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A study of a highly efficient resonance energy transfer between 7-*N,N*-diethylamino-4-methylcoumarin and 9-butyl-4-butylamino-1,8-naphthalimide

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This paper is dedicated to Dr. Geoff Hallas on his 65th birthday

Abstract

The quenching of the fluorescence of 7-*N,N*-diethylamino-4-methylcoumarin by 9-butyl-4-butylamino-1,8-naphthalimide has been studied in a variety of solvents. The resulting Stern–Volmer plots are non-linear since both radiative and non-radiative energy transfer mechanisms are in operation. The latter is very efficient with rate constants $>10^{12}\,\mathrm{dm}^3\,\mathrm{mol}^{-1}\,\mathrm{s}^{-1}$ and average donor–acceptor distances for the energy transfer of ≈2 nm. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Naphthalimide derivatives have been used in many areas of work for most of this century. At an early stage it was recognised that for the compounds to be coloured and, in particular, to be fluorescent, the naphthalimide ring needed to contain a strongly electron donating substituent such as a methoxy or amino group. To date, many hundreds of naphthalimide derivatives have been synthesised and have found wide application as luminescent dyes and brightners, fluorescent sensors, probes and labels. The earliest applications of naphthalimide derivatives were as dyestuffs for various fabrics but this usage has now been largely superseded and it is the fluorescence properties of these materials which provide the main current interest.

A significant number of naphthalimide derivatives have been synthesised for use as fluorescent probes. These are largely based on the 4-amino-1,8-naphthalimide structure (**1**) and include the Lucifer Yellow dyes which are water-solubilised by the introduction of sulphonate groups at the 3- and 6-positions. The latter are commercially available and can be used as fluorescent probes and labels in a variety of biochemical situations [1]. Derivatives of **1** and 3-amino-1,8-naphthalimide have also been shown to have potential as fluorescent pH sensors [2–4] and we have recently shown the sensitivity of several 4-(aminoalkyl)amino-1,8-naphthalimides to sub-ppm levels of Cu^{2+} [5]. The fluorescence properties of these systems can also be quite sensitive to changes in molecular structure [6,7] and the nature of the solvent [8,9].

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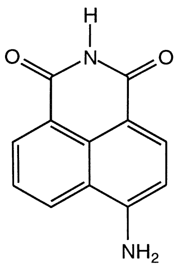

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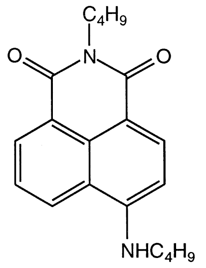

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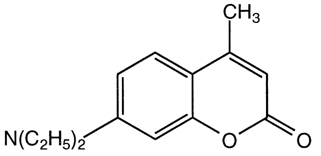

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A mixture of a naphthalimide such as 9-butyl-4-butylamino-1,8-naphthalimide (**2**) and 7-*N,N*-diethylamino-4-methylcoumarin (**3**) is used commercially for luminescent crack detection on surfaces. The mixture is applied to the surface under test, the surface excess removed and any cracks detected under UV light irradiation. The coumarin/naphthalimide mixture is employed because, although the naphthalimide fluoresces very efficiently in the green and yellow areas of the visible spectrum which are most sensitive for visual detection, it does not absorb in the near UV. A near-UV absorber such as **3** is therefore employed to sensitise the naphthalimide since visible excitation of the naphthalimide would interfere with detection of the fluorescence. As the absorption and emission properties of 4-amino-1,8-naphthalimides are quite sensitive to the solvent, we have studied the properties of **2** and **3** and the energy transfer between them as a function of solvent to provide information about the best solvent system to use for luminescent crack detection (as far as the photophysics are concerned). We find that both radiative and non-radiative energy transfer processes [10] are in operation and that the latter process is very efficient across a wide range of solvents. We report the details of this investigation here.

2. Materials and methods

7-*N,N*-diethylamino-4-methylcoumarin and 9-butyl-4-butylamino-1,8-naphthalimide were obtained from Brent Chemicals Ltd. and were purified by repeated recrystallisation from ethanol before use. All the solvents used in this work were spectroscopic grade (Aldrich Ltd.) and were used as received.

Absorption spectra were measured on a Pye-Unicam SP8-100 or a Hewlett-Packard HP8452A diode array spectrometer. Fluorescence spectra were measured on a modular spectrofluorimeter manufactured by Applied Photophysics Ltd. or a SPEX Fluoromax and were corrected for instrumental response. The errors on the absorption and fluorescence wavelengths quoted in Tables 1 and 2 are estimated as ± 1 nm and the extinction coefficients as ± 5%. Fluorescence quantum yields were determined relative to quinine sulphate in 0.1 M perchloric acid ($\Phi_f = 0.55$ [11]), fluorescein in 0.1 M sodium hydroxide solution ($\Phi_f = 0.90$ [6] [12]) and disulphonated perylene ($\Phi_f = 0.92$ [6]). The quantum yields quoted in Table 2 are estimated to be reliable to ± 10%.

Table 1
Absorption properties of 7-*N,N*-diethylamino-4-methylcoumarin and 9-butyl-4-butylamino-1,8-naphthalimide in various solvents. λ_{max} is the absorption maximum and ε is the extinction coefficient in $dm^3 mol^{-1} cm^{-1}$

Solvent	7-*N,N*-Diethylamino -4-methylcoumarin		9-Butyl-4-butylamino-, 18-naphthalimide	
	λ_{max} (nm)	log ε	λ_{max} (nm)	log ε
Toluene	360	4.38	420	4.17
Cyclohexane	351	4.45	403	4.13
Ethyl acetate	360	4.41	425	4.15
2-Propanol	372	4.37	442	4.27
Ethanol	374	4.36	444	4.22
Methanol	375	4.36	444	4.26
Acetonitrile	370	4.39	431	4.31

Fluorescence decay profiles were measured by the single photon counting technique [13] using either an Edinburgh Instruments model 199 Fluorescence Decay Time Spectrometer or the Synchrotron Radiation Source at the CLRC Daresbury Laboratory in single bunch mode [14]. The decay profiles were analysed by computer convolution using χ^2 values and the distribution of the residuals as "goodness of fit" criteria. The resulting fluorescence lifetime values are estimated to have error limits of ± 0.2 ns.

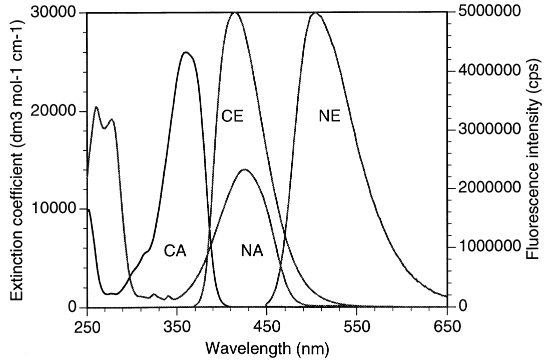

Fig. 1. Absorption and fluorescence emission spectra of 7-*N,N*-diethylamino-4-methylcoumarin (CA and CE) and 9-butyl-4-butylamino-1,8-naphthalimide (NA and NE) in ethyl acetate. The two emission spectra have been normalised to 5,000,000 cps in the peak for the purposes of comparison.

3. Results and discussion

7-*N,N*-diethylamino-4-methylcoumarin (**3**) and 9-butyl-4-butylamino-1,8-naphthalimide (**2**) absorb strongly (ε≈20,000) in the near-UV and near-visible regions of the spectrum, respectively. The lowest energy absorption band for **3** lies in the region of 350–375 nm and that for **2** between 400 and 445 nm. Examples of the spectra of the two compounds are shown in Fig. 1 and absorption data as a function of solvent are given in Table 1. Both compounds experience a red shift in their absorption spectra with increasing solvent polarity which is not surprising given that the lowest energy absorption transition for both compounds has significant charge-transfer character. It is also noticeable that there are hydrogen-bonding effects in operation given the enhanced red-shifts observed in alcoholic solvents. The extinction coefficients for **3** are all quite similar but there is some evidence for increased absorption intensity for **2** in polar solvents.

Given the strength of the absorption transitions as exemplified by the extinction coefficients for the two compounds, it is not surprising to find that they also fluoresce strongly, with high quantum yields, in the near-UV/visible (**3**) and in the green/yellow visible (**2**) spectral regions (see Table 2). The emission spectra exhibit the same red-shift observed in the absorption spectra but the solvent effects are rather greater than those seen for the absorption spectra and spectral shifts of ⩾50 nm are observed for both compounds in polar solvents.

Table 2
Fluorescence properties of 7-*N,N*-diethylamino-4-methylcoumarin and 9-butyl-4-butylamino-1,8-naphthalimide in various solvents. λ_{max} is the emission maximum, Φ_f is the quantum yield and τ_f is the fluorescence lifetime

Solvent	7-*N,N*-Diethylamino-4-methylcoumarin			9-Butyl-4-butylamino-1,8-naphthalimide		
	λ_{max} (nm)	Φ_f	τ_f (ns)	λ_{max} (nm)	Φ_f	τ_f (ns)
Toluene	408	0.79	3.2	485	0.84	8.6
Cyclohexane	392, 395[a]	0.87, 0.32[a]	2.8, 2.75[a]	470	0.83	7.6
Ethyl acetate	416, 416[a]	0.80, 0.93[a]	3.1	500	0.75	9.5
2-Propanol	438	0.70	3.6	520	0.74	9.8
Ethanol	446, 451[a]	0.59, 0.59[a]	3.15, 3.1[a]	520	0.66	9.2
Methanol	450	0.36	2.05	525	0.58	8.3
Acetonitrile	432, 434[a]	0.75, 0.73[a]	3.4[a]	515	0.84	10.3

[a] Reference [18].

This indicates that the first excited singlet states of both compounds have higher dipole moments than the respective ground states and are therefore stabilised more by polar solvents.

As Fig. 1 shows, there is excellent overlap between the emission spectrum of **3** and the absorption spectrum of **2** in ethyl acetate and this is true of all the solvents used in this work. It is not surprising therefore to find that energy transfer readily occurs from **3** to **2** in solution. The fluorescence from 7-*N*,*N*-diethylamino-4-methylcoumarin (excited in the near UV around 370 nm) is significantly reduced when small amounts of 9-butyl-4-butylamino-1,8-naphthalimide are also present in the solution. As the emission from the coumarin decreases, emission from the naphthalimide increases in intensity. The naphthalimide absorbs minimally at these excitation wavelengths (Fig. 1) so the quenching of the fluorescence may be assigned to excited state processes rather than the ground states of the two molecules competing for the excitation light.

Measurements of the fluorescence intensity of **3** (taken at its fluorescence maximum in each solvent) as a function of the concentration of **2** are not linear, but exhibit upward curvature as exemplified by Fig. 2. This behaviour is typical of a situation where energy transfer is taking place from a donor molecule (in this case the coumarin) to an acceptor (the naphthalimide) by both radiative and non-radiative processes [10]. The former is effectively a type of inner-filter effect in that the coumarin fluorescence, which is generated in the middle of a 1 cm square cuvette, has to pass through approximately 0.5 cm pathlength of naphthalimide solution before it reaches the outside of the cuvette and is detected i.e. a mechanism of the type

$$^1\mathbf{3}^* \rightarrow \mathbf{3} + h\nu_\mathrm{f} \tag{1a}$$

$$\mathbf{2} + h\nu_\mathrm{f} \rightarrow {}^1\mathbf{2}^* \tag{1b}$$

is in operation where the first excited singlet states of the two compounds are denoted by $^1\mathbf{2}^*$ and $^1\mathbf{3}^*$ and the ground states by **2** and **3**. The reduction in the intensity of the coumarin fluorescence at any wavelength can therefore be expected to exhibit a Beer's Law dependence on the naphthalimide concentration.

The second mechanism in operation involves the interaction

$$^1\mathbf{3}^* + \mathbf{2} \rightarrow \mathbf{3} + {}^1\mathbf{2}^* \tag{2}$$

This will almost certainly take place via a dipole–dipole interaction since the transitions in both the donor and acceptor are strongly allowed. The theory of dipole–dipole energy transfer has been developed by Förster [15]. In his treatment the energy transfer rate constant (k_ET) is given by

$$k_\mathrm{ET} = \frac{1}{\tau_\mathrm{D}}\left(\frac{R_0}{r}\right)^6 \tag{3}$$

where τ_D is the excited state lifetime of the donor in the absence of acceptor, r is the donor-acceptor separation and R_0 is a distance given by Eq. (4):

$$R_6^0 = \frac{9000\ \ln\ 10\kappa^2\Phi_\mathrm{D}}{128\pi^5 N_\mathrm{A} n^4}\int_0^\infty \frac{F_\mathrm{D}(\bar{\nu})\varepsilon_\mathrm{A}(\bar{\nu})\mathrm{d}\bar{\nu}}{\bar{\nu}^4} \tag{4}$$

where κ^2 is a factor which describes the relative orientations of the donor and acceptor ($=2/3$ for a random orientation), Φ_D is the donor emission quantum yield in the absence of the acceptor, n is the refractive index of the medium and the integral defines the amount of overlap between the normalised emission spectrum of the donor ($F_\mathrm{D}(\bar{\nu})$) and the acceptor absorption spectrum ($\varepsilon_A(\bar{\nu})$). In

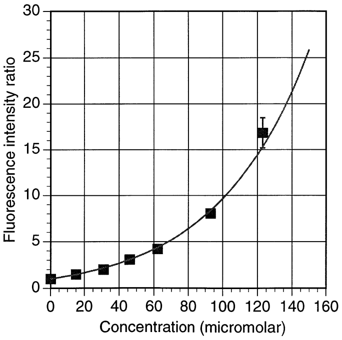

Fig. 2. Plot of I_0/I_f for the quenching of the fluorescence of 7-*N*,*N*-diethylamino-4-methylcoumarin by 9-butyl-4-butylamino-1,8-naphthalimide in ethyl acetate. The curve results from fitting Eq. (6) to the data.

this treatment, R_0 corresponds to the donor–acceptor distance at which 50% of the excited donors undergo energy transfer to an acceptor and is usually known as the critical distance. Values of R_0 are typically 5–10 nm when the transitions in both donor and acceptor are allowed and there is good overlap between the donor emission and acceptor absorption spectra [16]. These conditions are certainly fulfilled for the two compounds studied here as Tables 1 and 2 and Fig. 1 show.

This non-radiative energy transfer should obey the Stern–Volmer relationship, i.e.

$$\frac{\Phi_0}{\Phi_f} = \frac{I_0}{I_f} = 1 + k_{ET}\tau_D[A] \tag{5}$$

where Φ_0 (I_0) is the fluorescence quantum yield (fluorescence intensity) of the donor in the absence of the acceptor and Φ_f (I_f) is the fluorescence quantum yield (fluorescence intensity) of the donor in the presence of a concentration $[A]$ of the acceptor. Eq. (5) will strictly only be valid for a single, fixed donor–acceptor distance. In this work, there will be a range of distances all with their own kET values. However, the assumption of Stern–Volmer kinetics appears to adequately model the observed quenching behaviour when combined with the effect of the radiative energy transfer as given below.

Eq. (5), when combined with the Beer's Law dependence of the radiative transfer, yields the following relationship between the fluorescence intensities I_0 and I_f and the concentration of the acceptor:

$$\frac{I_0}{I_f} = (1 + k_{ET}\tau_D[A]).10^{\varepsilon 1[A]} \tag{6}$$

(Note: if fluorescence quantum yields are used, then the radiative transfer term must be integrated over the whole of the donor emission/acceptor absorption spectra [10].)

The observed quenching curves were iteratively fitted to this relationship using $k_{ET}\tau_D$ and $\varepsilon 1$ as variable parameters to yield acceptable fitted curves such as the one shown in Fig. 2. The values of $k_{ET}\tau_D$ and $\varepsilon 1$, which result from this procedure together with the derived values of k_{ET}, are given in Table 3. As can be seen from this table, the energy transfer rate constants, which must be regarded as values averaged over all the donor–acceptor distances r, are much larger than the rate constants for diffusion-controlled reactions ($k_{diff} \approx 10^{10}$ dm^3 mol^{-1} s^{-1}) in these solvents. They indicate that the non-radiative energy transfer mechanism is very efficient in these systems and operates over distances rather larger than those involved in contact between the two molecules. This is further borne out by the R_0 values [calculated from Eq. (4)], which are also given in Table 3, all of which are in the region of 8.5–10 nm; towards the upper limit of the expected values for non-radiative energy transfer [16]. Sivaram et al. [17] have reached similar conclusions for energy transfer from **3** to rhodamine-6G, although their energy transfer rate constant (in 2-methoxyethanol) was approximately one-tenth the values we find here. This reflects the weaker overlap between donor emission and acceptor absorption in the 7-*N,N*-diethylamino-4-methylcoumarin/rhodamine-6G system.

Table 3
Parameters for the radiative and non-radiative energy transfer between 7-*N,N*-diethylamino-4-methylcoumarin and 9-butyl-4-butylamino-1,8-naphthalimide in various solvents

Solvent	$\varepsilon 1$ (dm^3 mol^{-1})	$k_{ET}\tau_D$ (dm^3 mol^{-1})	10^{-12} k_{ET} (dm^3 mol^{-1} s^{-1})	R_0 (nm)	r (nm)
Toluene	11,000	8500	2.50	8.52	1.91
Cyclohexane	10,000	5000	1.79	8.49	2.05
Ethyl acetate	11,600	6500	2.10	9.04	2.09
2-Propanol	7650	9500	2.64	9.54	2.07
Ethanol	10,900	7700	2.44	9.19	2.07
Methanol	4900	7000	3.41	8.70	1.99
Acetonitrile	7000	9000	2.65	9.81	2.15

Finally, it is notable that the "average" donor–acceptor distance [obtained from Eq. (3)] is almost independent of the solvent (Table 3). The variations in k_{ET} with solvent are almost completely explained by the variation in R_0 with solvent. This is very useful from a practical viewpoint in that there are no restraints (as far as the energy transfer step is concerned) on the choice of solvent system that can be used and other properties such as viscosity and volatility can be optimised.

Acknowledgements

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