′-*N*,*N*-dimethylaminopropyl)amino-9-butyl-1,8-naphthalimide (**2**) and 4-propylamino-9-butyl-1,8-naphthalimide (**3**). The first two compounds exhibit anomalous behaviour in terms of their emission properties, whereas **3** is considered to be a reference compound.

All three compounds absorb in two spectral regions of the UV-visible above 200 nm. The lowest energy band is in the region of 420–440 nm and a pair of higher energy absorption bands lie in the region of 260–290 nm (see Fig. 2). In both cases, extinction coefficients of 10–20,000 $dm^3\ mol^{-1}\ cm^{-1}$ are recorded, indicating that these absorption features are π–π^* transitions. The behaviour of the absorption properties of all three compounds with changes in the nature of the solvent are virtually identical; with increasing solvent polarity and/or hydrogen bonding ability, the visible absorption band undergoes a red-shift of up to 25 nm whilst the UV bands are unaffected (Table 1). This behaviour is expected as the lowest energy transition involves considerable charge-transfer character [24]. The fluorescence maxima of the three compounds undergo a larger red-shift with increasing solvent polarity with emission maxima varying from approximately 460 to 530 nm (Table 2).

At this stage, the absorption and emission properties of the three compounds are very similar. However, when the efficiency of the fluorescence of the three compounds is measured in terms of their fluorescence quantum yields, very significant differences appear (Table 2). Compound **3** is strongly fluorescent across the whole range of solvents employed in our work whereas **1** and **2**, where the alkyl substituent on the 4-amino group is replaced with a dialkylaminoalkyl group, exhibit much weaker emission in the more polar solvents. The suddenness of the change in emission efficiency is illustrated in Fig. 3. This change in fluorescence efficiency has also been noted for a very similar compound to **1** by de Silva et al., although they only reported measurements in cyclohexane and ethanol [31].

It is not surprising, therefore, to find that the fluorescence kinetics of these compounds are also very solvent dependent and that **1** and **2** exhibit a step-change in the nature of their kinetics at the same point in the solvent series at which they exhibit the diminution in their fluorescence quantum yields. As with its fluorescence yields, the decay kinetics of compound **3** are consistently monoexponential in all solvents (Figs. 4 and 5). In non-polar solvents, compounds **1** and **2** are also monoexponential (Fig. 4) but in polar solvents either bi- or tri-exponential (for **1** in DMF and DMSO) models are required to adequately fit the experimentally observed decays as Fig. 5 shows. The parameters required for an acceptable fit to the experimental emission kinetics are shown in Table 3 for the solvents used in this study.

We have previously suggested that the metal ion sensing properties of **1** are caused by the formation of an intramolecular exciplex between the distal dimethylamino group at the 4-position and the naphthalimide ring [23]. The exciplex formation quenches the fluorescence and leads to complex emission kinetics. There is no evidence for exciplex emission in Fig. 2 but this would certainly explain the complex emission kinetics observed for **1** and **2** in more polar solvents. Exciplex formation is often accompanied by charge transfer between the two components of the exciplex and de Silva's group have postulated that photoinduced electron transfer (PET) occurs in compounds such as these [32]. The exciplex formation will be energetically favourable if

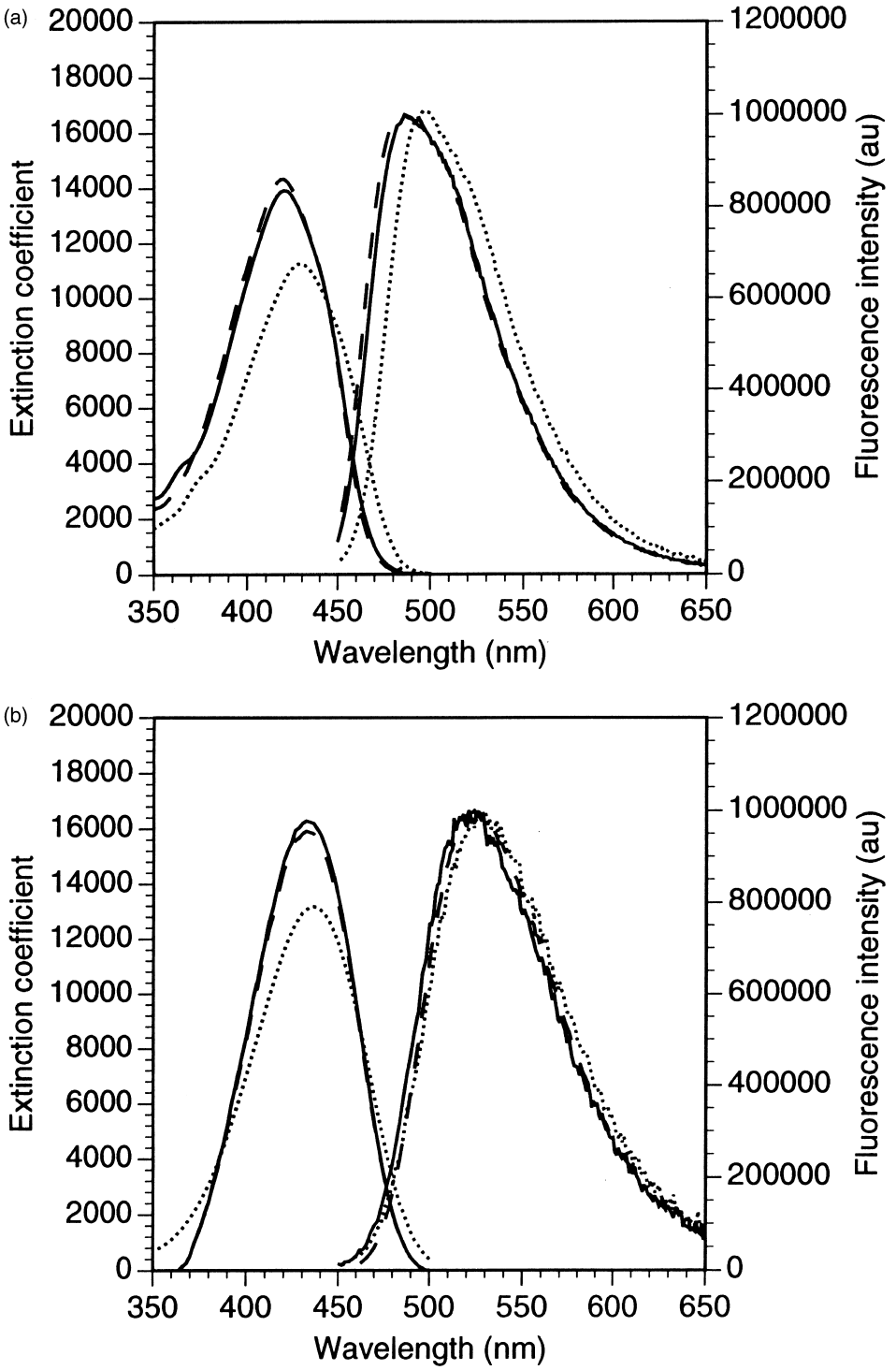


Fig. 2. Absorption and fluorescence spectra of **1–3** in (a) toluene and (b) acetonitrile. **1** (—), **2** (- - -), 3 (· · · ·).

Table 1
Absorption properties of naphthalimides **1–3**

Solvent	**1**	**2**	**3**
	λ_{max} (log ε)	λ_{max} (log ε)	λ_{max} (log ε)
Methylcyclohexane	430 (3.71), 412 (3.83) 272 (4.01), 260 (4.09)	438 (sh), 420 278, 260	430 (3.99), 410 (4.13) 272 (4.33), 260 (4.41)
1,4-Dioxane	422 (4.13), 276 (sh) 262 (4.33)	428 (4.10), 278 (sh) 264 (4.30)	422 (4.12), 278 (sh) 264 (4.36)
Toluene	420 (4.14)	428 (4.04)	420 (4.17)
1-Chlorobutane	418 (4.20), 276 (4.32) 260 (4.40)	428 (4.07), 278 (4.22) 262 (4.27)	420 (4.17), 278 (4.31) 260 (4.30)
Diethyl ether	418 (4.17), 276 (4.32) 260 (4.36)	424 (4.17), 276 (4.39) 260 (4.40)	420 (4.17), 276 (4.31) 260 (4.35)
Ethyl acetate	424 (4.13), 278 (4.26)	430 (4.09), 280 (4.24)	426 (4.16), 278 (4.29)
2-Propanol	438 (4.18), 282 (4.25) 260 (4.29)	442 (4.14), 284 (4.21) 260 (4.24)	443 (4.21), 284 (4.28) 260 (4.30
Acetone	430 (4.16)	436 (4.08)	431 (4.14)
Ethanol	436 (4.34), 282 (4.41) 260 (4.45)	442 (4.13), 282 (4.21) 260 (4.24)	442 (4.17), 284 (4.25) 260 (4.30)
Methanol	436 (4.17), 282 (4.23) 260 (4.26)	440 (4.16), 284 (4.22) 260 (4.25)	442 (4.20), 284 (4.27) 260 (4.28)
Dimethyl formamide	438 (4.15), 284 (4.26)	440 (4.13), 284 (4.24)	440 (4.17), 284 (4.28)
Acetonitrile	430 (4.20), 280 (4.30) 260 (4.33)	436 (4.12), 280 (4.22) 262 (4.25)	430 (4.21), 280 (4.32) 260 (4.35)
Dimethyl sulphoxide	444 (4.15), 284 (4.28) 264 (4.45)	444 (4.13), 285 (4.24) 264 (4.22)	444 (4.16), 284 (4.29) 264 (4.26)

Table 2
Fluorescence maxima (λ_{max}) and quantum yields for compounds **1–3** in various solvents together with the solvent dielectric constants (ε)

Solvent	ε	**1**		**2**		**3**	
		λ_{max} (nm)	ϕ_f	λ_{max} (nm)	ϕ_f	λ_{max} (nm)	ϕ_f
MCH	2.0	460, 481	0.95	469, 491	0.87	459, 477	0.91
1,4-Dioxane	2.2	503	0.93	506	1.00	502	1.0
Toluene	2.4	488	0.86	495	0.77	482	0.94
Diethyl ether	4.3	489	0.55	493	0.52	488	0.63
Ethyl acetate	6.0	506	0.55	509	0.68	503	0.83
2-Propanol	19.9	523	0.061	525	0.27	524	0.7
Acetone	20.7	513	0.038	521	0.18	516	0.76
Ethanol	24.6	526	0.018	531	0.11	531	0.42
Methanol	32.7	526	0.03	532	0.18	529	0.58
DMF	36.7	527	0.018	528	0.12	525	0.76
Acetonitrile	37.5	522	0.018	528	0.07	524	0.58
DMSO	46.7	530	0.013	532	0.13	532	0.74

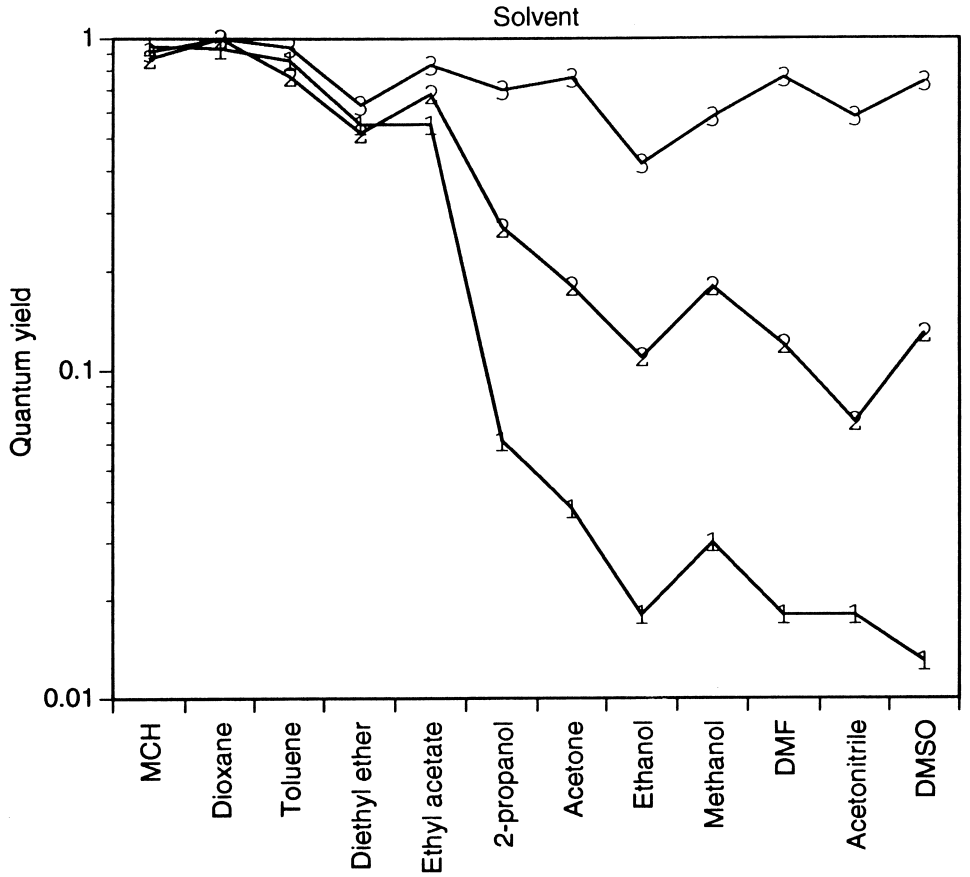


Fig. 3. Fluorescence quantum yields of **1–3** as a function of the solvent range used in this study.

$$\Delta G_{\text{exciplex}} = IP - EA - C - \Delta H_s - \Delta E_{0-0} < 0 \quad (1)$$

where IP and EA are the ionization energy and electron affinity of the electron donor and acceptor parts of the exciplex respectively, C is the Coulomb interaction energy between the two ionic centres, ΔH_s is the solvation energy of the exciplex and ΔE_{0-0} is the excitation energy of the naphthalimide [33]. In our case, it is only ΔH_s which varies significantly as the solvent is changed and the first observation we can make is that $\Delta G_{\text{exciplex}}$ as given in Eq. (1) must be fairly close to zero if the exciplex formation can be switched on or off by a change of solvent. The low $\Delta G_{\text{exciplex}}$ values are probably not surprising since the lowest excited state in the 4-aminonaphthalimides already has a substantial degree of charge-transfer character [24] and a further interaction involving charge transfer/PET would not be highly favourable.

ΔH_s will be comprised of a number of solute–dipole interaction terms but will be dominated by a dipole–dipole interaction term [1]:

$$\Delta H_{\text{DD}} = -\mu_{\text{S1}}.(\mu_{\text{exciplex}} - \mu_{\text{S1}}).[f(\varepsilon) - f(n^2)]/a^3 \quad (2)$$

For the energy of this interaction (ΔH_{DD}) to be exothermic, the dipole moment of the exciplex

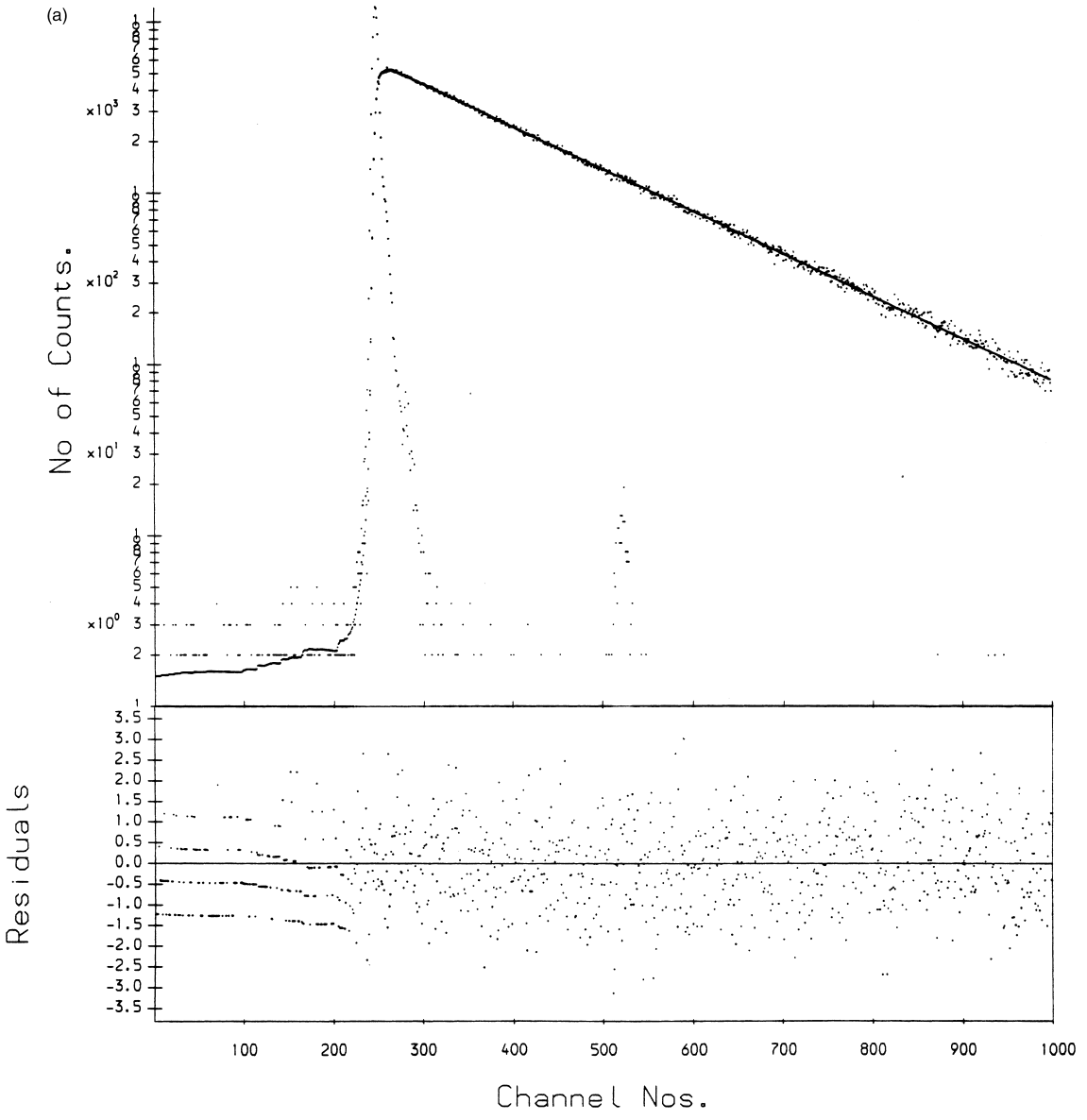


Fig. 4. Fluorescence decay profiles for **1–3** [(a)–(c) respectively] in toluene. The lamp profile and the experimental and fitted decay profiles (parameters given in Table 3) are shown together with the residuals from the fit. Time calibration = 0.0472 ns per channel.

(μ_{exciplex}) must be greater than the dipole moment of the first excited singlet state of the amino-naphthalimide (μ_{S1}). In addition, it would appear that the solvent function $f(\varepsilon) - f(n^2)$ has to have a value in the region of 0.5 [i.e. $f(\varepsilon) - f(n^2)$ for 2-propanol)] for the ΔH_{DD} value to be sufficiently exothermic to make the overall exciplex formation exothermic (i.e. $\Delta G_{\text{exciplex}} < 0$).

We can put forward a kinetic model for the exciplex formation of the form

$$N + h\upsilon \rightarrow {}^1N^* \qquad \text{Excitation} \tag{3}$$

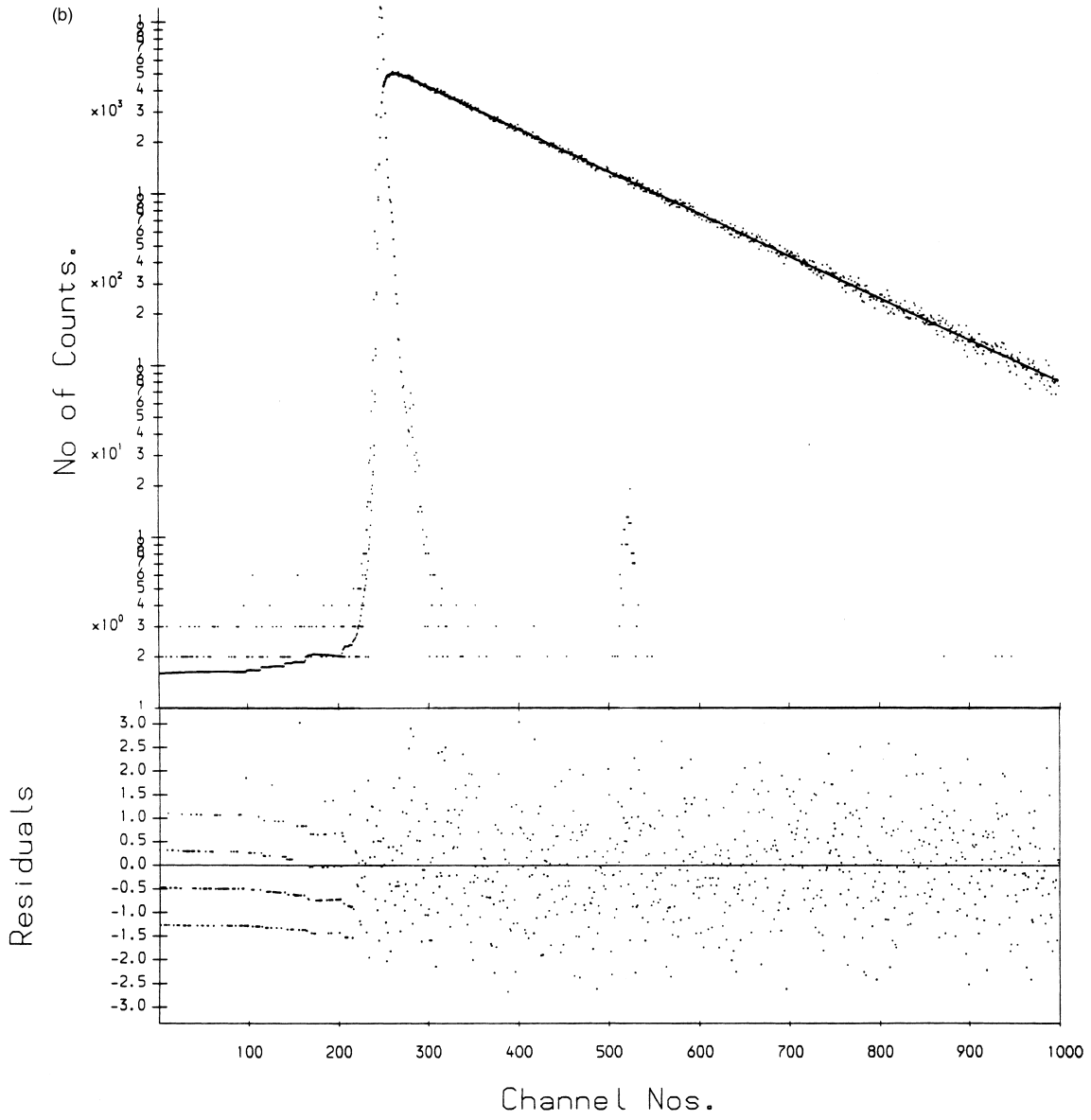


Fig. 4. (*continued*)

$$^1N^* \rightarrow N + h\upsilon \quad \text{Fluorescence} \tag{4}$$

Rate constant k_1

$$^1N^* \rightarrow N \quad \text{Non-radiative decay} \tag{5}$$

Rate constant k_2

$$^1N^* \rightarrow {}^1(\text{Exciplex})^* \quad \text{Exciplex formation} \tag{6}$$

Rate constant k_3

$$^1(\text{Exciplex})^* \rightarrow {}^1N^* \quad \text{Exciplex break-up} \tag{7}$$

Rate constant k_4

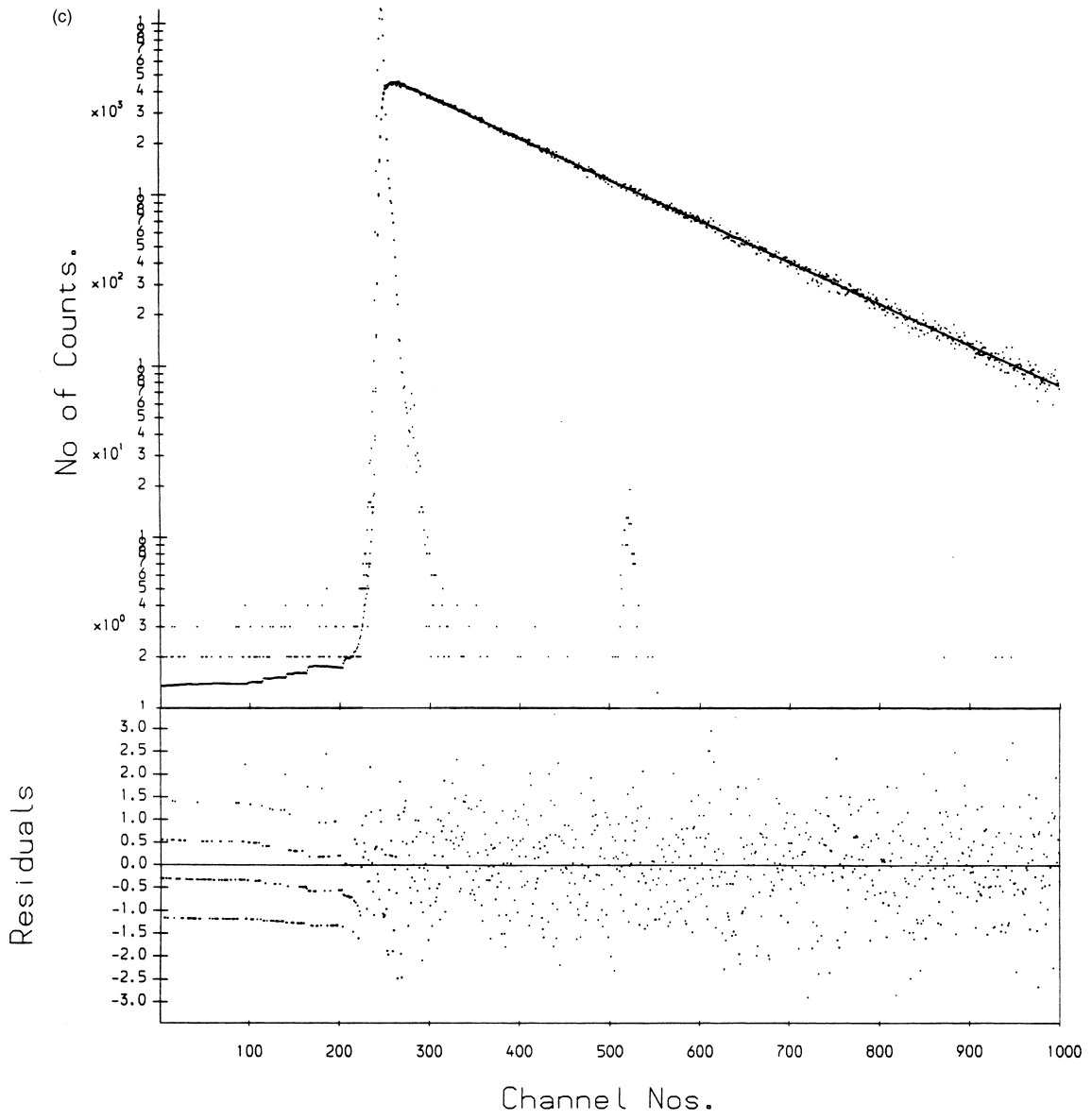


Fig. 4. (*continued*)

^{1}(Exciplex)$^* \rightarrow N$ Decay of exciplex

Rate constant k_5 (8)

where N is the naphthalimide and $^1X^*$ represents the first excited singlet state of either the naphthalimide or the exciplex.

This model fully predicts the observed behaviour of **1** and **2** and can be used to relate their fluorescence quantum yields [ϕ_f, Eq. (9)] and decay kinetics [Eq. (10)–(12)] to the rate constants k_1 to k_5 [Eq. (4)–(8)] [34,35].

$$\phi_f = \frac{k_1(k_4 + k_5)}{(k_1 + k_2)(k_4 + k_5) + k_3 k_5} \quad (9)$$

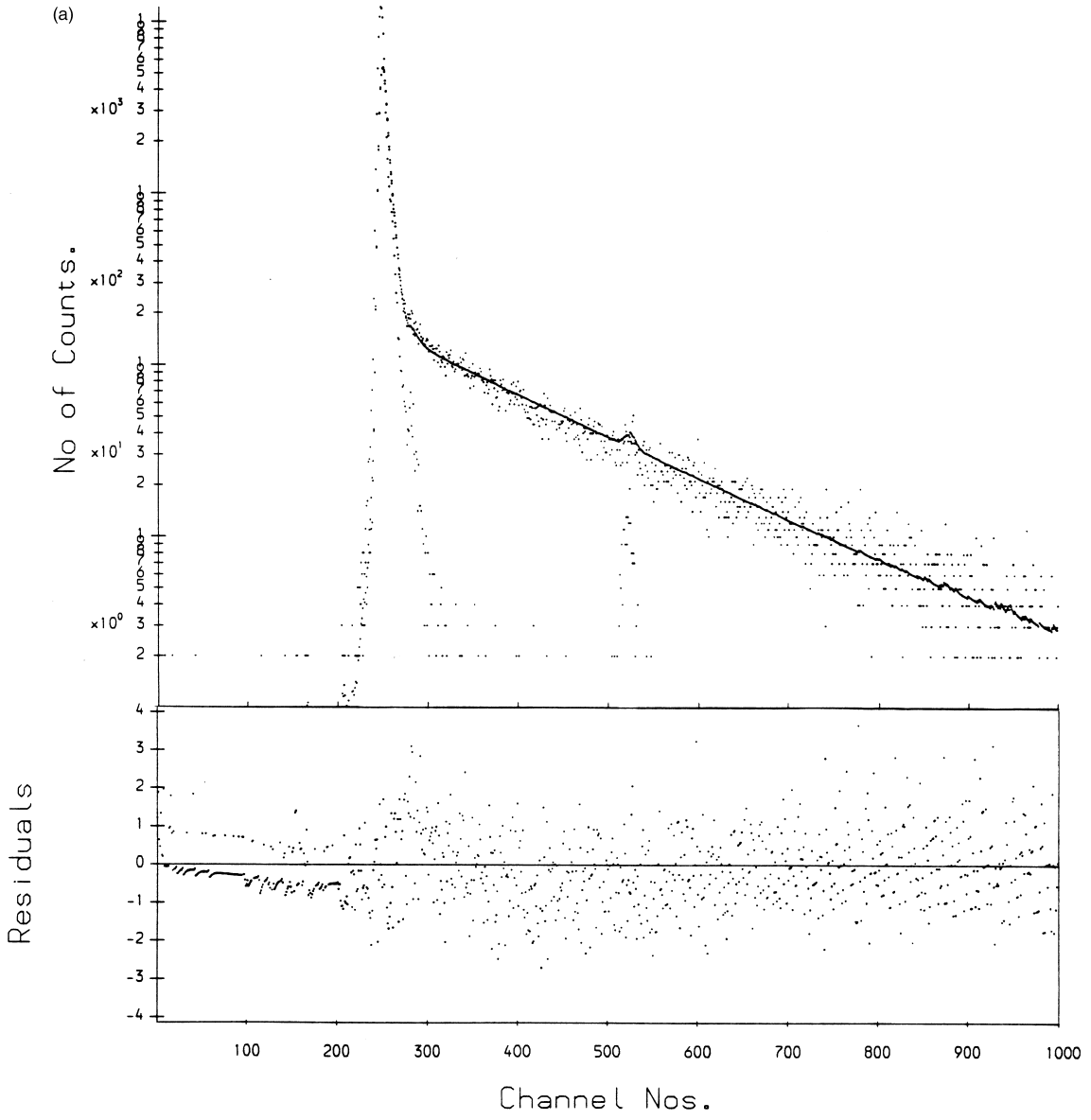


Fig. 5a. Fluorescence decay profiles for **1–3** [(a)–(c) respectively] in acetonitrile. The lamp profile and the experimental and fitted decay profiles (parameters given in Table 3) are shown together with the residuals from the fit. Time calibration = 0.0472 ns per channel.

$$\left[{}^1N^*\right] = C_1 e^{-\lambda_1 t} + C_2 \mathrm{e}^{-\lambda_2 t} \tag{10}$$

$$\lambda_{1,2} = \frac{1}{2}\Big[k_1 + k_2 + k_3 + k_4 + k_5 \mp \sqrt{(k_4 + k_5 - k_1 - k_2 - k_3)^2 + 4k_3k_4}\Big] \tag{11}$$

$$\frac{C_1}{C_2} = \frac{(\lambda_2 - k_1 - k_2 - k_3)}{(k_1 + k_2 + k_3 - \lambda_1)} \tag{12}$$

If we assume (i) that there is no significant exciplex emission (the emission spectra of **1–3** shown in Fig. 2b are virtually identical and support this)

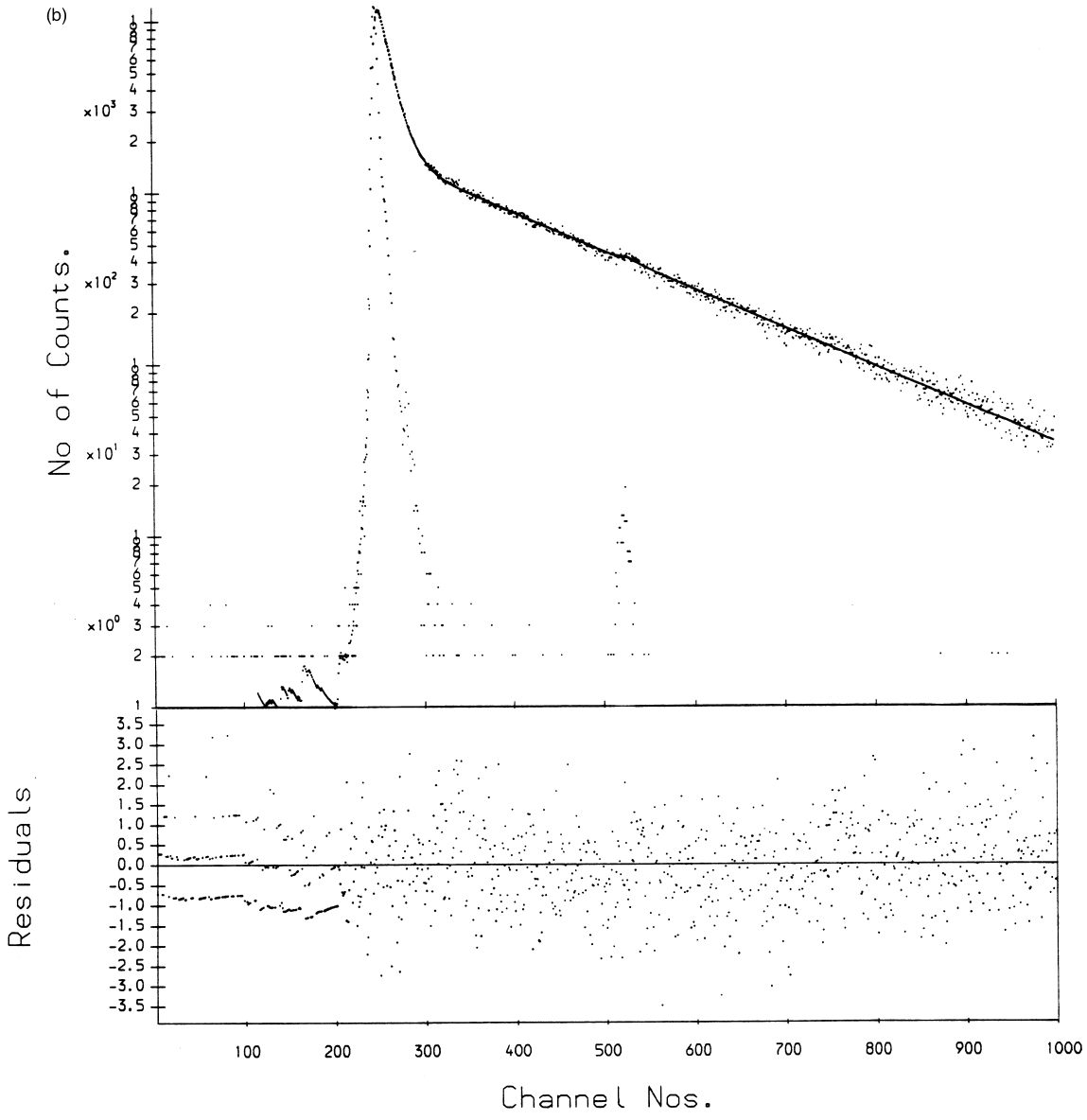


Fig. 5. (*continued*)

such that the measured quantum yields for **1** and **2** may be equated with ϕ_f and (ii) that the values for k_1 and k_2 for **1** and **2** in a given solvent are the same as k_1 and k_2 for **3** in the same solvent, then it is possible to solve Eq. (9)–(12) for rate constants k_3–k_5. The results of these calculations are shown in Table 4. The values of k_3–k_5 for 1 in DMF and DMSO have to be viewed with considerable caution since a biexponential fit is not optimal for these systems — hence the results of both bi- and tri-exponential fits presented in Table 3.

For both compounds **1** and **2**, the rate constant for exciplex formation exhibits an excellent correlation with solvent polarity, increasing by a factor of nearly 6 for **1** and a factor of nearly 10 for **2** over the range of solvents where clear biexponen-

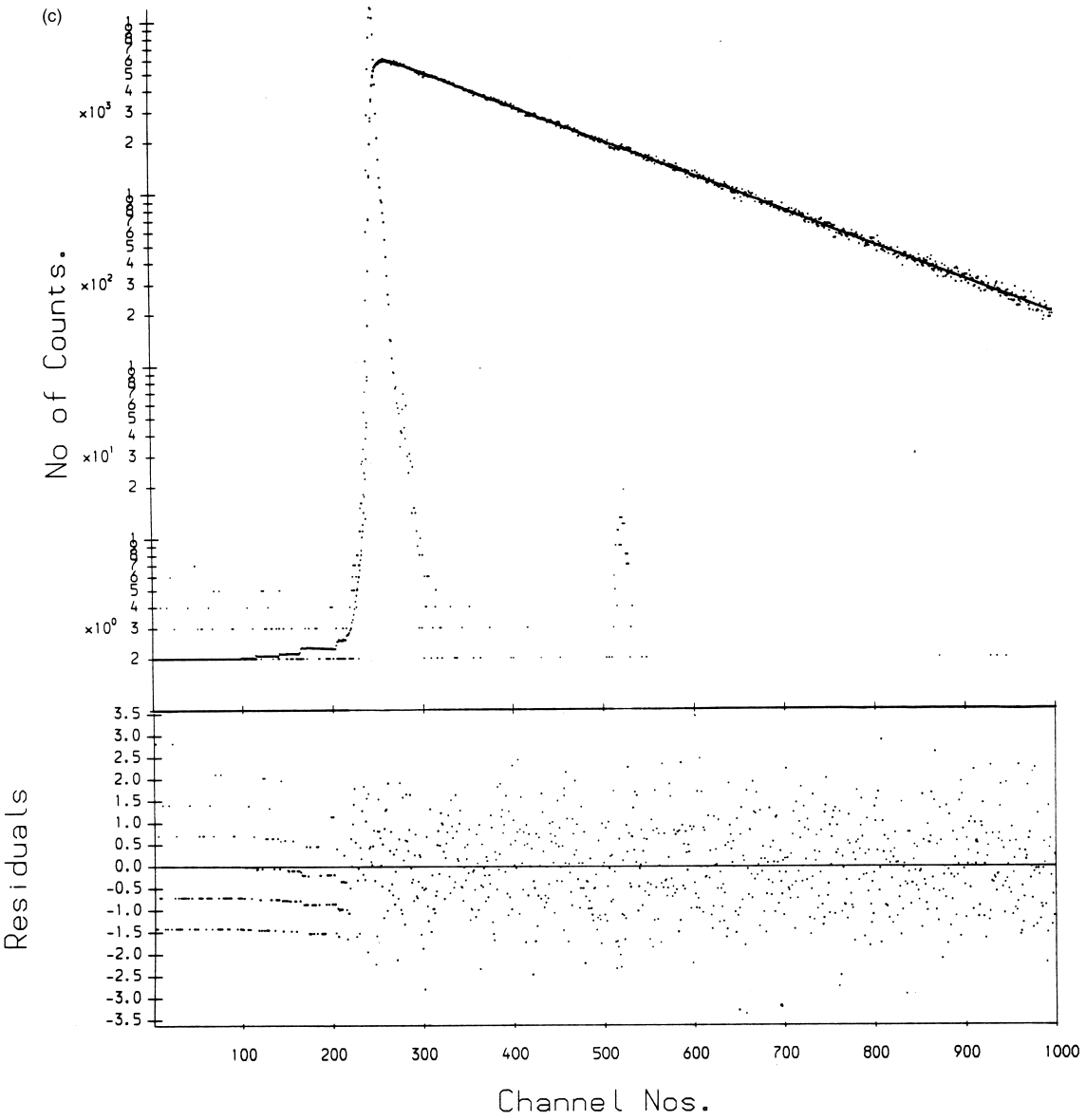


Fig. 5. (*continued*)

tial emission kinetics are observed. This indicates that exciplex formation is favoured by the more polar solvents which can stabilise any PET which occurs. The distance between the fluorophore (4-aminonaphthalimide) and the receptor (*N*,*N*-dimethylamino group) is also clearly significant. The ϕ_f values for **1** are much smaller than the corresponding quantum yields for **2**, reflecting the much greater size of rate constant k_3 for **1** relative to **2**. These observations are in complete accord with the common observation that intramolecular exciplex formation becomes less efficient the

Table 3
Calculated parameters (a = pre-exponential factor, τ = lifetime) for single or multi-exponential fits to the fluorescence decay profiles for compounds **1**–**3** in various solvents

Compound	Solvent	a_1	τ_1 (ns)	a_2	τ_2 (ns)	a_3	τ_3 (ns)
1	MCH	1.000	7.53				
	1,4-Dioxane	1.000	8.63				
	Toluene	1.000	8.26				
	Diethyl ether	1.000	9.69				
	Ethyl acetate	1.000	9.39				
	2-Propanol	0.994	0.76	0.006	9.26		
	Acetone	0.982	0.34	0.018	8.45		
	Ethanol	0.994	0.32	0.006	9.00		
	Methanol	0.988	0.20	0.012	8.75		
	DMF	0.963	0.15	0.037	6.50		
		0.972	0.12	0.013	1.88	0.015	7.86
	Acetonitrile	0.993	0.15	0.007	8.15		
	DMSO	0.971	0.14	0.029	8.55		
		0.983	0.11	0.007	1.41	0.010	9.82
2	MCH	1.000	7.61				
	1,4-Dioxane	1.000	9.88				
	Toluene	1.000	8.31				
	Diethyl ether	1.000	9.58				
	Ethyl acetate	1.000	6.47				
	2-Propanol	0.905	3.23	0.095	9.55		
	Acetone	0.975	0.99	0.025	9.12		
	Ethanol	0.899	1.77	0.101	8.61		
	Methanol	0.860	1.39	0.140	8.05		
	DMF	0.895	0.99	0.105	9.50		
	Acetonitrile	0.917	0.59	0.083	9.04		
	DMSO	0.915	1.26	0.085	9.77		
3	MCH	1.000	7.76				
	1,4-Dioxane	1.000	10.18				
	Toluene	1.000	8.43				
	Diethyl ether	1.000	9.98				
	Ethyl acetate	1.000	9.39				
	2-Propanol	1.000	9.69				
	Acetone	1.000	9.72				
	Ethanol	1.000	9.12				
	Methanol	1.000	8.17				
	DMF	1.000	10.25				
	Acetonitrile	1.000	10.17				
	DMSO	1.000	10.55				

longer the carbon chain joining the two components of the exciplex [33].

Rate constant k_5, for the decay of the exciplex, is remarkably constant across the solvent series; an average value of $1.09\pm0.4\times10^8\ s^{-1}$ encompasses all of the observed values except for **1** in DMF and DMSO where we have previously expressed reservations about the values of k_3–k_5 recovered from the experimental data. On the other hand, rate constant k_4, for the break-up of the exciplex to reform the excited naphthalimide, exhibits considerable variation with solvent. For both compounds, k_4 varies by approximately an order of magnitude between the least polar (2-propanol) and the more polar solvents used. It is surprising to find that k_4 is accelerated by a more polar solvent.

Table 4
Rate constants (all$\times 10^{-8}$ s^{-1}) for exciplex formation, break-up and decay for compounds **1** and **2** in more polar solvents

Solvent	k_1	k_2	**1**			**2**		
			k_3	k_4	k_5	k_3	k_4	k_5
2-Propanol	0.72	0.31	12.20	0.12	0.96	1.87	0.15	1.09
Acetone	0.78	0.25	28.2	0.53	1.18	8.32	1.08	0.72
Ethanol	0.46	0.64	30.0	0.24	1.06	4.10	0.40	1.22
Methanol	0.71	0.51	48.2	0.36	1.37	5.14	0.98	1.10
DMF	0.74	0.23	63.3	1.45	2.52	8.15	0.72	1.28
Acetonitrile	0.57	0.41	63.5	0.86	0.81	14.7	1.24	1.18
DMSO	0.70	0.25	69.2	0.75	2.47	6.43	0.50	1.12

Once the fluorescence has been switched off in a polar solvent, the addition of a transition metal ion such as Cu^{2+} switches the emission back on again [23]. Protons have the same effect; both species presumably interact with the distal nitrogen of the dimethylamino group such that its lone pair is no longer available to take part in exciplex formation. We therefore have a system which can be switched on or off in terms of its fluorescence depending on the nature of the solvent medium and the presence of certain cations.

Acknowledgements

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