Highly Solvatochromic Emission of Electron Donor–Acceptor Compounds Containing Propanedioato Boron Electron Acceptors

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Light-induced electron transfer occurs in bifunctional compounds consisting of 1,3-diphenylpropanedioato boron oxalate or fluoride electron acceptors and simple aromatic electron-donor groups, linked by a methylene bridge; fluorescence from the highly polar charge-transfer excited state is remarkably efficient and shows an exceptionally large solvatochromicity.

Recently, we described a series of unusually strongly fluorescence piperidine-based electron donor–acceptor systems, which on account of their large excited-state dipole moments (20–30 D) (1 D $\simeq 3.34 \times 10^{-30}$ Cm) display very large solvatochromic shifts of their emission bands.[1,2] These compounds are finding interesting applications as fluorescent probes of polarity and mobility on a microscopic scale.[3]

We are engaged in a project[4] in which the favourable properties of propanedioato boron complexes (diketoboronates) as photoexcitable electron acceptors[5] are used to effect light-induced electron transfer in bi- and tri-chromophoric systems. In this communication we report the solvent dependent fluorescence of bichromophoric compounds **1**, **2** and **3**, which combine a unique fluorescence solvatochromicity with rather high fluorescence quantum yields (Table 1). As an example, the optical absorption and fluorescence spectra of compound **3** in a number of solvents are shown in Fig. 1.

Following common practice,[6] the solvatochromic sensitivity is expressed as the slope of a plot of the emission wavenumber σ_{CT} *vs.* the solvent polarity parameter Δf [eqn. (1)]. This slope is related to the excited-state dipole moment μ_e according to eqn. (2), where ε is the relative dielectric permittivity, n is the refractive index of the solvent and ρ is the radius of the solvent cavity.

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \tfrac{1}{2}\frac{n^2 - 1}{2n^2 + 1} \tag{1}$$

$$\sigma_{CT} = \sigma_{CT}(0) - \frac{2\mu_e^2}{hc\rho^3}\Delta f \tag{2}$$

While the solvatochromic sensitivity of **2** (3.6×10^4 cm^{-1}) is similar to the most sensitive polarity probes known,[1,2] the values obtained for **1** (4.9×10^4 cm^{-1}) and **3** (5.1×10^4 cm^{-1}) clearly exceed the latter.

We note in passing that the application of the powerful propanedioato boron electron acceptors [the effective redox potentials (in acetonitrile *vs.* SCE) in the excited singlet state are 2.5 V for **1** and **2**, 2.3 V for **3**] allows the use of weak electron-donating groups (E_{ox} *vs.* SCE = 1.79 V for 1,2,4,5-

Table 1. Fluorescence data of compounds **1**, **2** and **3**: emission wavenumber and quantum yields (in parentheses; reference 9,10-diphenylanthracene, $\phi_f = 0.9$)

	$\sigma/10^{-3}$ cm^{-1}		
Solvent (Δf)	**1**	**2**	**3**
Cyclohexane (0.100)	—[a]	22.3 (0.32)	—[a]
Benzene[b]	22.5 (0.60)	18.6 (0.36)	21.6 (0.37)
Di-n-butyl ether (0.194)	21.9 (0.27)[c]	18.8 (0.28)	22.3 (0.31)
Diisopropyl ether (0.237)	20.7 (0.13)	17.5 (0.28)	20.8 (0.17)
Diethyl ether (0.251)	19.2 (0.08)	17.5 (0.12)	19.7 (0.18)
Ethyl acetate (0.292)	16.3 (0.002)	15.0 (0.005)	17.2 (0.03)
Tetrahydrofuran (0.308)	—[d]	14.8 (0.002)	16.9 (0.02)
Dichloromethane (0.319)	16.6 (0.01)	14.7 (0.006)	16.1 (0.02)
$-2\mu^2/hc\rho^3$ ($\times 10^{-3}$, cm^{-1})	48.7 ± 8.3	35.8 ± 1.2	51.2 ± 3.0

[a] Only acceptor fluorescence, no CT emission observed. [b] Not included in solvatochromicity analysis. [c] Obtained by deconvolution of local and CT fluorescence bands. [d] No CT emission observed.

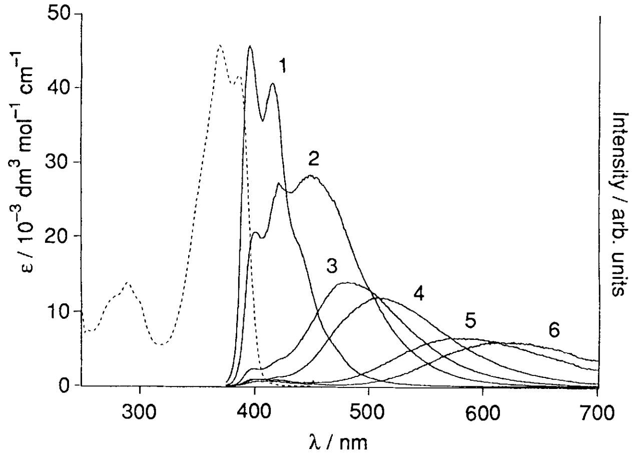


Fig. 1 Optical absorption spectrum of compound **3** in ethyl acetate (dashed line) and fluorescence spectra in cyclohexane (*i*), di-n-butyl ether (*ii*), diisopropyl ether (*iii*), diethyl ether (*iv*), ethyl acetate (×4) (*v*) and dichloromethane (×4) (*vi*)

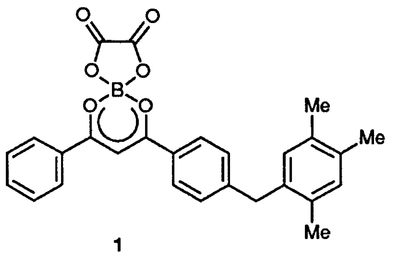
tetramethylbenzene,[7] 1.51 V for 1,4-dimethylnaphthalene[8]). We find that light-induced electron transfer occurs quantitatively in **2** even in cyclohexane, whereas for **1** and **3** a slightly polar solvent is required for rapid electron transfer: in the case of **1** an efficiency of 70% is achieved in di-n-butyl ether, as derived from the quenching of the characteristic acceptor fluorescence relative to an appropriate reference compound.

From the solvatochromic shift an estimate of the dipole moment of the charge-transfer (CT) excited state can be derived if the solvent cavity radius ρ is known. We estimate this parameter simply from the molecular volume in the solid state, assuming a density of 0.9 g cm^{-3}. This yields dipole moments of the emissive states of 31, 27 and 31 D for **1**, **2** and **3**, respectively. The possible errors in these numbers are obviously large, but it is clear that there are differences between the dipole moments of the three compounds.

Semi-emprical quantum chemical calculations (AM1/UHF)[9] of the radical anion of the acceptor model 1,3-diphenylpropanedioato boron oxalate indicate that the excess of negative charge is mainly located on the oxygen atoms surrounding boron and on the carbonyl oxygens of the oxalate ligands. According to the calculations, there is little delocalization of the negative charge into the phenyl rings, even though the system is planar in the reduced state. This result is qualitatively consistent with the large dipole moments of the charge-transfer states estimated above.† The differences in the dipole moments of the charge-transfer states of **1** and **2** may be related to conformational differences. It is possible that the formally positively charged aromatic moiety can be brought closer to the acceptor group in **2**.

The quantum efficiencies of fluorescence in nonpolar solvents are fairly large, considering the large distance of charge separation. CT emission involving similar or even greater donor–acceptor distances has been reported in a few cases,[10] but invariably the quantum yields were low.

For compound **2** the decay times of the CT fluorescence have been measured. From these and the quantum yields (Table 1), the rate constants of fluorescence and radiationless decay have been calculated. The results are shown in Table 2.



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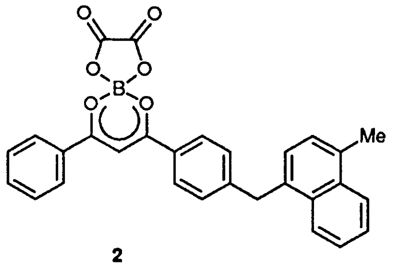

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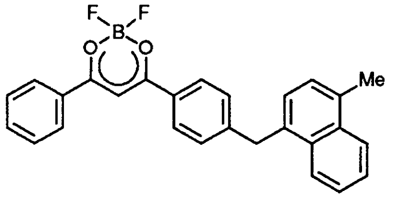

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Table 2. Fluorescence decay times and calculated rate constants of fluorescence and non-radiative decay of compound **2**

Solvent	τ/ns	$k_f/10^6\,s^{-1}$	$k_d/10^6\,s^{-1}$
Di-n-butyl ether	16	18	45
Benzene	21	17	31
Diisopropyl ether	13	9	68
Diethyl ether	9	4	107
Ethyl acetate	3	2	332

The fluorescence rate constant k_f decreases rapidly with decreasing energy in a series of progressively more polar solvents, indicating that it is likely that much of the transition probability is borrowed from the strongly allowed higher-lying acceptor transition[11,2] (from optical absorption spectra $f \approx 0.7$; fluorescence $k_f = 4 \times 10^8\,s^{-1}$). In addition, we see that k_d increases with solvent polarity. This is a well-known consequence of the energy-gap law of radiationless transitions, or from a different point of view, of electron transfer in the Marcus inverted region.

Preliminary evidence from transient absorption spectroscopy and photoacoustic calorimetric measurements indicates that excitation of the bichromophoric compounds discussed here (and of acceptor reference compounds) gives rise to the formation of long-lived transient species. The nature of these species and quantitative aspects of their formation are currently being investigated in order to elucidate the pathways of nonradiative decay.

The strongly fluorescent and polarity sensitive compounds discussed here, and the functionally similar but structurally very different compounds discussed previously,[1,2] offer unique potential for applications as polarity sensors, but also for an enhancement of our understanding of fundamental

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† The neglect of μ_g in eqn. (2) leads to an underestimation of μ_e by approximately 2 D. We consider the application of a more complete treatment, which takes the magnitude of μ_g and the relative orientations of μ_g and μ_e into account, hardly worthwhile in view of the rather crude assumptions that are made.

issues such as solvation in organic solvents and the decay processes of CT excited states. Work along these lines is in progress.

Received, 26th April 1991; Com. 1/01977E

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