

## Highly Efficient Through-Bond-Mediated Electronic Excitation Energy Transfer Taking Place over 12 Å

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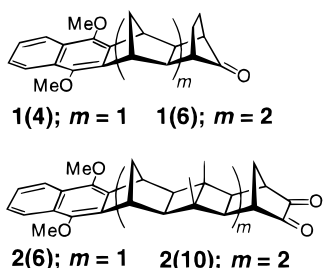
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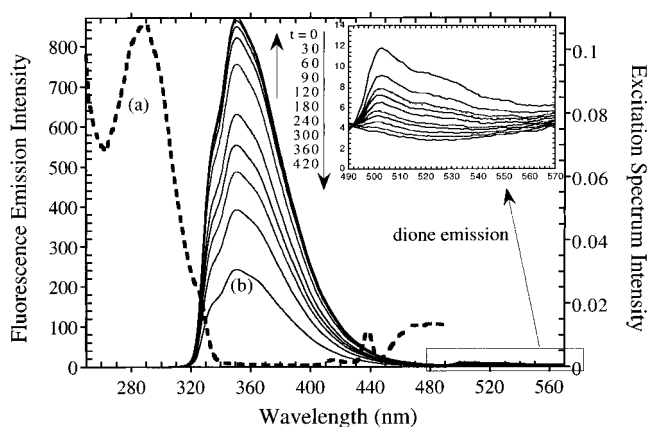
There is ample documentary evidence that both triplet and singlet electronic excitation energy transfer (EET) can take place over substantial distances in rigid donor–{saturated hydrocarbon bridge}–acceptor (D–B–A) systems by a type of electron exchange mechanism involving through-bond (TB) coupling with the bridge orbitals (hereafter referred to as the TB mechanism).<sup>1–4</sup> As expected for the TB mechanism, the EET rates display a strong exponential distance dependence of the form shown by eq 1, in which  $n$  is the number of bonds in the bridge relay, and  $\beta$  is an attenuation coefficient with experimentally determined values in the range of 2–2.5 per bond.<sup>2,3</sup>

$$k_{EET} = A \exp(-\beta n) \quad (1)$$

For example, an experimental value of  $\beta \approx 2$  per bond was obtained for TB-mediated singlet–singlet EET in the four-bond and six-bond dimethoxynaphthalene (DMN)–bridge–ketone systems **1(4)** and **1(6)**.<sup>2</sup> Using this value of  $\beta$  leads to a predicted TB-mediated EET rate of ca.  $10^5 \text{ s}^{-1}$  for the 10-bond homologue **1(10)**, in which the interchromophore separation is ca.  $12.5 \text{ \AA}$ .<sup>5</sup> Indeed, rates of ca.  $10^5 \text{ s}^{-1}$  have been observed for intramolecular triplet–triplet EET in D–{steroid bridge}–A systems having interchromophore separations of 11–13 Å.<sup>4</sup>



We communicate here that the rate of TB-mediated intramolecular singlet–singlet EET in the novel 10-bond DMN–bridge–



**Figure 1.** Fluorescence spectra of **2(10)** in *n*-hexane: (a) excitation spectrum with  $\lambda_{em} = 505 \text{ nm}$  (dashed line) and (b) emission spectra as a function of irradiation time (0–420 min) ( $\lambda_{ex} = 295 \text{ nm}$ ). Inset shows the decrease in dione emission with irradiation time concomitant with the increase observed in DMN emission.

dione **2(10)**<sup>6</sup> is 5 orders of magnitude faster than that predicted for **1(10)** and observed in the steroid systems exhibiting comparable interchromophore separations. The efficiency of energy transfer (>99.5% calculated based on the measured rate) is also much larger than that observed in flexibly linked systems containing the same donor:acceptor chromophores.<sup>1</sup>

An important motivation in extending our TB-mediated singlet–singlet EET studies to the diones **2(n)** was to eliminate as much as possible the competing and complicating Förster-mediated singlet–singlet EET process. It is well-known that singlet–singlet EET between aromatic chromophores and 1,2-diones cannot occur by the Förster resonance mechanism due to the very low dione absorption transition probability, as reflected by the small Förster critical radii ranging between 3.3 and 7 Å.<sup>7</sup>

Irradiation of the DMN–bridge–dione compounds at 295 nm strongly favors excitation of the DMN moiety in preference to the dione which has an extinction at this wavelength of just  $\sim 15 \text{ M}^{-1}\text{cm}^{-1}$ . The fluorescence spectra from these compounds show characteristic DMN emission (Figure 1) that is quenched in **2(6)** and **2(10)** relative to a DMN model compound, yet despite negligible direct excitation of the dione moiety, there is also clearly emission characteristic of the dione around 500 nm (inset Figure 1). This is compelling evidence for the occurrence of intramolecular EET from the DMN to the dione. Further evidence for this is provided by the fluorescence excitation spectrum of **2(10)** monitored in the dione's emission region at 505 nm (see also Figure 1) that shows intensity across the DMN absorption spectrum profile (i.e. excitation of the DMN chromophore leads to emission from the dione). Although the absolute intensity of the dione emission is rather weak, when normalized to the very low fluorescence quantum yield of the dione group, energy transfer in this compound is deemed to be remarkably efficient.

Monitoring the kinetics of the appearance and decay of the emission of the acceptor following excitation of the donor provides one of the most direct methods of determining the efficiency and rate of energy transfer. The time-resolved fluorescence decay profiles obtained from **2(6)** and **2(10)** in *n*-hexane, recorded at 505 nm (acceptor region) following 295 nm excitation (DMN absorption), are shown in Figure 2 and indicate that the rise in

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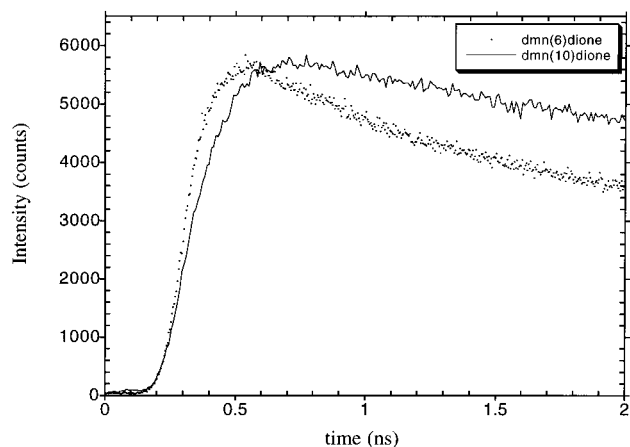
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**Figure 2.** Time-resolved fluorescence decay profiles of **2(6)** (dots) and **2(10)** (solid line) in *n*-hexane ( $\lambda_{\text{ex}} = 295$  nm,  $\lambda_{\text{em}} = 505$  nm).

dione emission intensity is virtually instantaneous on the time scale of the experiment. The decays in Figure 2 are the raw data and are therefore a convolution of the instrument's temporal response function and the true decay profile parameters.<sup>8</sup> A rise time of  $\sim 40$  ps (which is approaching the time resolution of our present instrumentation) was obtained for **2(10)** by fixing one of the decay lifetimes in the nonlinear least squares, iterative reconvolution analysis<sup>8</sup> to the fluorescence lifetime of the dione (11.6 ns) determined from decays recorded on longer time scales. The observed rise time for the dione emission in **2(10)** corresponds to a rate for EET from DMN to the dione of  $2.5 \times 10^{10} \text{ s}^{-1}$ . No rise time was resolvable for **2(6)** within the time-resolution of our instrument and the rate is thus estimated to be  $> 10^{11} \text{ s}^{-1}$ . Collection of fluorescence data in these experiments was hampered by a significant reduction in emission count rate throughout the duration of the data acquisition that is attributed to photolysis of the dione groups as discussed below.

Subjecting a solution of **2(10)** in *n*-hexane to prolonged irradiation at 295 nm led to a dramatic increase in the intensity of the DMN emission band at 330–400 nm during irradiation and a concomitant decrease in emission from the dione (Figure 1). This finding can only be explained in terms of EET taking place from the locally excited DMN chromophore to the dione group that then undergoes coupling and other reactions<sup>9</sup> with the consequent switching on of the DMN fluorescence.

If one assumes an energy transfer rate of ca.  $10^{13} \text{ s}^{-1}$  for the 4-bond analogue **2(4)** then an estimate for  $\beta$  of only ca. 1.0 per bond for the **2(n)** series is obtained, which is about one-half that found in other systems.<sup>2,3</sup> This diminished  $\beta$  value<sup>10</sup> for the **2(n)** series, plus the sheer speed with which TB-mediated singlet–singlet EET takes place within **2(10)** are quite without precedent.

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.<sup>2a</sup> The spectral overlap

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(10) If the assumed EET rate for **2(4)** is taken to be  $10^{14} \text{ s}^{-1}$  (in which case EET would take place within a molecular vibration), then  $\beta$  increases to 1.38 per bond, a value that is still substantially smaller than that observed for other systems.<sup>2,3</sup> We are endeavoring to obtain an experimental value for  $\beta$  in **2(n)** by measuring the rate of EET in the recently synthesized 12-bond homologue **2(12)**.

**Table 1.** Rates of Intramolecular Singlet–Singlet EET in *n*-hexane Solvent

molecule	$k_{\text{eet}} (\text{s}^{-1})$
<b>1(4)</b>	$1.17 \times 10^{10}$ <sup>a</sup>
<b>1(6)</b>	$1.93 \times 10^8$ <sup>a</sup>
<b>2(6)</b>	$> 10^{11}$
<b>2(10)</b>	$2.5 \times 10^{10}$

<sup>a</sup> Reference 2c.

integrals for resonance and exchange interactions between the DMN emission and the dione absorption for the system under discussion here are calculated to be  $6.6 \times 10^{-18} \text{ cm}^3 \text{ M}^{-1}$  and  $1.16 \times 10^{-5} \text{ cm}$ , respectively. These values can be compared with those reported for the **1(n)** compounds in cyclohexane ( $0.259 \times 10^{-18} \text{ cm}^3 \text{ M}^{-1}$  and  $2.26 \times 10^{-6} \text{ cm}$ , respectively).<sup>2a</sup> If a resonance dipole–dipole mechanism were dominant, the rate of EET for **2(10)** is calculated to be of the order of  $10^6$ – $10^7 \text{ s}^{-1}$ , which is far less than observed. The larger exchange overlap integral calculated for the DMN–bridge–diones compared to that of the DMN–bridge–ketone system cannot account for the 2 orders of magnitude increase in the observed rate of energy transfer in **2(10)** compared with, for example, **1(6)**<sup>2c</sup> (Table 1).

Preliminary CIS/6-31G(d)<sup>11</sup> calculations on the first excited states of model DMN–norbornane, 7-norbornane, and norbornane-2,3-dione chromophores, all possessing  $C_s$  symmetry, reveal that they have  $^1A'$ ,  $^1A''$ , and  $^1A'$  symmetries, respectively. Thus, singlet–singlet EET in the series **2(n)** is electronically allowed, whereas in **1(n)** this is electronically forbidden. However, vibronic coupling of the  $A'$  ( $^1L_b$ ) with the low-lying  $^1A''$  ( $^1L_a$ ) state of DMN should facilitate rapid EET in **1(n)**,<sup>12</sup> so we do not believe that electronic symmetry lies at the heart of the anomalous behavior of **2(10)**. A possible cause might lie in interrelay interference effects in the hydrocarbon bridges of **1(n)** and **2(n)**. Such effects, which are known to play important roles in determining the magnitude and distance dependence of coupling through saturated hydrocarbon bridges,<sup>13</sup> might be constructive in **2(n)** but destructive in **1(n)**, owing to the different symmetry of the highest lying lone pair orbital of the oxygen atom(s), which is  $a'$  for **2(n)** yet  $a''$  in **1(n)**. This possibility is being further explored computationally.<sup>14</sup>

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**Supporting Information Available:** Experimental details for the synthesis of **2(10)** and deconvolution of fluorescence decay profiles for **2(6)** and **2(10)** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(14) Energy transfer, and not electron transfer, is almost certainly occurring in **2(n)** because, although electrochemical studies suggest that the latter process is 0.3 eV exergonic in *n*-hexane, the sensitized dione emission in both **2(6)** and **2(10)** is identical with that of a dione model system lacking the DMN chromophore.