

Intramolecular singlet–singlet energy transfer in antenna-substituted azoalkanes

Uwe Pischel,^a Fang Huang^b and Werner M. Nau^{*b,c}

^a REQUIMTE/Department of Chemistry, Faculty of Sciences, University of Porto, R. Campo Alegre, 4169-007 Porto, Portugal

^b Department of Chemistry, University of Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland

^c School of Engineering and Science, International University Bremen, Campus Ring 1, D-28759 Bremen, Germany. E-mail: w.nau@iu-bremen.de

Received 18th September 2003, Accepted 3rd November 2003

First published as an Advance Article on the web 2nd December 2003

Two novel azoalkane bichromophores and related model compounds have been synthesised and photophysically characterised. Dimethylphenylsiloxy (DPSO) or dimethylnaphthylsiloxy (DNSO) serve as aromatic donor groups (antenna) and the azoalkane 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) as the acceptor. The UV spectral window of DBO (250–300 nm) allows selective excitation of the donor. Intramolecular singlet–singlet energy transfer to DBO is highly efficient and proceeds with quantum yields of 0.76 with DPSO and 0.99 with DNSO. The photophysical and spectral properties of the bichromophoric systems suggest that energy transfer occurs through diffusional approach of the donor and acceptor within a van der Waals contact at which the exchange mechanism is presumed to dominate. Furthermore, akin to the behaviour of electron-transfer systems in the Marcus inverted region, a rate of energy transfer 2.5 times slower was observed for the system with the more favourable energetics, *i.e.* singlet–singlet energy transfer from DPSO proceeded slower than from DNSO, although the process is more exergonic for DPSO (−142 kJ mol^{−1} for DPSO *versus* −67 kJ mol^{−1} for DNSO).

Introduction

2,3-Diazabicyclo[2.2.2]oct-2-ene (DBO) is a bicyclic azoalkane which has applications as a fluorescent probe for supramolecular assemblies, *e.g.* cyclodextrin- or cucurbituril-based host–guest systems,^{1,2} for the detection of antioxidants or nucleotides,^{3–5} and as a fluorescent label to study biopolymer dynamics.^{6–9} In particular, the exceptionally long fluorescence lifetime of DBO¹⁰ in solution (up to 1 μs), along with distinct novel quenching mechanisms, *i.e.* aborted hydrogen and electron transfer,^{11,12} open a wide dynamic range for the assessment of weak or remote interactions while maintaining a high selectivity towards the quencher. The low energy n_π* transition of DBO allows selective excitation of the chromophore (λ_{max} = 378 nm hexane). However, the extinction coefficient of this transition is comparatively small (ε₃₇₈ ≈ 180 M^{−1}cm^{−1} in alkanes),² due to poor spatial overlap between the n_π and π* orbitals.

For many applications, it is essential to improve the absorption properties, while preserving the advantageous fluorescent properties, of the azoalkane. We have now investigated the feasibility of attaching an antenna for efficient light absorption and subsequent singlet energy transfer to the azoalkane. Numerous studies regarding intramolecular energy transfer involving singlet–^{13–17} as well as triplet–excited states have been reported.^{18,19} Variation of excited-state energies and spacer properties, *e.g.* flexibility and intra-chromophore distances, has provided valuable insights into the mechanistic details of this basic photophysical process.^{20,21} Although azoalkanes have been the subject of intermolecular energy-transfer studies,^{22–25} the only *intramolecular* study deals with triplet–triplet energy transfer from carbonyl chromophores to azoalkanes.²⁶

Morrison and co-workers have introduced the dimethylphenylsiloxy (DPSO) group as an antenna for singlet–singlet energy transfer (SSET) to keto functions in steroidal molecules.^{27–29} Owing to its high excitation energy, the DPSO antenna can undergo efficient, highly exergonic energy transfer

to an acceptor chromophore, and has a short excited-state lifetime, which reduces competitive intermolecular quenching reactions. Energy-transfer studies from DPSO to DBO appeared particularly promising, since DBO offers a UV spectral window between 250 and 300 nm, which should allow very selective excitation of the DPSO antenna. In addition to DPSO, we planned to study the dimethylnaphthylsiloxy (DNSO) group as a new antenna function. This was intended to allow the influence of the thermodynamics on the energy-transfer process to be investigated.

Two bichromophoric compounds with a phenyl or naphthyl moiety linked by a siloxy spacer to the bridgehead position of DBO (**1a** and **2a**) were also synthesised as part of this project (Chart 1). These molecules were photophysically characterised by UV absorption as well as steady-state and time-resolved fluorescence spectroscopy and compared with the antenna model compounds lacking the DBO acceptor (**1b** and **2b**).

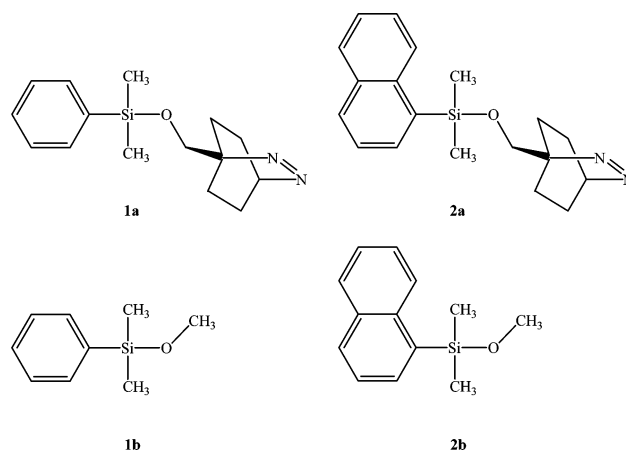


Chart 1 Structures of the bichromophoric azoalkanes (**1a** and **2a**) and antenna model compounds (**1b** and **2b**).

Experimental

Materials

1-(Hydroxymethyl)-2,3-diazabicyclo[2.2.2]oct-2-ene²⁶ and chlorodimethylnaphthylsilane³⁰ were synthesised according to literature procedures. All other chemicals and solvents for the synthesis were used as received from Aldrich. Column chromatography was performed with 70–230 μm silica gel from Merck. Cyclohexane was of spectroscopic quality from Fluka. Fluorescence grade benzene (Fluka) and naphthalene (National Bureau of Standards) were used as fluorescence standards.

Spectroscopic measurements

The absorption spectra were recorded using a Perkin-Elmer Lambda 19 spectrometer. All fluorescence measurements were performed in degassed solutions (3 freeze–pump–thaw cycles) at ambient temperature (24 °C). A home-made quartz cell with a high vacuum Teflon stopcock was used. Fluorescence spectra were recorded with a Glen Spectra Fluorolog Spex spectrometer. Fluorescence lifetimes were determined using an Edinburgh FLS900 single-photon counting setup operated by a 1.5 ns pulse width hydrogen flash lamp (nF900). The resulting data were analysed by means of monoexponential decay functions and a re-convolution function for the excitation light pulse. The concentration of bichromophoric compounds was kept low (10^{-5} – 10^{-4} M) to exclude competitive intermolecular quenching.

Synthesis of the antenna-substituted azoalkanes **1a** and **2a**

General procedure. A solution of 1 mmol 1-(hydroxymethyl)-2,3-diazabicyclo[2.2.2]oct-2-ene, 1.3 mmol triethylamine, and 1.5 mmol chlorodimethylarylsilane in 10 ml dry dichloromethane was stirred at room temperature under argon for 24 h. The resulting reaction mixture was extracted with 2×5 ml water and the resulting organic layer was dried over Na_2SO_4 . After filtration and solvent evaporation, a yellowish oil was obtained. Column chromatography with hexane–ethylacetate (1 : 1) yielded the product as colourless oil.

1-(Dimethylphenyl)siloxymethyl-2,3-diazabicyclo[2.2.2]oct-2-ene (1a**).** Yield 69%. UV/Vis (cyclohexane): λ 253 (log ϵ = 2.28), 259 (2.44), 264 (2.44), 270 (2.30), 379 (2.22) nm. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 0.44 [6 H, s, $(\text{CH}_3)_2\text{Si}$], 1.07–1.16 (2 H, m, CH_2), 1.28–1.38 (2 H, m, CH_2), 1.52–1.62 (4 H, m, CH_2), 4.17 (2 H, s, CH_2O), 5.12 (1 H, t, J = 3.5 Hz, CH), 7.37–7.41 (3 H, m, CH aryl), 7.60–7.64 (2 H, m, CH aryl) ppm. $^{13}\text{C-NMR}$ (126 MHz, CDCl_3): δ -1.8 [2 C, $(\text{CH}_3)_2\text{Si}$], 21.6 (2 C, CH_2), 23.1 (2 C, CH_2), 61.9 (CH), 67.4 (C_q), 68.6 (CH_2O), 127.8 (2 C, CH aryl), 129.6 (2 C, CH aryl), 133.6 (CH aryl), 137.8 (C_q aryl) ppm. Elemental analysis calcd for $\text{C}_{15}\text{H}_{22}\text{SiN}_2\text{O}$: C, 65.65; H, 8.08; N, 10.21; found: C, 65.75; H, 8.02; N, 10.15%.

1-(Dimethylnaphth-1-yl)siloxymethyl-2,3-diazabicyclo[2.2.2]oct-2-ene (2a**).** Yield 19%. UV/Vis (cyclohexane): λ 262 (log ϵ = 3.58), 273 (3.81), 283 (3.89), 294 (3.73), 379 (2.24) nm. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 0.61 [6 H, s, $(\text{CH}_3)_2\text{Si}$], 1.11–1.16 (2 H, m, CH_2), 1.26–1.35 (2 H, m, CH_2), 1.54–1.61 (4 H, m, CH_2), 4.18 (2 H, s, CH_2O), 5.12 (1 H, t, J = 3.5 Hz, CH), 7.46–7.53 (3 H, m, CH aryl), 7.79 (1 H, dd, J = 1.5 and 5.8 Hz, CH aryl), 7.85–7.91 (2 H, m, CH aryl), 8.32–8.34 (1 H, m, CH aryl) ppm. $^{13}\text{C-NMR}$ (126 MHz, CDCl_3): δ -0.6 [2 C, $(\text{CH}_3)_2\text{Si}$], 21.6 (2 C, CH_2), 23.2 (2 C, CH_2), 61.9 (CH), 67.4 (C_q), 68.7 (CH_2O), 125.0 (CH aryl), 125.5 (CH aryl), 126.0 (CH aryl), 128.3 (CH aryl), 128.9 (CH aryl), 130.4 (CH aryl), 133.3 (CH aryl), 133.9 (C_q aryl), 135.8 (C_q aryl), 136.9 (C_q aryl) ppm. Elemental analysis calcd for $\text{C}_{19}\text{H}_{24}\text{SiN}_2\text{O}$: C, 70.33; H, 7.46; N, 8.63; found: C, 70.32; H, 7.46; N, 8.70%.

Synthesis of the antenna model compounds **1b** and **2b**

General procedure. 2.3 mmol of sodium were dissolved in 3 ml methanol and 1.4 mmol of chlorodimethylarylsilane were added dropwise. The mixture was stirred for 2 h at room temperature. The solvent was evaporated and the residue was treated with 5 ml of freshly distilled diethyl ether. After filtration, the solvent was removed by evaporation and the resulting oil was purified by Kugelrohr microdistillation to yield a colourless product.

Methoxydimethylphenylsilane (1b**).** Yield 39%. UV/Vis (cyclohexane): λ 253 (log ϵ = 2.26), 259 (2.43), 264 (2.42), 270 (2.29) nm. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 0.39 [6 H, s, $(\text{CH}_3)_2\text{Si}$], 3.45 (3 H, s, CH_3O), 7.36–7.43 (3 H, m, CH aryl), 7.56–7.60 (2 H, m, CH aryl) ppm. $^{13}\text{C-NMR}$ (126 MHz, CDCl_3): δ -2.4 [2 C, $(\text{CH}_3)_2\text{Si}$], 50.7 (CH_3O), 127.9 (2 C, CH aryl), 129.6 (2 C, CH aryl), 133.4 (CH aryl), 137.4 (C_q aryl) ppm. Elemental analysis calcd for $\text{C}_9\text{H}_{14}\text{SiO}$: C, 65.00; H, 8.49; found: C, 64.29; H, 8.04%.

Methoxydimethylnaphth-1-ylsilane (2b**).** Yield 30%. UV/Vis (cyclohexane): λ 262 (log ϵ = 3.59), 273 (3.81), 283 (3.89), 294 (3.72) nm. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 0.57 [6 H, s, $(\text{CH}_3)_2\text{Si}$], 3.48 (3 H, s, CH_3O), 7.47–7.57 (3 H, m, CH aryl), 7.76 (1 H, d, J = 7.1 Hz, CH aryl), 7.88–7.93 (2 H, m, CH aryl), 8.33 (1 H, d, J = 8.1 Hz, CH aryl) ppm. $^{13}\text{C-NMR}$ (126 MHz, CDCl_3): δ -1.0 [2 C, $(\text{CH}_3)_2\text{Si}$], 50.6 (CH_3O), 125.0 (CH aryl), 125.5 (CH aryl), 126.1 (CH aryl), 128.0 (CH aryl), 128.9 (CH aryl), 130.4 (CH aryl), 133.3 (CH aryl), 133.9 (C_q aryl), 135.5 (C_q aryl), 136.9 (C_q aryl) ppm. Elemental analysis calcd for $\text{C}_{13}\text{H}_{16}\text{SiO}$: C, 72.17; H, 7.45; found: C, 72.04; H, 7.39%.

Results and discussion

Absorption properties

The UV spectra of the individual chromophores in cyclohexane are shown in Fig. 1. The aryl residues in the antenna model compounds show characteristic vibrationally structured π, π^* transitions, with a weaker band for the phenyl moiety in **1b** (λ_{max} = 259 nm, ϵ = 275 $\text{M}^{-1} \text{cm}^{-1}$), due to its symmetry-forbidden nature, and a red-shifted absorption with a high transition probability (λ_{max} = 283 nm, ϵ = 7800 $\text{M}^{-1} \text{cm}^{-1}$) for the naphthalene chromophore in **2b**. The symmetry-allowed but, due to poor spatial overlap of the participating n and π^* orbitals, orbital-forbidden transition³¹ of the azoalkane at 379 nm has an ϵ value of ca. 170 $\text{M}^{-1} \text{cm}^{-1}$ in hydrocarbon solvents.

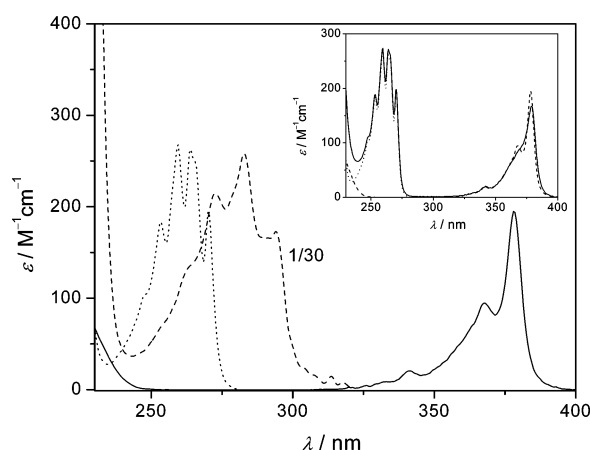


Fig. 1 Absorption spectra of the antenna model compounds **1b** (···) and **2b** (---; divided by 30) and the parent DBO (—). Note that the absorption of compounds **1b** and **2b** occurs in the spectral window of DBO, therefore allowing exclusive excitation of the antenna. The inset shows the absorption spectrum of the bichromophore **1a** (—) in comparison to the individual components, the antenna model **1b** (···) and the parent DBO (---), all in cyclohexane.

Table 1 Photophysical data for the investigated compounds (see Chart 1) in cyclohexane

	τ_f^a /ns	Φ_f^b	$\Phi_{\text{SSET}}^{c,d}$	$k_{\text{SSET}}^{c/s^{-1}}$	$J_{d-d}/\text{cm}^6 \text{ mol}^{-1}$	$J_{\text{ex}}^e/\text{cm}$	$k_{\text{inter}}^f/\text{M}^{-1} \text{ s}^{-1}$
1a	0.63	0.014	0.76	1.2×10^9	4.6×10^{-15}	1.3×10^{-5}	1.3×10^8
1b	2.61	0.040					
2a	0.33	0.008	0.99	3.0×10^9	4.8×10^{-14}	1.2×10^{-4}	1.5×10^{10}
2b	54.0	0.279					

^a Measured by single photon counting; 5% error. ^b Measured by steady-state fluorescence spectroscopy using benzene ($\Phi_f = 0.06$) or naphthalene ($\Phi_f = 0.19$) in cyclohexane as standards;³⁴ 10% error. ^c Equations for calculation are given in the text. ^d Quantum yields for energy transfer are based on time-resolved data. ^e Note that these values differ significantly from the Dexter spectral overlap integrals calculated by Engel *et al.*²⁴ for the intermolecular energy transfer between DBO and benzene ($J_{\text{ex}} = 2.0 \times 10^{-7} \text{ cm}$) or naphthalene ($J_{\text{ex}} = 6.8 \times 10^{-5} \text{ cm}$) in isoctane. ^f Intermolecular fluorescence quenching rate constants of benzene or naphthalene by DBO in isoctane taken from ref. 24.

The spectra of the bichromophoric systems are a superposition of the two separated chromophores, as shown in the inset of Fig. 1 for **1a** and the individual chromophores **1b** and DBO. Neither the spectral shapes nor the oscillator strengths are altered, which rules out a sizable electronic interaction between the two chromophores in the ground state. In fact, the only difference is that the spectra of the bichromophoric compounds reveal a marginal red shift (*ca.* 1 nm) of the maximum of the n, π^* transition of the azoalkane residue compared to the parent DBO. This effect may be indicative of the presence of the remote aryl groups, which should increase the apparent polarisability in the surroundings of the azo chromophore.³² Recent studies of DBO in various solvents have revealed a marked dependence of the absorption maximum on the polarisability of the environment: the higher the polarisability, the more red-shifted (and more intense) is the absorption.²

Note in particular the large UV window of DBO and the perfect spectral match of the antenna absorptions in the bichromophoric systems (Fig. 1), which render them quite unique. In photophysically related donor–acceptor combinations of dimethoxynaphthalene and bicyclic (di)ketones, selective excitation of the donor has only been achieved by exploiting the differences in molar absorption coefficients.³³

Fluorescence measurements

To investigate intramolecular singlet–singlet energy transfer in the antenna-substituted azoalkanes, steady-state as well as time-resolved fluorescence measurements were performed. Selective excitation of the antenna results, in both cases, in a weak residual fluorescence of the aromatic moiety ($\lambda_{\text{max}} = 295 \text{ nm}$ for **1a** and 345 nm for **2a**). The emission spectra are dominated by the characteristic broad band of DBO, with a maximum at 430 nm . In both cases, the excitation spectrum, with $\lambda_{\text{obs}} = 430 \text{ nm}$, matched the absorption spectrum of the bichromophore, which provides the signature of energy transfer from the aryl residue to the azoalkane chromophore. This is exemplified in Fig. 2, which shows the fluorescence emission and

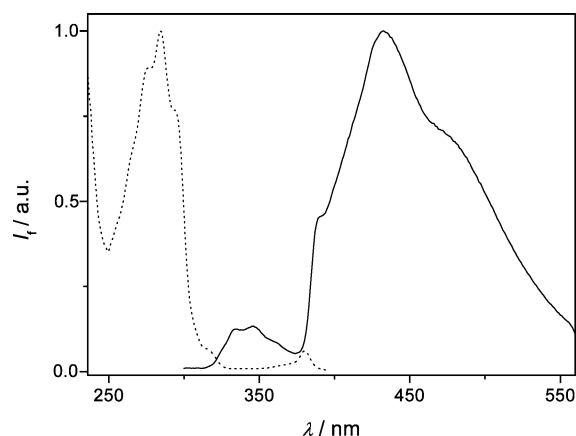


Fig. 2 Fluorescence emission (—; $\lambda_{\text{exc}} = 283 \text{ nm}$) and excitation (···; $\lambda_{\text{obs}} = 430 \text{ nm}$) spectra of **2a** in cyclohexane ($2.1 \times 10^{-5} \text{ M}$).

excitation spectra of the DNSO-substituted azoalkane **2a** in cyclohexane. In order to quantify the fluorescence properties, the emission quantum yields of the aryl residues in the antenna model compounds (**1b** and **2b**) and the bichromophoric systems (**1a** and **2a**) were determined (*cf.* Table 1). Benzene and naphthalene were used as reference standards ($\Phi_f = 0.06$ and 0.19 , respectively, in cyclohexane).³⁴

The shortened fluorescence lifetimes of the antenna in **1a** and **2a** compared to their respective model compounds, **1b** and **2b**, as obtained from single-photon counting-based measurements (*cf.* Table 1 and Fig. 3) are in line with the steady-state fluorescence quenching results. Deviations from monoexponential decay behaviour were not observed. The lifetimes are not dependent on the concentration of the bichromophoric system within the examined concentration range (10^{-5} – 10^{-4} M), which mitigates against intermolecular association and static quenching in the nonpolar solvent. As will be shown below, a contact-quenching mechanism is operative, for which deviations from monoexponential decay kinetics are only expected on a picosecond timescale.³⁵

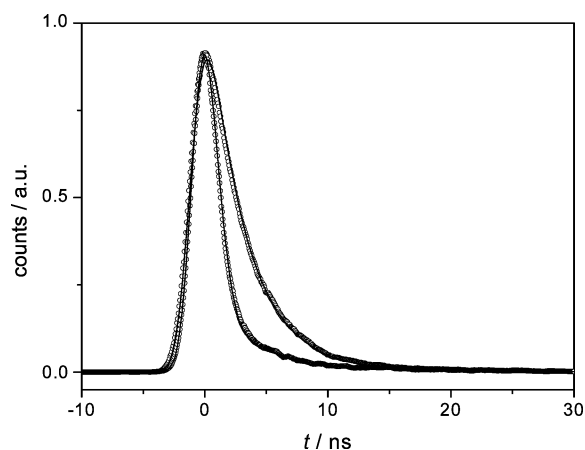


Fig. 3 Time-resolved fluorescence decay kinetics of **1a** (lower trace) and **1b** (upper trace) in cyclohexane ($[\mathbf{1a}] = 3.5 \times 10^{-4} \text{ M}$, $[\mathbf{1b}] = 1.9 \times 10^{-3} \text{ M}$; $\lambda_{\text{exc}} = 270 \text{ nm}$, $\lambda_{\text{obs}} = 295 \text{ nm}$). The solid lines represent reconvolution fits taking into account the lamp profile.

The assignment of the mechanism of intramolecular fluorescence quenching as singlet–singlet energy transfer from the arene to the azo chromophore requires attention. First, the fraction of naphthalene fluorescence which is lost due to intramolecular quenching is fully converted, within instrumental error, to DBO emission (*cf.* Fig. 2). Second, electron transfer, the most likely competitive quenching mechanism, is expected to be strongly endergonic in nonpolar cyclohexane for both phenyl and naphthyl. Even if the calculation is done for a polar solvent (acetonitrile),³⁶ only slightly exergonic thermodynamics applies for the oxidation of DBO ($\Delta G_{\text{et}} \approx -30 \text{ kJ mol}^{-1}$ for naphthalene and *ca.* -5 kJ mol^{-1} for benzene), while photo-reduction of DBO is already an uphill process ($\Delta G_{\text{et}} \approx +34 \text{ kJ mol}^{-1}$ for naphthalene and *ca.* $+33 \text{ kJ mol}^{-1}$ for benzene). Electron transfer is therefore not expected to compete with the

strongly exergonic singlet–singlet energy transfer (-142 kJ mol^{-1} for **1a** and -67 kJ mol^{-1} for **2a**).^{15,18,36,37}

Note that the fluorescence lifetime of the DBO chromophore remains unaffected for the phenyl derivative **1a** (270 versus 275 ns for the parent DBO in cyclohexane), but is shortened for the naphthyl derivative **2a** (106 ns). The weak quenching of DBO fluorescence by naphthalene is presumably induced by intramolecular exciplex formation, which is known for the quenching of n, π^* excited states by arenes.^{10,38,39} The naphthyl group is a stronger quencher than the phenyl group, as is also indicated by the *intermolecular* quenching rate constants of DBO, which are $1.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for benzene¹⁰ and $6.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for naphthalene.

Rate and efficiency of singlet–singlet energy transfer

The efficiency of singlet–singlet energy transfer (Φ_{SSET}) and the associated intramolecular rate constant (k_{SSET}) can be determined by using eqn. 1 and 2. The indices (a) and (b) refer to the compounds in Chart 1.

$$\Phi_{\text{SSET}} = 1 - \frac{\Phi_{\text{f(a)}}}{\Phi_{\text{f(b)}}} = 1 - \frac{\tau_{\text{f(a)}}}{\tau_{\text{f(b)}}} \quad (1)$$

$$k_{\text{SSET}} = \frac{\Phi_{\text{SSET}}}{\tau_{\text{f(a)}}} \quad (2)$$

The results are shown in Table 1. The quantum yields were calculated on the basis of the fluorescence lifetimes, which is made possible by the monoexponentiality of the decays. The use of steady-state fluorescence quantum yields leads, within error limits, to virtually the same values (0.66 for **1a** and 0.97 for **2a**). The intramolecular rate constant for SSET can be calculated from the lifetimes as $1.2 \times 10^9 \text{ s}^{-1}$ for the phenyl-substituted azo chromophore **1a** and as $3.0 \times 10^9 \text{ s}^{-1}$ for **2a**. These values are of the same order of magnitude as those observed for related bichromophoric systems with similar donor–acceptor spacing.⁴⁰

Strikingly, these rate constants seem to contradict the thermodynamic data for energy transfer (see above), *i.e.* the process is a factor of 2.5 *slower* for the thermodynamically favoured case **1a**, for which singlet–singlet energy transfer is 75 kJ mol^{-1} more exergonic than for **2a**. This inverted effect has previously been observed for *intermolecular* singlet–singlet energy transfer between aromatics and azoalkanes.^{22–24} In essence, we have reached the inverted region, where energy transfer is slowed down, regardless of favourable thermodynamics, due to decreased Franck–Condon overlap between the initial and final states, akin to the Marcus inverted region for electron transfer.⁴¹

The dominant quantities are the spectral overlap integrals (J) of the donor emission and the acceptor absorption, which enter directly the expressions (eqn. 3 and 4) for the rate constants of energy transfer according to the dipole–dipole (Förster, $k_{\text{d-d}}$) or the exchange (Dexter, k_{ex}) mechanisms.²¹ Note that the absorption band is normalised in Dexter theory such that a small absolute extinction coefficient of the acceptor (in this case, the azo chromophore) reduces the energy-transfer rate only for the dipole–dipole mechanism.

$$k_{\text{d-d}} = \frac{1}{\tau_{\text{D}}} \left(\frac{R_0}{R} \right)^6 \quad (3)$$

$$\text{where } R_0^6 = \frac{9000 \ln 10 (\kappa^2 \Phi_{\text{D}})}{128 \pi^5 n^4 N_{\text{A}}} J_{\text{d-d}} \quad (4)$$

$$k_{\text{ex}} = \frac{2\pi}{\hbar} K J_{\text{ex}} e^{(-2R/L)}$$

The spectral overlap integrals according to Förster ($J_{\text{d-d}}$) and Dexter (J_{ex}) theory¹⁴ were obtained by numerical integration and are presented in Table 1. Note that the absolute values for J are comparable to those obtained for similar intramolecular systems composed of 1,4-dimethoxynaphthalene and diketones.³³ For the phenyl case, **1a**, the excitation energy of the donor exceeds significantly that of the acceptor. This causes a mismatch of donor emission and acceptor absorption bands (*cf.* Fig. 4) and reduces J for both mechanisms. With the known fluorescence quantum yields and lifetimes in the absence of quencher (see values for **1b** and **2b** in Table 1), and by assuming a constant specific orbital interaction K (in eqn. 4, only for Dexter mechanism), the expectation factors by which energy transfer for **2a** should be faster than for **1a** can be calculated. Factors of 3.5 for the Förster mechanism and 9.2 for the Dexter mechanism are obtained, in qualitative agreement with experiment, but at variance with expectations based on the thermodynamics alone. The faster energy-transfer rates for **2a** are mainly due to the larger J values, while the differences in the radiative decay rates (which enter eqn. 3 as the ratio of Φ_{D} and τ_{D}) somewhat moderate the net effect in the dipole–dipole case.

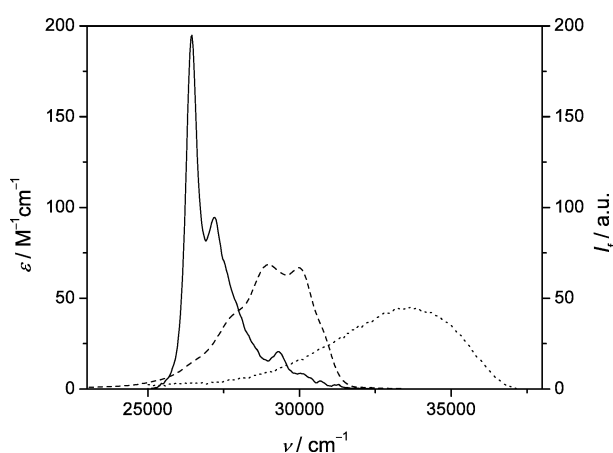


Fig. 4 Absorption spectrum of the parent DBO (—) and fluorescence spectra of the antenna model compounds **1b** (···; $\lambda_{\text{exc}} = 249 \text{ nm}$) and **2b** (---; $\lambda_{\text{exc}} = 283 \text{ nm}$) in cyclohexane (fluorescence spectra normalised to same area as absorption spectrum). Note the very poor spectral overlap for the **1b**–DBO donor–acceptor pair.

Mechanism of energy transfer

Singlet–singlet energy transfer by the exchange mechanism requires orbital overlap, *i.e.* contact between probe and quencher. Fluorescence resonance energy transfer can occur over larger distances, as can be judged from the critical transfer distance, R_0 (eqn. 3).

With known spectral data and $\kappa^2 = 2/3$, the critical transfer radii for **1a** and **2a** can be calculated as $R_0 = 5.4$ and 11.1 Å , respectively. These critical radii provide the distance at which energy transfer and the deactivation by other processes occur at the same rate. However, to account for the experimentally observed energy-transfer efficiencies, which are greater than 50% (Table 1), energy transfer must occur at a shorter mean distance (R), which can be derived from eqn. 5.

$$\Phi_{\text{SSET}} = \frac{1}{1 + \left(\frac{R}{R_0} \right)^6} \quad (5)$$

Mean distances of 4.5 and 5.2 Å result for **1a** and for **2a**, respectively, which suggest that probe and quencher come effectively within van der Waals contact to undergo quenching (the sum of the radii of probe and quencher is *ca.* 5 Å). This means that singlet–singlet energy transfer in the bichromophoric systems proceeds predominantly by the exchange

mechanism, which is generally anticipated when forbidden acceptor transitions are involved (in this case, the orbital-forbidden n, π^* transition of DBO).^{20,21} Previous studies on intermolecular energy transfer-induced fluorescence quenching of aromatics by azoalkanes have also led to the conclusion that an exchange mechanism operates.^{22–25,42} For example, steric hindrance effects were observed, which stress the requirement for orbital overlap between donor and acceptor orbitals.²⁵

The efficient quenching demonstrates that donor and acceptor must rapidly come into contact within the excited-state lifetime of the donor, *i.e.* within several nanoseconds. In fact, mutual diffusion of the two ends of a very short polymer chain is expected to occur on a timescale as fast as 1 ns.⁸ The observed timescale for energy transfer is, therefore, consistent with the idea that energy transfer is promoted by a diffusive intramolecular collision between the donor and acceptor.⁴⁰ Intramolecular diffusion should occur faster for the phenyl derivative **1a**, since the phenyl group has a higher diffusion coefficient. The fact that intramolecular quenching in **1a** is nevertheless slower reflects the less favourable electronic requirement for energy transfer (small overlap integral), *i.e.* not every collision between the phenyl and DBO residues may lead to quenching. In fact, the intermolecular fluorescence quenching rate constants of benzene and naphthalene by DBO (k_{inter} values in Table 1) demonstrate that the quenching of benzene, in contrast to naphthalene, is not diffusion controlled.²⁴

Comparison of the quenching rate constants for the intramolecular and the intermolecular reaction (Table 1) reveals also that the differentiation between the rate constants for the two aromatic chromophores is much less pronounced for the intramolecular case (the k_{SET} values differ by a factor of 2–3) compared to the intermolecular case (the k_{inter} values differ by a factor of 100). This trend is in line with the idea that intrachain diffusion becomes an additional factor in determining the quenching rates. Note that the intramolecular diffusion coefficients of a chromophore in, for example, a polymer chain are typically 10 times smaller than the corresponding free intermolecular diffusion coefficients,^{35,43} such that the impact of electronic factors on the overall rate is less pronounced. In other words, the kinetics shifts from purely reaction controlled for the intermolecular case to partially diffusion controlled for the intramolecular case. In addition, any participation of fluorescence resonance energy transfer, which is likely to compete to an unknown extent for the intramolecular system, will tend to reduce the differential rates (see expectation factors above). The combined arguments account for the observation that the “inverted effect” on singlet–singlet energy transfer is less pronounced for the bichromophoric systems studied here than for the intermolecular reaction.

Conclusions

Two new bichromophoric DBO derivatives have been photo-physically characterised. Both perform very efficient singlet–singlet energy transfer by an exchange mechanism, which is induced by intramolecular diffusion to form van der Waals contact between donor and acceptor. An inverted effect of the intramolecular quenching rate constants on the thermodynamics of energy transfer was observed; however, this is less pronounced than for the intermolecular reaction. While the DPSO group in **1a** exhibits a weak absorption band like DBO, the DNSO group in **2a** shows an ϵ value which is *ca.* 50 times higher, which greatly improves the absorption features of DBO while performing an almost quantitative and irreversible singlet–singlet energy transfer. DNSO is therefore a suitable antenna for DBO. Unfortunately, the naphthyl group also causes some exciplex-induced quenching of the long-lived DBO chromophore, which certainly limits the scope of the antenna approach to remedy the weak absorption properties of DBO.

Acknowledgement

Financial support by the Schweizerischer Nationalfonds (NRP 47 “Supramolecular Functional Materials”) is gratefully acknowledged.

References and notes

- W. M. Nau and X. Zhang, An exceedingly long-lived fluorescent state as a distinct structural and dynamic probe for supramolecular association: an exploratory study of host–guest complexation by cyclodextrins, *J. Am. Chem. Soc.*, 1999, **121**, 8022–8032.
- C. Marquez and W. M. Nau, Polarizabilities inside molecular containers, *Angew. Chem., Int. Ed.*, 2001, **40**, 4387–4390.
- W. M. Nau, A fluorescent probe for antioxidants, *J. Am. Chem. Soc.*, 1998, **120**, 12614–12618.
- C. Marquez, U. Pischel and W. M. Nau, Selective fluorescence quenching of 2,3-diazabicyclo[2.2.2]oct-2-ene by nucleotides, *Org. Lett.*, 2003, **5**, 3911–3914.
- G. Gramlich, J. Zhang and W. M. Nau, Increased antioxidant reactivity of vitamin C at low pH in model membranes, *J. Am. Chem. Soc.*, 2002, **124**, 11252–11253.
- R. R. Hudgins, F. Huang, G. Gramlich and W. M. Nau, A fluorescence-based method for direct measurement of submicrosecond intramolecular contact formation in biopolymers: an exploratory study with polypeptides, *J. Am. Chem. Soc.*, 2002, **124**, 556–564.
- W. M. Nau and X. Wang, Biomolecular and supramolecular kinetics in the submicrosecond time range: the fluorazophore approach, *ChemPhysChem*, 2002, **3**, 393–398.
- W. M. Nau, F. Huang, X. Wang, H. Bakirci, G. Gramlich and C. Marquez, Exploiting long-lived molecular fluorescence, *Chimia*, 2003, **57**, 161–167.
- F. Huang and W. M. Nau, A conformational flexibility scale for amino acids in peptides, *Angew. Chem., Int. Ed.*, 2003, **42**, 2269–2272.
- W. M. Nau, G. Greiner, H. Rau, J. Wall, M. Olivucci and J. C. Scaiano, Fluorescence of 2,3-diazabicyclo[2.2.2]oct-2-ene revisited: solvent-induced quenching of the n, π^* -excited state by an aborted hydrogen atom transfer, *J. Phys. Chem. A*, 1999, **103**, 1579–1584.
- W. M. Nau, G. Greiner, J. Wall, H. Rau, M. Olivucci and M. A. Robb, The mechanism for hydrogen abstraction by n, π^* excited singlet states: evidence for thermal activation and deactivation through a conical intersection, *Angew. Chem., Int. Ed.*, 1998, **37**, 98–101.
- A. Sinicropi, U. Pischel, R. Basosi, W. M. Nau and M. Olivucci, Conical intersections in charge-transfer induced quenching, *Angew. Chem., Int. Ed.*, 2000, **39**, 4582–4586.
- H. E. Zimmerman, T. D. Goldman, T. K. Hirzel and S. P. Schmidt, Rod-like organic molecules. Energy-transfer studies using single-photon counting, *J. Org. Chem.*, 1980, **45**, 3933–3951.
- H. Oevering, J. W. Verhoeven, M. N. Paddon-Row, E. Cotsaris and N. S. Hush, Long-range exchange contribution to singlet–singlet energy transfer in a series of rigid bichromophoric molecules, *Chem. Phys. Lett.*, 1988, **143**, 488–495.
- J. Kroon, A. M. Oliver, M. N. Paddon-Row and J. W. Verhoeven, Observation of a remarkable dependence of the rate of singlet–singlet energy transfer on the configuration of the hydrocarbon bridge in bichromophoric systems, *J. Am. Chem. Soc.*, 1990, **112**, 4868–4873.
- F. Schael, M. B. Rubin and S. Speiser, Electronic energy transfer in solution in naphthalene–anthracene, naphthalene–acridine and benzene–DANS bichromophoric compounds, *J. Photochem. Photobiol., A*, 1998, **115**, 99–108.
- S. Speiser and F. Schael, Molecular structure control of intramolecular electronic energy transfer, *J. Mol. Liq.*, 2000, **86**, 25–35.
- G. L. Closs, M. D. Johnson, J. R. Miller and P. Piotrowiak, A connection between intramolecular long-range electron, hole, and triplet energy transfers, *J. Am. Chem. Soc.*, 1989, **111**, 3751–3753.
- P. J. Wagner and P. Klán, Intramolecular triplet energy transfer in flexible molecules: electronic, dynamic, and structural aspects, *J. Am. Chem. Soc.*, 1999, **121**, 9626–9635.
- N. J. Turro, Energy transfer processes, *Pure Appl. Chem.*, 1977, **49**, 405–429.
- S. Speiser, Photophysics and mechanisms of intramolecular electronic energy transfer in bichromophoric molecular systems: solution and supersonic jet studies, *Chem. Rev.*, 1996, **96**, 1953–1976.
- K. Razi Naqvi and C. Steel, Exchange-induced resonance energy transfer, *Chem. Phys. Lett.*, 1970, **6**, 29–32.

- 23 P. S. Engel and C. Steel, Photochemistry of aliphatic azo compounds in solution, *Acc. Chem. Res.*, 1973, **6**, 275–281.
- 24 P. S. Engel, L. D. Fogel and C. Steel, Singlet energy transfer to azoalkanes, *J. Am. Chem. Soc.*, 1974, **96**, 327–332.
- 25 C. C. Wamser, L. Lou, J. Mendoza and E. Olson, Singlet electronic energy transfer to azoalkanes: separation of collisional and long-range mechanisms by steric and solvent-viscosity effects, *J. Am. Chem. Soc.*, 1981, **103**, 7228–7232.
- 26 P. S. Engel, D. W. Horsey, J. N. Scholz, T. Karatsu and A. Kitamura, Intramolecular triplet energy transfer in ester-linked bichromophoric azoalkanes and naphthalenes, *J. Phys. Chem.*, 1992, **96**, 7524–7535.
- 27 Z.-Z. Wu, J. Nash and H. Morrison, Organic photochemistry. 97. Antenna-initiated photochemistry in polyfunctional steroids. Photoepimerization of 3 α -(dimethylphenylsiloxy)-5 α -androstane-6,17-dione and its 3 β isomer by through-bond exchange energy transfer, *J. Am. Chem. Soc.*, 1992, **114**, 6640–6648.
- 28 Z.-Z. Wu and H. Morrison, Organic photochemistry. 95. Antenna-initiated photochemistry of distal groups in polyfunctional steroids. Intramolecular singlet and triplet energy transfer in 3 α -(dimethylphenylsiloxy)-5 α -androstane-17-one and 3 α -(dimethylphenylsiloxy)-5 α -androstane-11,17-dione, *J. Am. Chem. Soc.*, 1992, **114**, 4119–4128.
- 29 J. K. Agyin, L. D. Timberlake and H. Morrison, Steroids as photonic wires. Z \rightarrow E olefin photoisomerization involving ketone singlet and triplet switches by through-bond energy transfer, *J. Am. Chem. Soc.*, 1997, **119**, 7945–7953.
- 30 T. R. van den Anker and C. L. Raston, Polymer- and metal-oxide-supported alkali metal naphthalenides: application in the generation of lithium and sodium reagents, *J. Organomet. Chem.*, 1998, **550**, 283–300.
- 31 W. M. Nau, n, π^* Photochemistry beyond ketones, *EPA Newsl.*, 2000, **70**, 6–29.
- 32 K. A. Zachariasse, A. L. Maçanita and W. Kühnle, Chain length dependence of intramolecular excimer formation with 1,*n*-bis-(1-pyrenylcarboxy)alkanes for *n* = 1–16, 22, and 32, *J. Phys. Chem. B*, 1999, **103**, 9356–9365.
- 33 N. Lokan, M. N. Paddon-Row, T. A. Smith, M. La Rosa, K. P. Ghiggino and S. Speiser, Highly efficient through-bond-mediated electronic excitation energy transfer taking place over 12 Å, *J. Am. Chem. Soc.*, 1999, **121**, 2917–2918.
- 34 S. L. Murov, I. Carmichael and G. L. Hug, *Handbook of Photochemistry*, Marcel Dekker, Inc., New York, 2nd edn., 1993.
- 35 X. Wang, E. N. Bodunov and W. M. Nau, Fluorescence quenching kinetics in short polymer chains: dependence on chain length, *Opt. Spectrosc.*, 2003, **95**, 603–613.
- 36 To calculate the electron transfer energetics with the Rehm–Weller equation [ΔG_{et} (kJ mol^{−1}) = 96.5(E_{ox} – E_{red} – E^* + C)], and for the energy-transfer energetics [$\Delta G_{\text{SSET}} = E^*(\text{Acceptor}) - E^*(\text{Donor})$], the following photophysical and electrochemical parameters (versus SCE in acetonitrile unless otherwise stated) were used: for DBO, $E^* = 3.30$ eV (318 kJ mol^{−1}),¹⁰ $E_{\text{ox}} = 1.45$ V (cf. W. M. Nau, W. Adam, D. Klapstein, C. Sahin and H. Walter, Correlation of oxidation and ionization potentials for azoalkanes, *J. Org. Chem.*, 1997, **62**, 5128–5132) and $E_{\text{red}} = -2.80$ V (cf. W. M. Nau and U. Pischel, “Inverted” solvent effect on charge transfer in the excited state, *Angew. Chem., Int. Ed.*, 1999, **38**, 2885–2888); for naphthalene, $E^* = 3.99$ eV (385 kJ mol^{−1}),³⁴ $E_{\text{ox}} = 1.60$ V⁴¹ and $E_{\text{red}} = -2.29$ V⁴¹; for benzene $E^* = 4.75$ eV (460 kJ mol^{−1}),³⁴ $E_{\text{ox}} = 2.35$ V (cf. S. Fukuzumi, K. Ohkubo, T. Suenobu, K. Kato, M. Fujitsuka and O. Ito, Photoalkylation of 10-alkylacridinium ion via a charge-shift type of photoinduced electron transfer controlled by solvent polarity, *J. Am. Chem. Soc.*, 2001, **123**, 8459–8467) and $E_{\text{red}} = -3.31$ V versus SCE in 1,2-dimethoxyethane (cf. F. Gerson, H. Ohya-Nishiguchi and C. Wydler, Indirect determination of the half-wave reduction potential of benzene and of [2.2]paracyclophane, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 552–553). The Coulomb term (C) was taken as −0.06 eV.
- 37 G. L. Closs, P. Piotrowiak, J. M. MacInnis and G. R. Fleming, Determination of long distance intramolecular triplet energy transfer rates. A quantitative comparison with electron transfer, *J. Am. Chem. Soc.*, 1988, **110**, 2652–2653.
- 38 P. J. Wagner, R. J. Truman, A. E. Puchalski and R. Wake, Extent of charge transfer in the photoreduction of phenyl ketones by alkylbenzenes, *J. Am. Chem. Soc.*, 1986, **108**, 7727–7738.
- 39 C. Coenjarts and J. C. Scaiano, Reaction pathways involved in the quenching of the photoactivated aromatic ketones xanthone and 1-azaxanthone by polyalkylbenzenes, *J. Am. Chem. Soc.*, 2000, **122**, 3635–3641.
- 40 An interaction of both chromophores mediated by the spacer orbitals, i.e. a superexchange mechanism, was also considered. Its participation in the overall mechanism is presumably negligible, since considerable flexibility of the spacer chain reduces the probability of a favourable arrangement of σ orbitals.^{15,17} For triplet energy transfer in bichromophoric ω -aryloxyalkanophenones with flexible tethers, it was found that through-space energy transfer by the exchange mechanism is overwhelmingly predominant¹⁹.
- 41 G. J. Kavarnos and N. J. Turro, Photosensitization by reversible electron transfer: theories, experimental evidence, and examples, *Chem. Rev.*, 1986, **86**, 401–449.
- 42 M. Gisin and J. Wirz, Photolysis of the azo precursors of 2,3- and 1,8-naphthoquinodimethane, *Helv. Chim. Acta*, 1976, **59**, 2273–2277.
- 43 S. J. Hagen, J. Hofrichter and W. A. Eaton, Rate of intrachain diffusion of unfolded cytochrome *c*, *J. Phys. Chem. B*, 1997, **101**, 2352–2365.