

Photophysics of novel donor–{saturated rigid hydrocarbon bridge}–acceptor systems exhibiting efficient excitation energy transfer

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Abstract

Intramolecular singlet–singlet energy transfer is reported in a series of novel donor–{saturated rigid hydrocarbon bridge}–acceptor (D–B–A) molecules containing dimethoxynaphthalene (DMN) or dimethoxybenzene (DMB) as the energy donor chromophore, and a dione group as the acceptor. In the case of the DMN donor, the efficiency of energy transfer has been studied as a function of the bridge length with the number of sigma bonds linking the donor and acceptor groups ranging from 6 to 12. Highly efficient energy transfer is observed in all the D–B–A molecules studied, and the results are discussed with reference to the role of dipole–dipole and through-bond donor–acceptor coupling mechanisms. The energy transfer process facilitates efficient photosensitized decomposition of the dione moiety. These results are compared to data published on related donor–acceptor compounds. The chemical structure of the backbone linking the donor and acceptor is shown to have a marked effect on the photophysics of the molecules. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The study of the rate and efficiency of singlet–singlet excitation energy transfer (EET) between covalently linked donor and acceptor groups has attracted a great deal of interest in recent years from both theoretical and experimental standpoints. A significant body of experimental and theoretical work exists on an impressive array of systems with rigid, flexible or semi-rigid [1–3] linkages between the two moieties, where the two groups were of the same, or different type [4]. Whilst this work has provided valuable insight into the dynamics of intramolecular EET, an accurate determination of the donor–acceptor distance- and/or orientation dependence on the rate of EET is usually not possible with flexibly linked systems due to the fluctuations in the molecular structure and consequent variations in the interchromophore separation and orientation.

The determination of the mechanisms of EET and the dependencies of these mechanisms on interchromophore distance and orientation is a primary goal. One favourable approach to this end has been to design systems which are structurally well defined with the donor and acceptor groups

being linked covalently together by a backbone which is as rigid as possible. In this way, the separation between the two relevant groups and their orientation relative to one another can be controlled to the maximum extent. Work in our laboratories has concentrated in recent years on donor–acceptor systems based on norbornylogous backbones that provide a high degree of structural rigidity [5,6]. The synthesis of these bridge types has been well established and perfected to the extent where a wide variety of donor–acceptor chromophores can, and has been included in systems undergoing either energy or electron transfer, or in some cases both [7].

One consequence of the rigid bridging in these donor–acceptor systems has been the observation of significantly enhanced energy and electron transfer efficiencies and rates, as compared to non-linked or flexibly bridged compounds. This, along with ample other documentary evidence has provided confirmation that both triplet and singlet electronic EET can take place over substantial distances in rigid donor–{saturated hydrocarbon bridge}–acceptor (D–B–A) systems. The mechanisms of intramolecular EET in systems such as these have been discussed in detail elsewhere [8,9], but it is postulated that this long-range energy transfer occurs by a type of electron exchange mechanism involving through-bond (TB) coupling with the bridge orbitals (hereafter referred to as the TB mechanism) [10–16], in

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addition to the more commonly considered through space (e.g. Förster) dipole–dipole mechanism. The TB mechanism appears to provide an extremely efficient pathway for EET in certain molecules and it is evidently more widespread than previously thought.

In a recent communication [17], we reported that highly efficient electronic excitation energy transfer occurred in novel donor–{rigid bridge}–acceptor compounds with six and 10 sigma bonds connecting the donor dimethoxynaphthalene (DMN) and dione acceptor groups (DMN(6)Dione and DMN(10)Dione, Fig. 1(a)). The rate of intramolecular singlet–singlet EET in DMN(10)Dione was found to be significantly faster than that reported for the comparable molecule with a ketone group as the energy acceptor DMN(10)Ketone (Fig. 1(c)) [10–12] and observed in steroid systems with comparable interchromophore separations. The efficiency of energy transfer derived from the measured rate, was >99.5% which is also much larger than that observed in flexibly linked systems containing the same chromophores [1–3]. The rate of energy transfer in DMN(6)Dione was found to be beyond the time-resolution of our present apparatus, which made the determination of the distance dependence of EET in these molecules somewhat ambiguous, but through-bond interactions were implicated.

We have since synthesized a more complete series of the DMN–bridge–diones in which the number of sigma bonds between the donor and acceptor groups ranges from 6 to 12 (Fig. 1(a)). It was anticipated that by extending the rigid backbone to 12 bonds, the distance dependence of the energy transfer rate could be further investigated. For comparison, we have also synthesized and studied molecules equivalent to DMN(6)Dione but possessing a *cis*-linkage (or “kink”) in the linking backbone (Fig. 1(a), DMN(6-*cis*)Dione), and the six bond dimethoxybenzene (DMB) equivalent (Fig. 1(b), DMB(6)Dione). Despite the overall structural similarities between the molecules, there are noticeable differences between them and, as we report here, these differences provide a significant insight into the coupling between the donor and acceptor moieties. These molecules can be compared with the semi-flexible macrocyclic compounds studied in detail by Speiser and coworkers [1–3] and the ketone-containing molecules studied by Paddon-Row and co-workers (Fig. 1(c)) [10–12]. Suitable model compounds (Fig. 1(d)) were also synthesized and studied for comparison.

2. Experimental details

2.1. Synthesis

The DMN(6)Dione and DMN(10)Dione bichromophores were prepared as described previously [18–21]. Details of the syntheses of the other compounds are available through supporting information.

2.2. Photophysical measurements

Solutions of optical densities of ~ 0.1 (at 295 nm) in *n*-hexane were thoroughly degassed by a series of freeze-pump-thaw cycles to better than 10^{-6} Torr. Samples were kept in the dark except when being measured or irradiated for photodegradation studies. Absorption spectra were recorded on either a Hitachi 150-20 or Varian 50-BIO spectrophotometer. Corrected fluorescence spectra were recorded on Hitachi 4010 or 4500 spectrofluorimeters using 5 nm bandpass settings on both excitation and emission monochromators. Photodegradation experiments were conducted using the excitation beam of the Hitachi 4010 fluorimeter at 295 nm with a wide excitation slit.

Fluorescence decay measurements were carried out using time-correlated single photon counting methods employing as the excitation source the frequency doubled output of a synchronously pumped and cavity dumped, mode-locked argon ion/Rh6G dye laser system; details of which have been published elsewhere [22]. The excitation wavelength was in most cases 295 nm and the emission was monitored in either the naphthalene (350 nm) or the dione (507 nm) emission regions.

Transient absorption measurements were performed on a flash photolysis system using as the excitation source the frequency doubled (295 nm) output of a nanosecond optical parametric oscillator (Casix) pumped by the 355 nm frequency tripled output of a Nd:YAG laser (Continuum NY-61). The monitoring xenon lamp (Rofin, 150 W) intensity was pulsed (Applied Photophysics arc lamp pulsing unit, model 410) and spectrally dispersed through an imaging monochromator/spectrograph (Acton 308i), and detected by a fast photomultiplier/digitizing oscilloscope (Hamamatsu R928/Tektronix TDS 520) system.

All quantum chemical calculations were carried out using the GAUSSIAN program [23].

3. Results and discussion

3.1. Steady-state fluorescence studies

The absorption and emission spectra of the DMN(2), DMB and dione model compounds (Fig. 1(d)) are shown in Fig. 2. The extinction coefficient of the dione model is extremely low across the absorption region with some weak absorption below 350 nm and another band at ~ 470 nm ($\epsilon_{470} \approx 15 \text{ M}^{-1} \text{ cm}^{-1}$). The DMN(2) and DMB model compounds show characteristic absorptions around 290 nm with the DMN band being somewhat broader than that of the DMB compound. Irradiation at 295 nm will excite predominantly the DMB or DMN moieties. The dione model exhibits a very weak emission band around 505 nm when excited directly at 470 nm, whereas the emission from both the DMB- and DMN-model compounds is negligible at this wavelength.

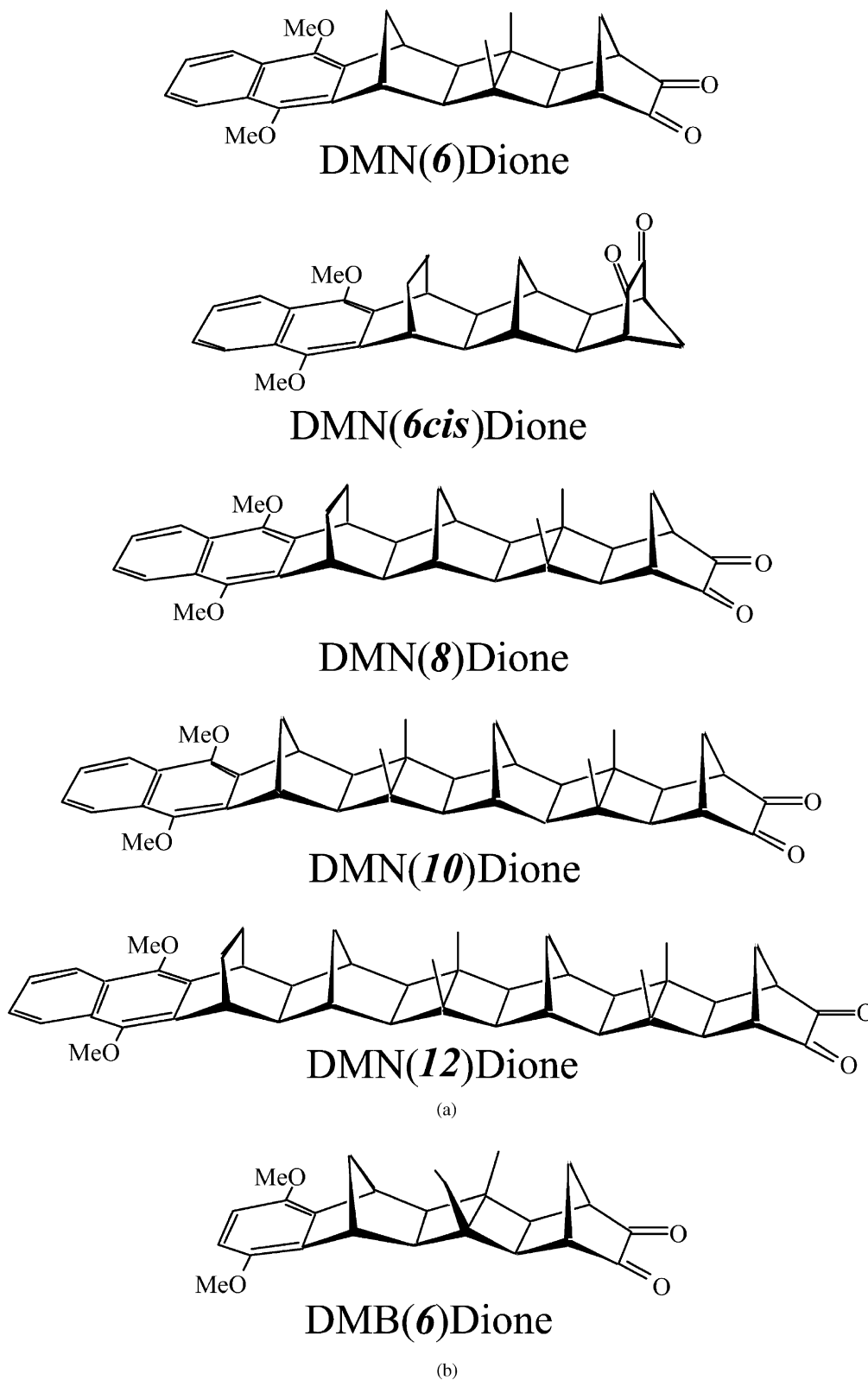


Fig. 1. Structures and abbreviations for the series of compounds studied: (a) dimethoxynaphthalene(*n*)diones (DMN(*n*)Dione); (b) dimethoxybenzene(6)dione (DMB(6)Dione); (c) dimethoxynaphthalene(*n*)ketone (DMN(*n*)Ketone) compounds studied previously [10–12] and (d) B–dione, DMN–B and DMB–B model compounds used. The DMN(2) was used as the standard model for the DMN(*n*)Dione series.

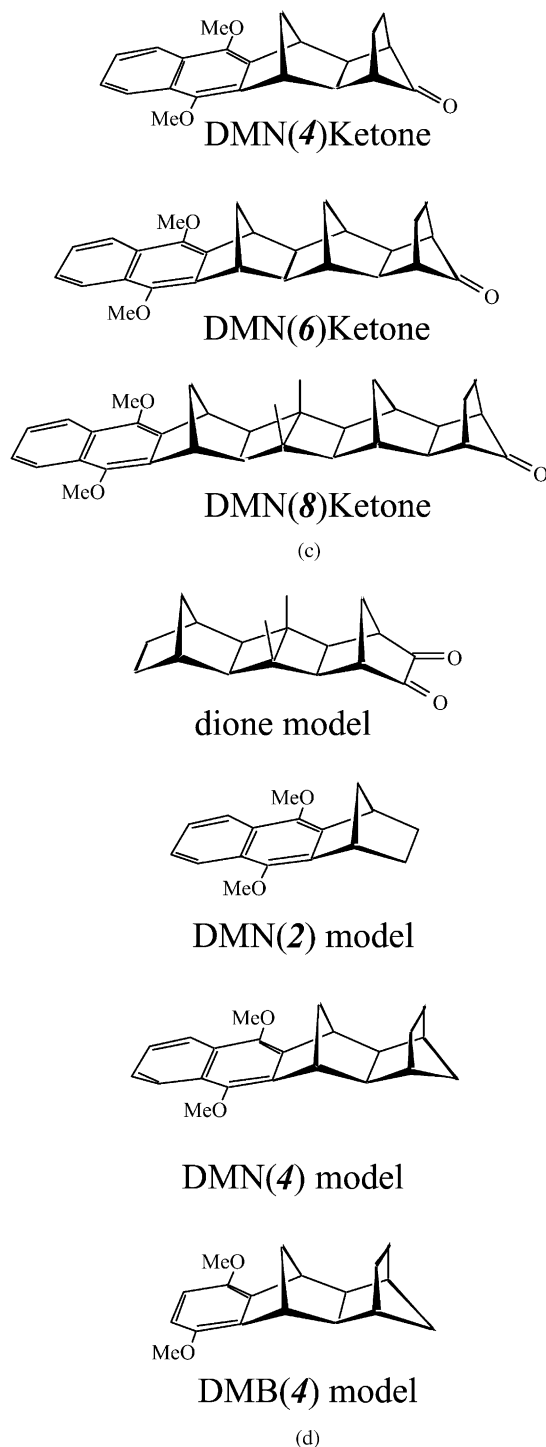


Fig. 1. (Continued).

The emission spectra of the DMN(2) model and DMN(*n*)Dione series of compounds in *n*-hexane following excitation at 295 nm (normalized for the fraction of light absorbed) are shown in Fig. 3(a). The fluorescence spectra from these compounds show characteristic DMN emission which is quenched significantly (up to 85%) in all the DMN(*n*)Dione compounds relative to the DMN(2) model

compound. Despite negligible direct excitation of the dione moiety, there is also clear evidence of a small but significant emission produced in the dione region (507 nm—inset Fig. 3(a)) following 295 nm excitation in the DMN(*n*)Dione compounds, in contrast to the DMN(2) model compound. Similar behaviour (~88% quenching and dione emission) is observed from the DMB-containing compounds (Fig. 3(b)).

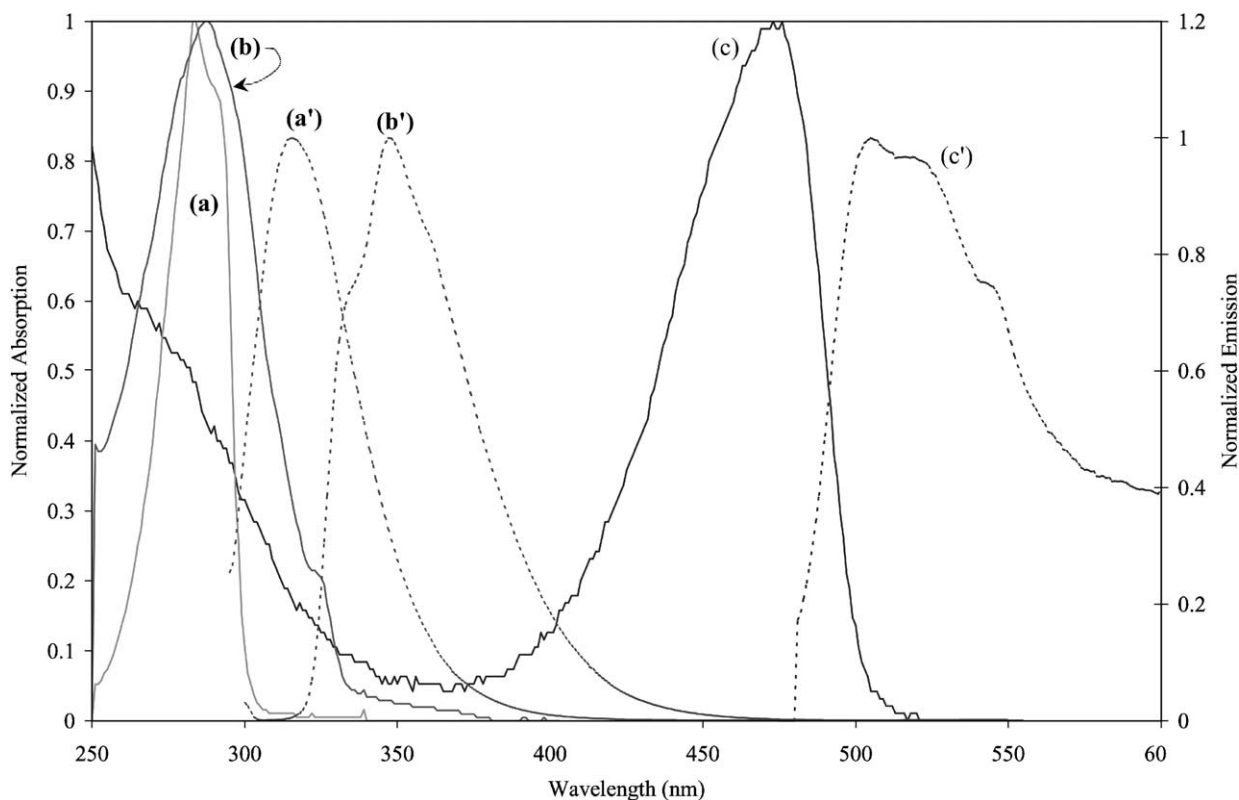


Fig. 2. Normalized absorption (solid lines) and emission spectra (broken lines with primed label) of: (a) DMB; (b) DMN(2); and (c) dione model compounds in *n*-hexane (for the fluorescence spectra of the DMB and DMN-model compounds, $\lambda_{\text{ex}} = 295$ nm while for the dione model compound, $\lambda_{\text{ex}} = 470$ nm).

It could be argued that the emission at 507 nm may result from some direct excitation of the dione at 295 nm, however, this is unlikely for several reasons. First, the absorption of the dione is very weak at 295 nm in the bichromophores and the solution absorbance is dominated by the aromatic groups. Secondly, the dione emission intensity is seen to vary between the various compounds studied which would not be expected if the dione were excited directly since there is only one dione per molecule and the spectra are normalized for the fraction of light absorbed at 295 nm. Thirdly, the fluorescence excitation spectra of the compounds monitored in the dione emission region at 505 nm (Fig. 4) indicate that the vast majority of this emission results from absorption across the aromatic chromophores' absorption spectrum profile (i.e. excitation of the DMN chromophore leads to emission from the dione).

The quenching of the aromatic emission, the observation of dione emission and the fluorescence excitation spectra of the 505 nm emission provide three pieces of strong evidence for the transfer of electronic excitation energy from the DMB or DMN chromophores to the dione group. The intensity of the emission at 505 nm is weak, but considering the low yield of emission expected from the dione group, EET from the DMB and DMN to the dione group appears to be remarkably efficient in all the compounds of these series. Quantifying the extent of energy transfer from steady-state measurements is, however, difficult for the reasons described below.

A surprising result illustrated in Fig. 3 is the almost total quenching of the DMN emission, and the corresponding highest emission in the dione region, in the DMN(6-*cis*)Dione compound compared with the other members of the series. If a through-bond mechanism is responsible for EET in these molecules, this result is an apparent transgression of the postulated "all-trans" rule for the TB mechanism which states that the coupling through a bridge is maximized for an all-trans (antiperiplanar) configuration of bridge bonds [24–26]. This behaviour is in contrast to that observed in the related DMN(6-*cis*)Ketone and DMN(8-*cis*)Ketone compounds reported by Kroon et al. [12] in which significantly reduced quenching of the DMN emission was observed as compared to the corresponding "all-trans" compounds.

Electrochemical measurements indicate that electron transfer from DMN and DMB to the dione group is thermodynamically possible [17], and thus might be proposed as the quenching process. The observation of the sensitized dione emission (i.e. following excitation of the aromatic species) being identical to that of a dione model system lacking the aromatic chromophore (excited at ~ 470 nm), is strong evidence that the 507 nm emission is the result of energy transfer from the aromatic group to the dione, rather than being a charge transfer emission band. Further evidence for this is the lack of any significant change in the emission spectra of the DMN(*n*)Dione series in solvents more polar

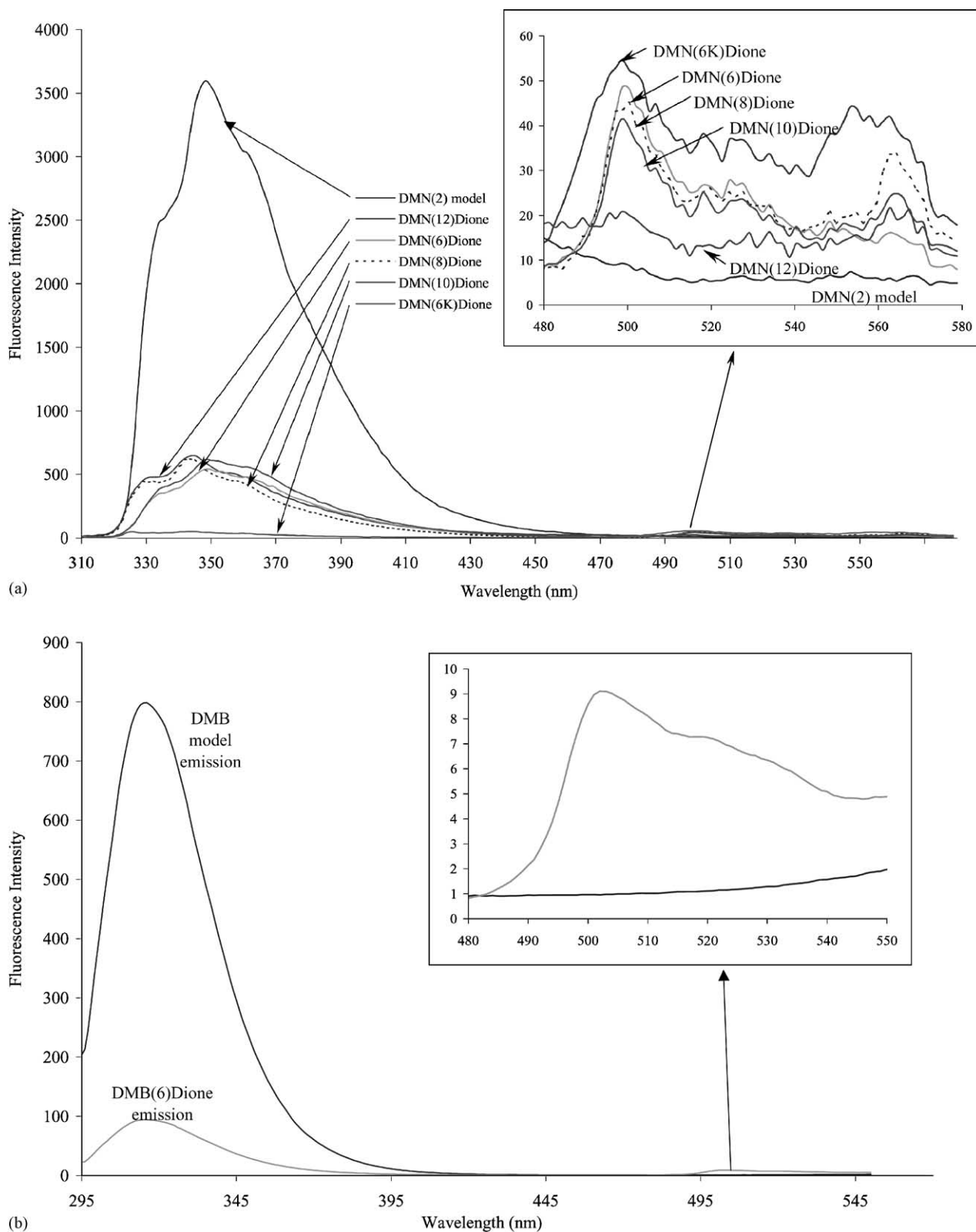


Fig. 3. Fluorescence spectra of: (a) the DMN(*n*)Dione series of compounds relative to the DMN model compound and (b) DMB(6)Dione relative to the DMB model compound, in *n*-hexane ($\lambda_{\text{ex}} = 295$ nm) corrected for fraction of light absorbed.

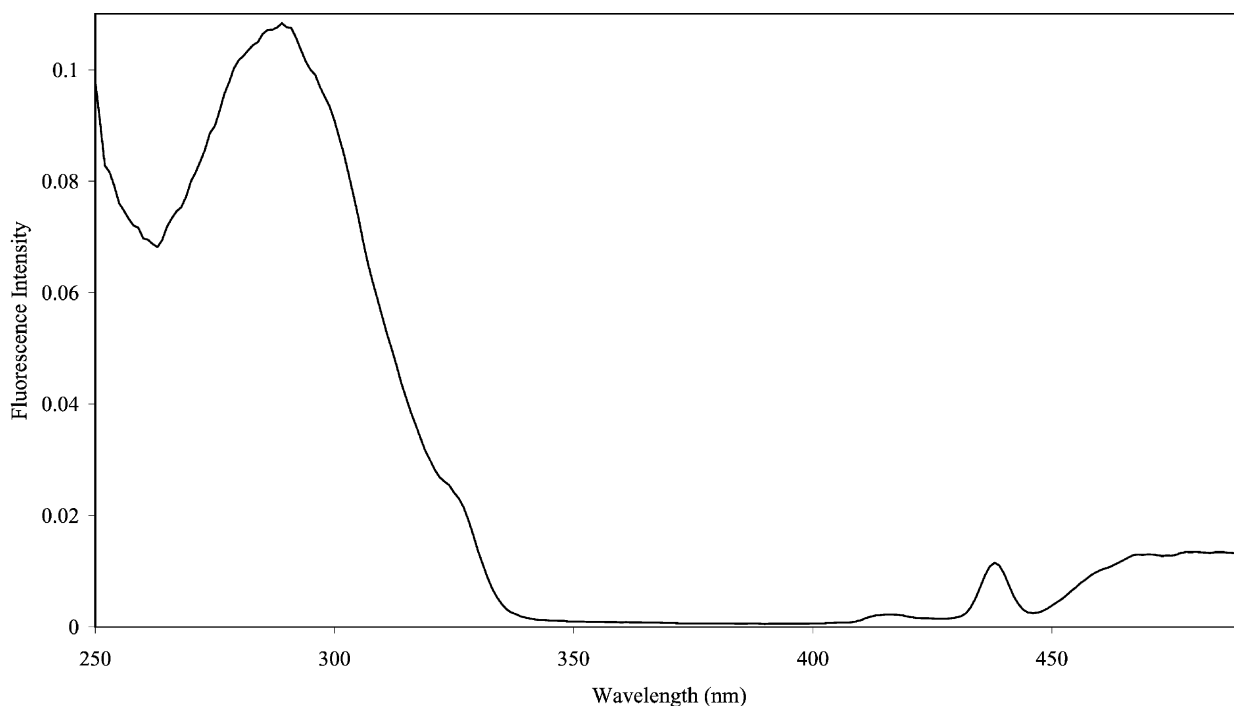


Fig. 4. Fluorescence excitation spectrum of DMN(10)Dione in *n*-hexane ($\lambda_{em} = 505$ nm).

than *n*-hexane such as acetonitrile. Laser flash photolysis experiments on 1,4-dimethoxynaphthalene (1,4-DMN), the DMN(2) model and DMN(6-*cis*)Dione, could detect no transient signals at 590 nm associated with aromatic radical ions. This null result is similar to the finding reported for the DMN(*n*)Ketone series [10–12], but of course does not rule out electron transfer since if the charge recombination is rapid, nanosecond flash photolysis measurements will not resolve the intermediate charge separated state.

The degree of steady-state fluorescence quenching indicated in Fig. 3 is influenced by a facile degradation pathway which leads to recovery of the donor emission as illustrated in Fig. 5(a) for DMN(10)Dione and Fig. 5(b) DMB(6)Dione. Subjecting solutions of all the DMN(*n*)Dione and DMB(*n*)Dione compounds in *n*-hexane to irradiation at 295 nm led to a dramatic increase in the intensity of the aromatic emission band at 330–400 nm during irradiation and a concomitant decrease in emission from the dione at 507 nm. This finding can be explained in terms of EET taking place from the locally excited aromatic chromophore to the dione group which then undergoes fragmentation reactions [27] with the consequent switching on of the aromatic fluorescence. That is, when the acceptor is removed through photochemical means, the aromatic emission recovers since EET no longer occurs. Indeed, steady state irradiation of a sample of DMN(6)Dione in hexane using a mercury lamp (308 nm) produced a complex intractable mixture of products which displayed a fluorescence spectrum similar to that displayed by the DMN chromophore. ^{13}C NMR analysis of the mixture revealed the absence of the 1,2-dione functional group. While we

are unsure as to the exact nature of this photodegradation process, we note firstly that the DMN and DMB model compounds do not undergo the degradation, secondly that no significant photodegradation was observed for the corresponding DMN(*n*)Ketone series of compounds [10–12], and thirdly, the degradation is observed in both the DMN and DMB-containing compounds. The dione group is therefore implicated as the photodegradation centre since diones are known to undergo photochemical reactions leading to loss of the dione functionality [27]. The fact that irradiation of the DMN(*n*)Dione and DMB(*n*)Dione compounds at 295 nm strongly favours excitation of the aromatic moiety in preference to the dione due to the latter's low extinction at this wavelength, suggests that the energy transfer process itself is inducing the degradation, that is, it is a photosensitized degradation. This photodegradation, while causing problems in the interpretation of the results, provides further compelling evidence for the occurrence of intramolecular EET from the aromatic groups to the dione, even in DMN(12)Dione. The emission intensity recorded from the aromatic groups following excitation is therefore higher, and that from the dione is lower, than would be the case in the absence of any photodegradation, and is dependent on the overall duration of the photoexcitation. The energy transfer process is therefore even more efficient than the steady-state emission intensities shown in Fig. 3 suggest, at least for the compounds with bridge lengths shorter than 12 bonds.

A closer investigation of the absorption and emission spectra of the DMN(*n*)Dione series of compounds (Fig. 6) reveals an interesting correlation between the shape and position of the absorption and emission bands, and the

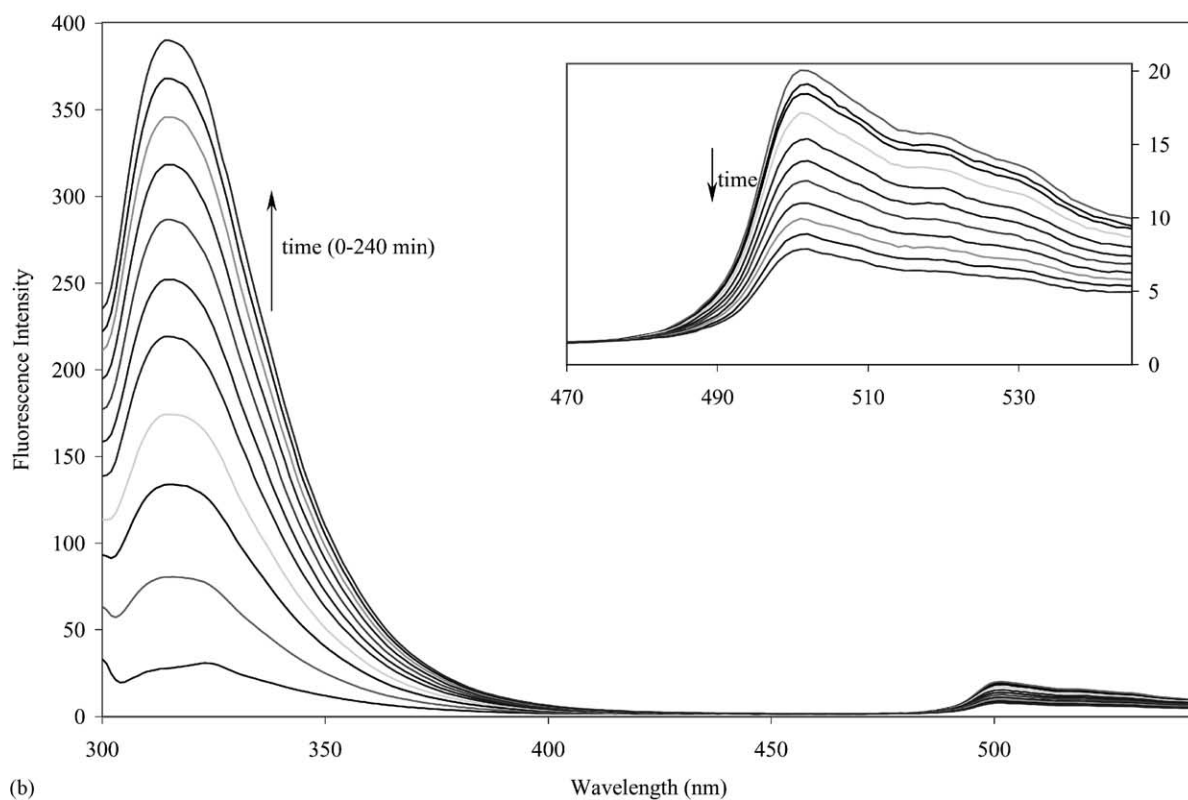
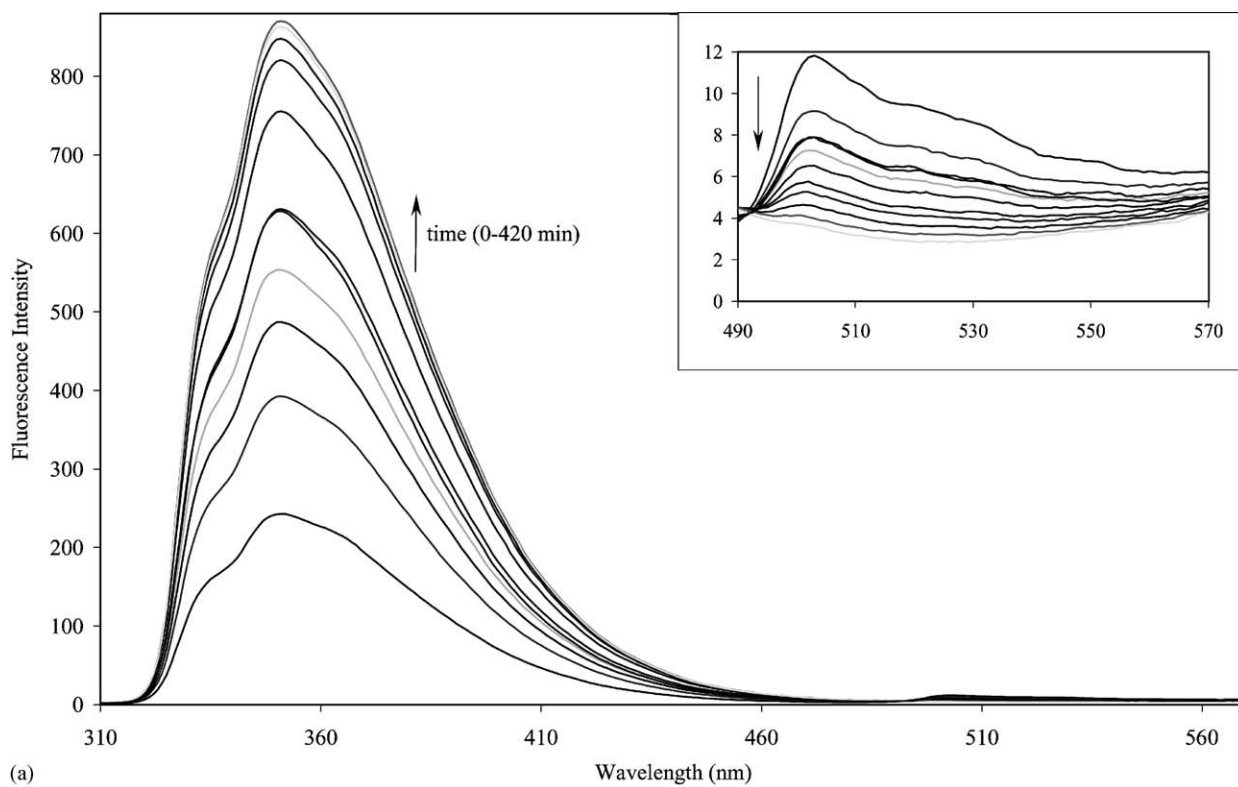


Fig. 5. Fluorescence spectra as a function of irradiation time for: (a) DMN(10)Dione (0–420 min) ($\lambda_{\text{ex}} = 295$ nm) and (b) DMB(6)Dione (0–240 min) in *n*-hexane. Inset shows the decrease in dione emission with irradiation time concomitant with the increase observed in DMN emission.

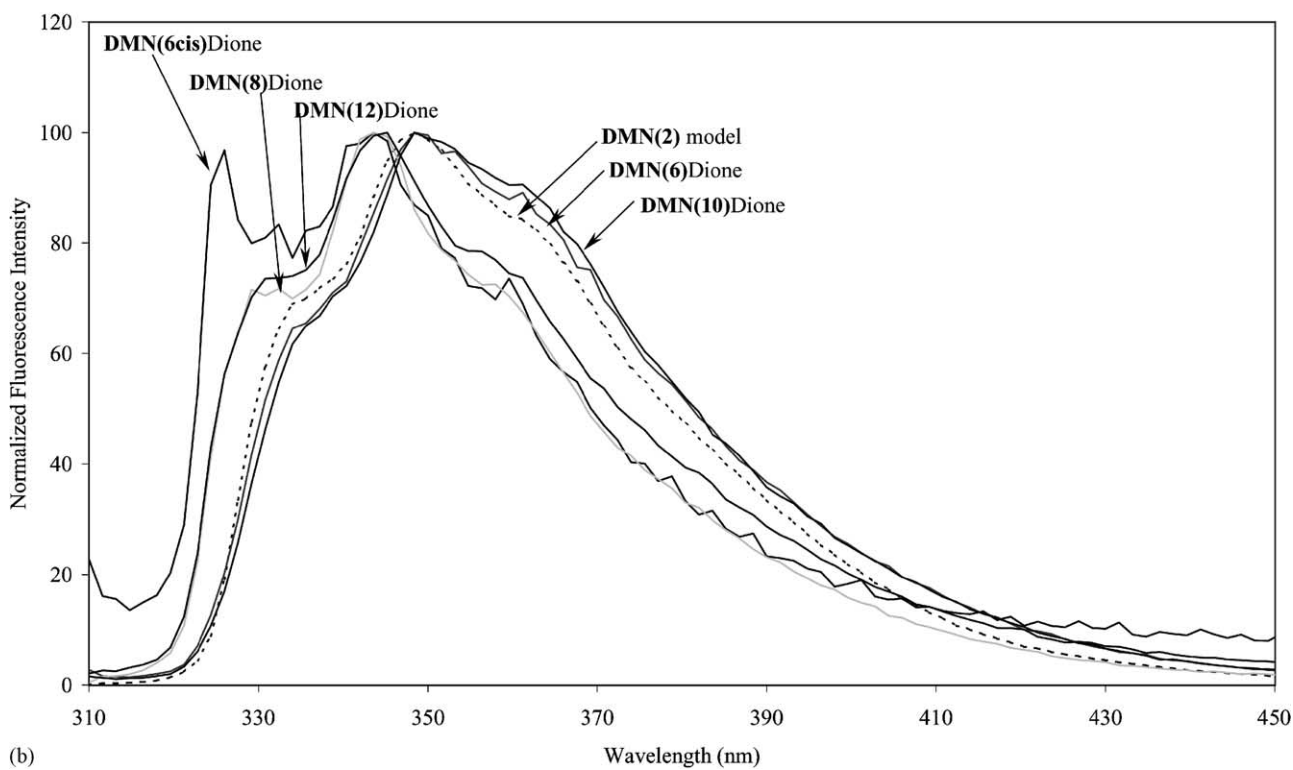
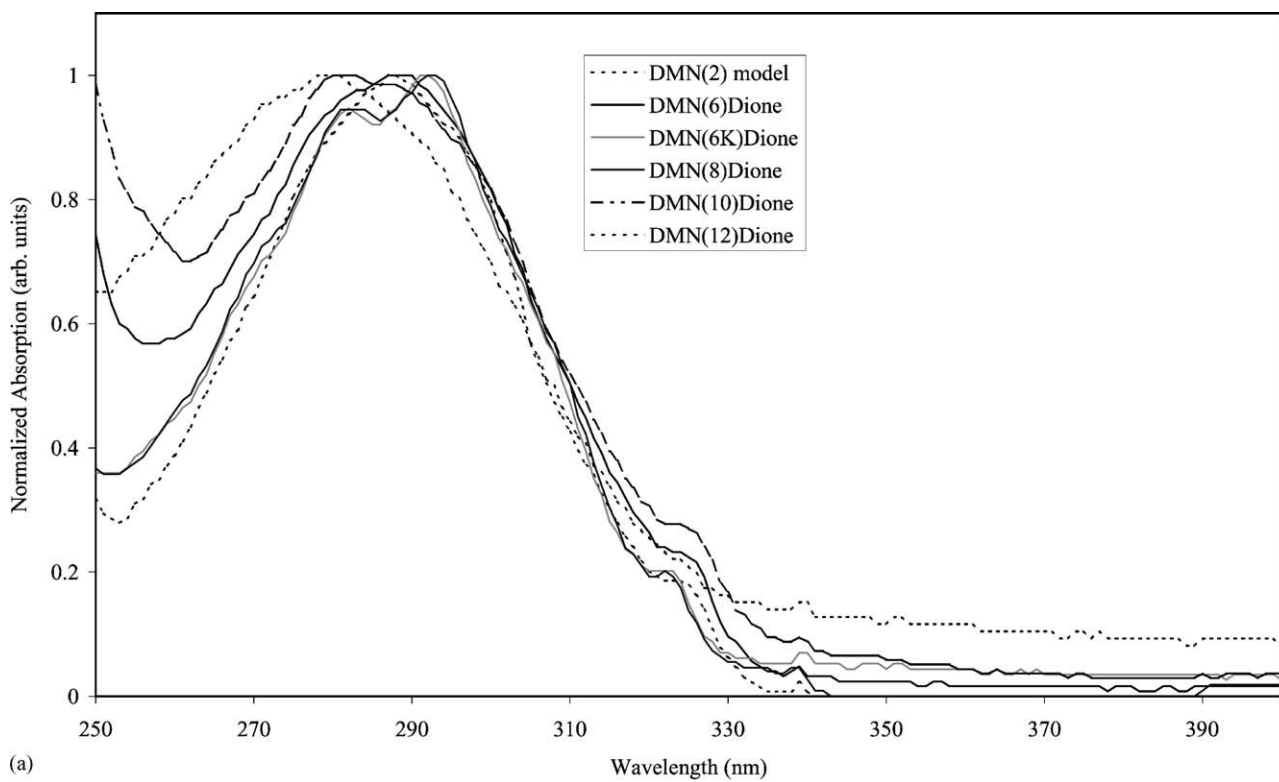


Fig. 6. Normalized (a) absorption and (b) emission spectra of the DMN(*n*)Dione series of compounds in *n*-hexane showing the dependence of the spectra on the bridging backbone structure.

structure of the linking backbone. The emission spectra of the DMN(2) model, DMN(6)Dione and the DMN(10)Dione are very similar to one another with an emission maximum at ~ 348 nm whereas the DMN(8)Dione and DMN(12)Dione have their emission maxima shifted 5 nm to higher energies. The “kinked” DMN(6-*cis*)Dione compound has its emission maximum most closely matching the 8 and 12 bond analogues, but with enhanced emission at ~ 325 nm. The absorption spectra of these compounds also differ slightly from one another with the DMN(8)Dione and DMN(6-*cis*)Dione compounds having identical absorption spectra, the DMN(6)Dione and DMN(2) model compound are similar to one another with DMN(6)Dione having some slight additional absorption at shorter wavelengths compared to the model. The absorption maxima of DMN(10)Dione and DMN(12)Dione are increasingly at higher energies. Inspection of the bridge structures of these molecules (Fig. 1) reveals that the DMN group in DMN(6)Dione and DMN(10)Dione is fused to the norbornane unit, whereas in DMN(6-*cis*)Dione, DMN(8)Dione and the DMN(12)Dione, it is fused to a bicyclo[2.2.2]octane unit. The spectral differences suggest that the backbone structure subtly affects the electronic energy levels of the aromatic chromophore. It might then be expected that the electronic coupling between the chromophore and the backbone may also be affected, which in turn can play a crucial role in determining the efficiency and rate of TB electronic energy transfer.

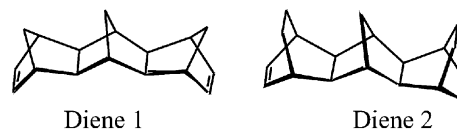


Fig. 7. Classical diene structures used in electronic coupling calculations. Diene 1 represents the norbornane bridge structure in molecules: DMN model, DMN(6)Dione, DMB(6)Dione and DMN(10)Dione, whereas diene 2 represents the bicyclo-octane bridge structure in molecules: DMN(6-*cis*)Dione, DMN(8)Dione and DMN(12)Dione.

Calculations of the electronic coupling between a chromophore and the two slightly different bridge structures have been carried out using the dienes (Fig. 7) since calculations of this type are known [28] to give useful insights into bridge–chromophore couplings. The two dienes were optimized at the HF/3-21G level and the π,π -splittings, $\Delta E(\pi)$, were calculated at the same level of theory. The qualitative results indicate that the strength of the electronic coupling between a chromophore and a bicyclo[2.2.2]octane unit, to which it is fused, is weaker (diene 2, $\Delta E(\pi) = 0.26$ eV) than that between the same chromophore and a norbornane unit (diene 1, $\Delta E(\pi) = 0.37$ eV), to which it is fused in the same manner. The absorption and emission spectra of 1,4-DMN in *n*-hexane are compared with those of the DMN(2) model compound in Fig. 8. There are noticeable differences between the spectra of the two compounds;

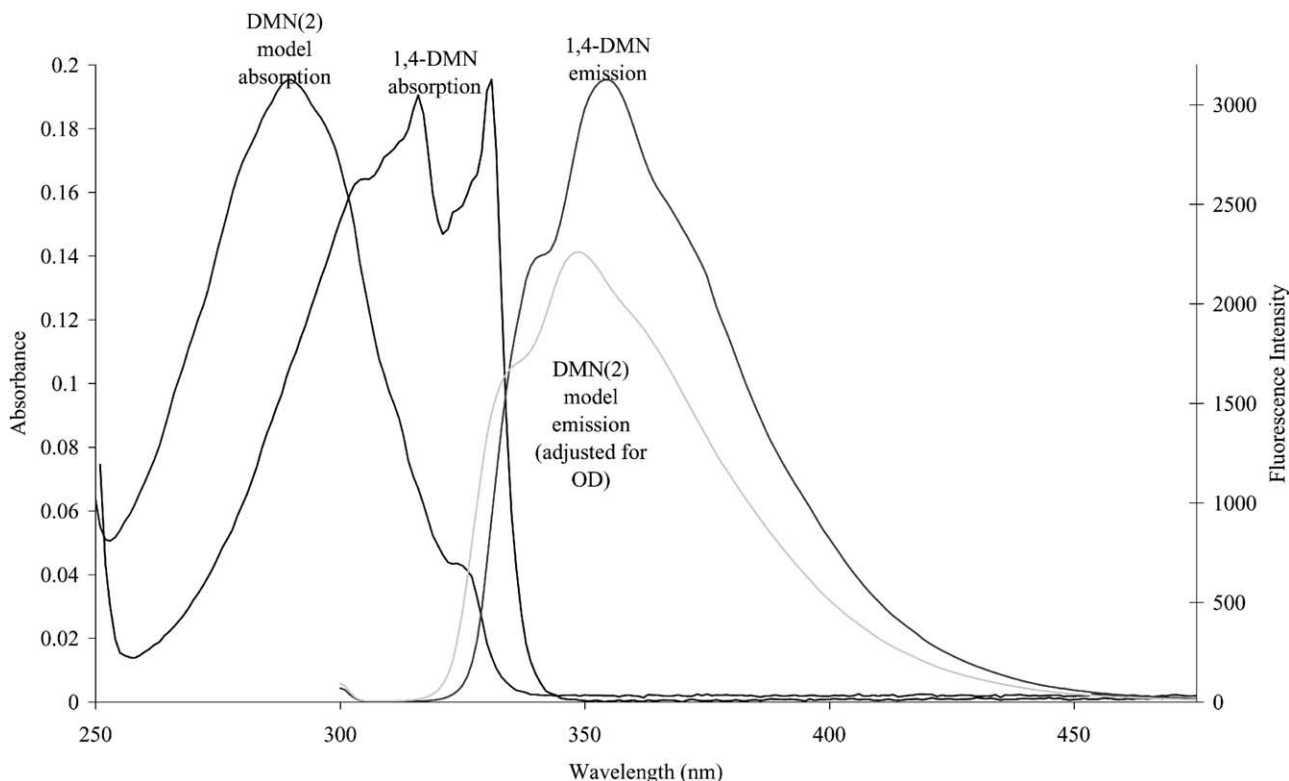


Fig. 8. Normalized absorption spectra and relative emission spectra of 1,4-DMN and the DMN model compound in *n*-hexane.

in particular, the absorption spectrum of the 1,4-DMN is markedly sharper and shifted significantly to the red of that of the DMN(2) model compound. It has been proposed that the methoxy substituents perturb the naphthalene π -system sufficiently to give the lowest excited singlet 1L_a character [10], and it appears that addition of the bridge at the 2,3-positions perturbs the π -system substantially further. The differences in the emission spectra of the two are less marked, although the quantum yield of the DMN(2) model compound is $\sim 77\%$ that of the 1,4-DMN parent. The fluorescence lifetimes of these two compounds are also significantly different ($\tau_f = 6.6$ ns for 1,4-DMN and ~ 9.9 ns for the DMN(2) model in *n*-hexane). These results show that the radiative rate constant is approximately halved by the presence of even just a short bridge at the 2,3-positions, compared with the DMN parent compound. The bridge clearly plays an important role in the spectroscopy and photophysics of these DMN-containing compounds.

3.2. Time-resolved fluorescence studies

Time-resolved fluorescence measurements can often help to clarify the fluorescence quenching phenomena, in particular by providing the rates of the quenching process. The fluorescence decay profiles of the DMN(*n*)Dione compounds and the DMN(2) model monitored in the DMN region are shown in Fig. 9. Unfortunately, the decays for

the bichromophores are complex to analyse, requiring in many cases triple exponential functions to achieve truly adequate fits to the data. The decay parameters recovered from analyses of these decays and the comparable decays of the DMB-containing compounds could not be unambiguously associated with particular species or rate processes. These observations are no doubt due to the interference in the measurements by photodegradation products which accumulate during collection of the decays and corrupt the collected decay profiles.

No clear trend between the recovered fluorescence decay parameters and the number of sigma bonds separating the DMN and the dione groups can be drawn. However, further evidence for the correlation noted above between the bridging backbone structure and the photophysics of the DMN moiety is provided by the observation that the fluorescence decay behaviour at longer times in the compounds containing the bicyclo[2.2.2]octane-based backbone (DMN(6-*cis*)Dione, DMN(8)Dione and DMN(12)Dione) is significantly different to that in the compounds with the norbornane-based backbone.

In order to obtain an indication of the rate of energy transfer, emission from the dione acceptor was monitored. Monitoring the kinetics of the appearance and decay of the emission of the dione acceptor group following excitation of the donor provides a more direct means of determining the efficiency and rate of energy transfer. The photodegra-

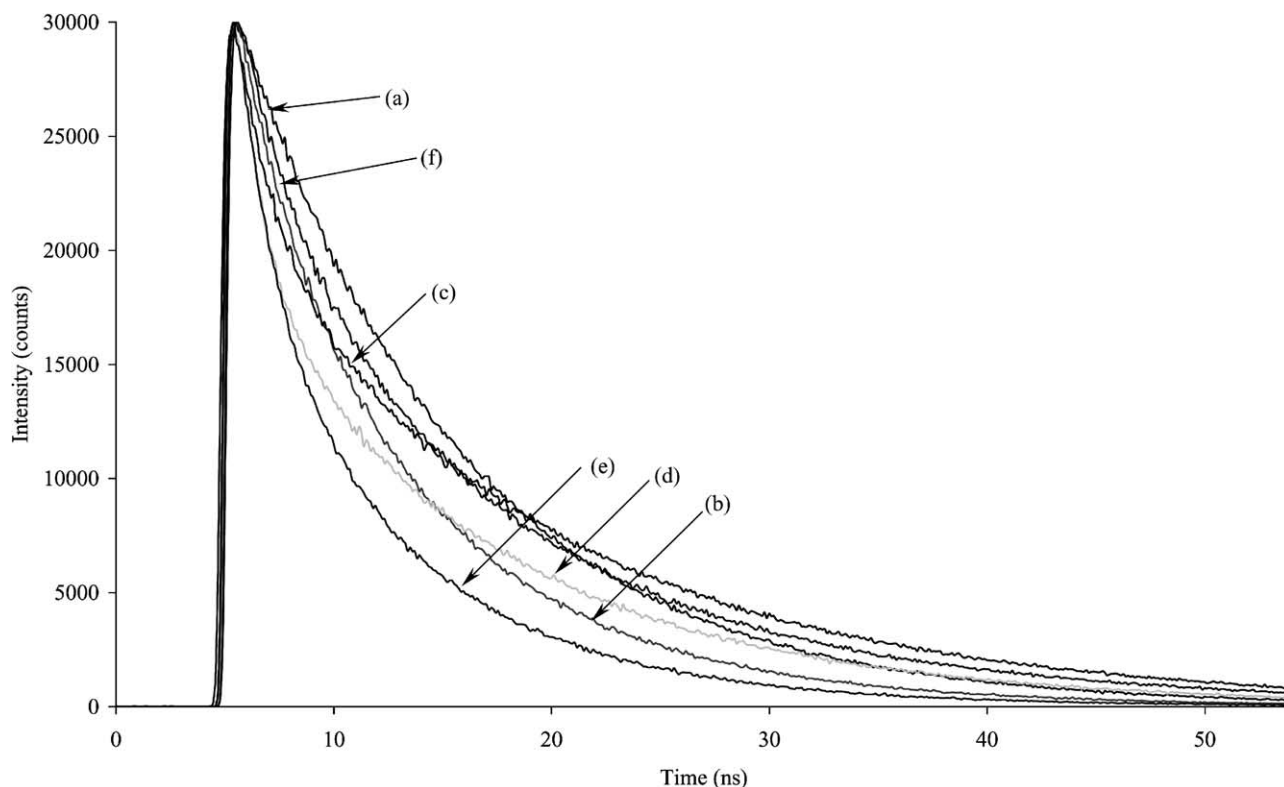


Fig. 9. Fluorescence decay profiles for the DMN(*n*)Dione series in *n*-hexane ($\lambda_{ex} = 295$ nm): (a) DMN(2) model; (b) DMN(6)Dione; (c) DMN(6-*cis*)Dione; (d) DMN(8)Dione; (e) DMN(10)Dione; and (f) DMN(12)Dione.

dation process discussed above complicates the steady-state measurements by increasing the emission intensity in the aromatic region while decreasing the emission intensity in the dione region with irradiation time. This is of little consequence in the time-resolved measurement of the acceptor emission rise-time since it should not affect the observed kinetics of formation of the dione emission, only overall intensity.

The time-resolved fluorescence decay profiles obtained from DMN(6)Dione and DMN(10)Dione in *n*-hexane, recorded at 505 nm (acceptor region) following 295 nm excitation (DMN absorption), were reported in our earlier paper [17]. In that work, we were only able to resolve a grow-in of the dione emission from DMN(10)Dione with a limit on the rise-time of ~ 40 ps (which is approaching the time resolution of our present instrumentation). The observed rise-time for the dione emission in DMN(10)Dione corresponds to a lower limit for the rate for EET from DMN to the dione of $2.5 \times 10^{10} \text{ s}^{-1}$. No rise-time was resolvable for DMN(6)Dione within the time-resolution of our instrument and the rate is thus estimated to be $> 10^{11} \text{ s}^{-1}$. A similar result was found in the present work for DMB(8)Dione. Collection of fluorescence data in these experiments was hampered by a significant reduction in emission count rate throughout the long duration of the data acquisition, which is attributed to photolysis of the dione groups as discussed above. This reduction in count rate at $\lambda_{\text{em}} = 505 \text{ nm}$ is further evidence that the emission being monitored is due to the dione rather than any residual DMN emission which would be expected to increase in line with the intensity changes observed in the steady-state spectra. We were unable to collect sufficient data with which to detect any rise-time from DMN(12)-Dione due to the weak dione emission, and the photodegradation process occurring during the measurement. The emission observed from the DMN(12)Dione is unexpectedly weak in comparison with the other compounds, considering the high degree of quenching of the DMN emission. It is possible that electron transfer may be competing with EET, particularly in this molecule, leading to the discrepancy between the DMN quenching and the dione emission intensity, although, as indicated above, no evidence for the electron transfer process has yet been detected. Through-bond EET and electron transfer would exhibit different distance dependence behaviour and it may be possible for a quenching contribution by electron transfer to become significant in molecules with longer bridges. Nevertheless, EET must play a significant role since sensitized photodegradation of the dione is still observed even in the DMN(12)Dione.

The results discussed above indicate that very rapid energy transfer is occurring within these molecules. However, the mechanism by which energy transfer is taking place; a Förster dipole–dipole mechanism, a Dexter direct through-space exchange mechanism, or a through-bond-mediated exchange process, needs to be addressed.

The rate of EET by either resonance or exchange mechanisms is dependent upon the degree of overlap of the donor

emission and the acceptor absorption spectra. The spectral overlap integrals for resonance, $J_{\text{resonance}}$, and exchange, J_{exchange} , interactions between the DMN emission and the dione absorption for the DMN(*n*)Dione molecules can be calculated using Eqs. (1) and (2), based on the spectral properties of the appropriate model compounds.

$$J_{\text{resonance}} = \int_0^{\infty} \bar{f}_{\text{D}}(\lambda) \varepsilon(\lambda) \lambda^4 d\lambda, \quad (\text{M}^{-1} \text{cm}^3) \quad (1)$$

with λ in cm, $\varepsilon(\lambda)$ is the absorption spectrum of the acceptor in $\text{M}^{-1} \text{cm}^{-1}$ and $\bar{f}_{\text{D}}(\lambda)$ the emission spectrum normalized to unity

$$J_{\text{exchange}} = \int_0^{\infty} \bar{f}_{\text{D}}(\nu) \bar{\varepsilon}(\nu) d\nu, \quad (\text{cm}) \quad (2)$$

with both the donor emission and acceptor absorption spectra normalised.

Values for $J_{\text{resonance}}$ and J_{exchange} are calculated to be $\sim 3.2 \times 10^{-18} \text{ cm}^3 \text{ M}^{-1}$ and $1.16 \times 10^{-5} \text{ cm}$, respectively using the spectroscopic properties of the relevant model compounds. These values can be compared with those reported for the DMN(*n*)Ketone compounds in cyclohexane ($0.259 \times 10^{-18} \text{ cm}^3 \text{ M}^{-1}$ and $2.26 \times 10^{-6} \text{ cm}$, respectively) [10]. In the case of resonance (Förster) interactions, the critical transfer distance R_0 can be calculated using Eq. (3) and represents the distance at which the probability of energy transfer via the dipole–dipole mechanism equals that of spontaneous emission:

$$R_0^6 = \frac{9000 \ln(10) \kappa^2 \phi_{\text{Df}} J_{\text{resonance}}}{128 \pi^5 n^4 N_{\text{AV}}} \quad (3)$$

where ϕ_{Df} is the donor fluorescence quantum yield (0.35), J the spectral overlap integral, n the refractive index (1.375) and N_{AV} Avogadro's number. The value of R_0 is also influenced by the orientation factor (κ^2) which accounts for the angle between the donor emission and acceptor absorption dipoles, and can vary from 0 to 4 corresponding to appropriate orientations of the donor emission and acceptor absorption dipoles [29]. Most implementations of Förster's theory involve systems consisting of a donor molecule surrounded by an ensemble of randomly oriented acceptor molecules, and under these conditions (for which the theory was originally derived), the κ^2 term can often be assumed as equal to 2/3. This is clearly inappropriate for the present system of molecules in which the orientation between the emission and absorption transition dipoles of a single donor and a single acceptor chromophore are well defined. The appropriate value of the κ^2 term has been discussed for the DMN(*n*)Ketone series [10], for which the $n-\pi^*$ transition dipole was assumed to be polarized perpendicular to the plane of symmetry, i.e. in the trigonal plane of the carbonyl group and perpendicular to the C=O bond. The S_0-S_1 transition of the donor chromophore mostly corresponds to a long-axis polarized 1L_b transition of the parent naphthalene molecule, thus giving the

orientation factor a value of zero in the DMN(*n*)Ketone series. However, as also suggested [10], if the lowest singlet state obtained some partial 1L_a character, the orientation between the donor emission and the acceptor absorption transition moments becomes more favourable for energy transfer between the DMN and the ketone group becoming finite.

There remains some ambiguity concerning the absolute orientation of the absorption transition dipole of the dione group with respect to the donor moiety emission dipole. Comparison with glyoxal, biacetyl and camphorquinone [30–32] suggests that the polarization of the absorption

transition in such molecules is perpendicular to the plane of the C–C bond. This is in contrast to the direction assumed for the carbonyl group in the DMN(*n*)Ketone series [10]. Ab initio MO calculations, at the CIS/6-31G(d) level of theory, suggest that the absorption transition dipole of the dione group in the current series of molecules lies in the plane of the norbornane backbone bisecting the C–C bond of the dione group (Fig. 10). Based on this orientation, and assuming long-axis polarization of the emission transition moment of the DMN group, the κ^2 value for each molecule in the DMN(*n*)Dione series was calculated from the angles determined from the energy minimized structures (Fig. 10),

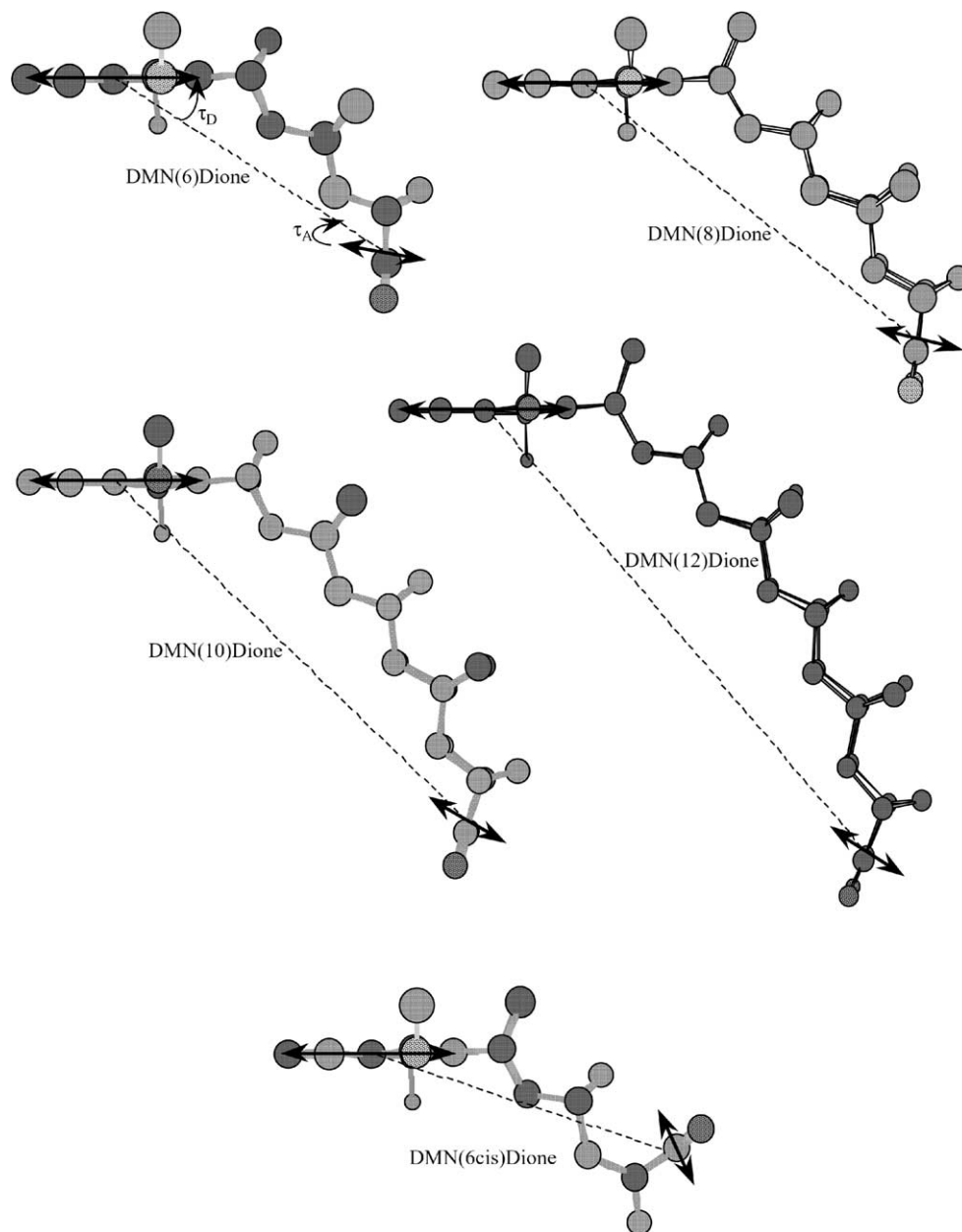


Fig. 10. Energy minimised structures of the compounds showing the relative orientations of the donor emission and acceptor absorption dipoles and the angles defined in Eq. (4).

Table 1

Chromophore centre-to-centre distances, κ^2 orientation terms, Förster critical energy transfer distances, calculated singlet–singlet EET efficiencies and rates assuming a Förster mechanism is operative, and experimentally determined rates for the dione series of molecules in *n*-hexane

Molecule	r (Å)	κ^2	R_0 (Å)	Eff _{eet} (%)	Förster k_{eet} (s ⁻¹)	Experimental k_{eet} (s ⁻¹)
DMN(6)Dione	9.2	1.46 (4.0)	8.6 (10.2)	40.2 (64.7)	6.8×10^7 (1.85×10^8)	>10 ¹¹
DMN(6- <i>cis</i>)Dione	9.3	2.07	9.1	47.0 (63.2)	9.0×10^7 (1.74×10^8)	>10 ¹¹
DMN(8)Dione	11.5	1.51	8.7	15.4 (32.5)	1.8×10^7 (4.85×10^7)	>10 ¹¹
DMN(10)Dione	14.1	1.24	8.4	4.2 (12.4)	4.4×10^6 (1.43×10^7)	2.5×10^{10}
DMN(12)Dione	15.9	1.24	8.4	2.1 (6.4)	2.2×10^6 (6.95×10^6)	–

using Eq. (4):

$$\kappa^2 = (\sin \theta_D \sin \theta_A \cos \varphi - 2 \cos \theta_D \cos \theta_A)^2 \quad (4)$$

where θ_D and θ_A are the angles between the donor emission and acceptor absorption transition moments and the line connecting the centres of these transition moments, and φ the azimuth (i.e. the angle between the projections of the transition moments on a plane perpendicular to the line through their centres) [29], as illustrated in Fig. 10. In these calculations, φ was set to zero.

The calculated κ^2 values listed in Table 1 illustrate that, if the assumed orientations of the DMN emission and dione absorption dipoles are correct, energy transfer would be significantly more favourable in the DMN/DMB(*n*)Diones compared with the DMN(*n*)Ketone compounds. Using Eq. (3) each value of κ^2 results in the values for the corresponding critical energy transfer distance R_0 for the individual molecules (Table 1), calculated assuming that the spectral overlap value is the same for each molecule. For comparison, if we assume κ^2 to have its maximum value of 4 (representing parallel absorption and emission dipoles in line with the separation vector [29]) a value for R_0 of ~ 10.2 Å is calculated. The weak oscillator strength of the dione along with the modest fluorescence quantum yield of the DMN chromophore (~ 0.35) [10] and the poor spectral overlap of the donor (DMB or DMN) emission and acceptor (dione) absorption combine to lead to critical energy transfer distances of less than 10 Å in all cases. The theoretical efficiencies for energy transfer via a Förster mechanism, Eff_{eet}, can be calculated as a function of r , the donor–acceptor separation using Eq. (5).

$$\text{Eff}_{\text{eet}} = \frac{R_0^6}{R_0^6 + r^6} \quad (5)$$

The values of r , taken as the centre-to-centre distances and the resultant values for Eff_{eet}, are also listed in Table 1. For comparison, the maximum expected energy transfer efficiencies and rates possible through a Förster-type mechanism based on $\kappa^2 = 4$ are also given in parentheses. These results indicate that, despite the short critical energy transfer distances in these molecules, energy transfer via the dipole–dipole (Förster) mechanism is possible although inefficient in the bichromophores with larger separations. However, the fluorescence quenching observed experimentally exceeds that calculated, even assuming the maximum

κ^2 value of 4. As discussed previously, the quenching values obtained experimentally are likely to be higher than those actually observed due to the effect of sensitized photodegradation.

If a resonance dipole–dipole mechanism dominates, the rate of such EET, k_{eet} , can be calculated using the relationship:

$$k_{\text{eet}} = \frac{1}{\tau_D} \left(\frac{R_0}{r} \right)^6 \quad (6)$$

where τ_D is the lifetime of the donor emission in the absence of energy transfer (9.9 ns). The calculated k_{eet} , values for the DMN(*n*)Dione series are also given in Table 1.

The rates of energy transfer, calculated assuming a Förster mechanism, are several orders of magnitude lower than our experimental observations indicate. As noted above, the absorption and emission dipole orientations used resulted in high values for the κ^2 term maximizing conditions for dipole–dipole energy transfer in these calculations. The calculated rates listed in Table 1 therefore represent upper limits to the expected rates of energy transfer in these molecules if the Förster mechanism were dominant. As mentioned above, we have been able to record a rise-time of the dione emission in only DMN(10)Dione whereas, based on these calculations, we would expect to be able to easily observe a grow-in of the dione emission in all the compounds of the series if this mechanism were dominant. An energy transfer rate of $\sim 10^7$ s⁻¹ should also be quite obvious in the DMN fluorescence decay, even in the presence of the photodegradation occurring.

These results suggest that the observed EET in the DMB(*n*)Dione and DMN(*n*)Dione compounds is most likely not occurring by a purely dipole–dipole mechanism but rather may involve an exchange-type mechanism. Clearly, this mechanism cannot be due to a classical Dexter through-space exchange process because of the large interchromophore separations in our systems which greatly exceed direct through space orbital overlap of donor and acceptor. The most likely mechanism, therefore, is a through-bond-mediated exchange mechanism. The experimental data of Table 1 indicate that such through bond transfer is remarkably efficient in this series of molecules.

Our results for the rigid bichromophoric DMN–bridge–Dione and DMB–bridge–Dione systems can also be contrasted with those obtained by Speiser [8] for *semi-flexible*

bridged dione-based bichromophoric systems, possessing similar donor groups. Based on the observed very strong distance dependence of EET rates in the latter systems, Speiser et al. concluded that EET takes place by the classical Dexter direct, through-space exchange mechanism, a conclusion which implies the absence of a through-bond coupling mechanism. The contrasting results and conclusions drawn from our present study compared to the Speiser [8] study has been convincingly explained elsewhere [12] in terms of the effect of bridge conformation on the strength of through-bond coupling [7,12]. The semi-flexible bridges in the systems studied by Speiser et al. do not adopt the all-trans conformation which is a prerequisite for effective through-bond coupling and EET in these systems consequently, appears to proceed by way of the through-space-mediated exchange mechanism.

4. Conclusions

The DMN(*n*)Dione and DMB(6)Dione series of compounds studied show surprisingly highly efficient quenching of the aromatic groups' emission. This quenching has been attributed to excitation energy transfer from the aromatic group to the dione moiety, with the possibility of a contribution by a competing electron transfer process occurring in at least in some of the molecules studied. Energy transfer rates are higher than observed for the DMN(*n*)Ketone series [10] and related aromatic, semi-flexible bridge–dione systems [8]. Comparison with calculated rates for EET assuming a Förster dipole–dipole mechanism is operative dramatically underestimates the transfer efficiency. The results indicate that a facile through-bond super-exchange coupling mechanism is responsible for energy transfer in these systems. A characteristic of these molecules is the efficient photosensitized degradation of the dione moiety following excitation of the aromatic chromophore. There are also subtle effects of the linkage structure on the photophysics of these molecules which could have an impact on the electronic coupling and should be considered in studies of energy and electron transfer in bridged chromophore systems.

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