Bis(BF$_2$)-2,2′-bidipyrrins, a class of BODIPY dyes with new spectroscopic and photophysical properties†

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The photophysical and spectroscopic characterization of four new dimeric bis(BF$_2$)-2,2′-bidipyrrins (BisBODIPYs) recently synthesized and characterized (*Chem. Eur. J.*, 2008, **14**, 2976–2983) has been undertaken along with that of the component BODIPY monomers. The monomers display the typical photophysical properties of this family; (i) narrow and intense single absorption band in the visible range at 530 nm; (ii) intense, solvent independent emission (Φ_{fl} *ca.* 1); (iii) narrow emission band with a 200–400 cm^{-1} Stokes shifted emission, independent of solvent polarity; (iv) no absorption features for the singlet excited state; (v) very little triplet yield and no ability to sensitize singlet oxygen. The absorption spectra of the corresponding new dimers exhibit split band maxima in the visible range at about 490 and 560 nm, corresponding to an exciton splitting of *ca.* 2600 cm^{-1}. The luminescence in toluene is strong (Φ_{fl} *ca.* 0.7, τ = 3.4 ns), broad and Stokes shifted by *ca.* 2200 cm^{-1}, but both luminescence yield and Stokes shift are solvent polarity dependent; $\Phi_{fl} < 0.1$, $\tau < 1$ ns and the Stokes shift is close to 2700 cm^{-1} in acetonitrile. Solvent viscosity does not appear to play an important role and freezing of the solvents to 77 K in a solid matrix cancels the differences in luminescence parameters. Singlet and triplet excited state absorbance was measured in toluene and acetonitrile and the ability of these new dyes to sensitize singlet oxygen was examined. The nature and dynamics of the excited state is discussed in comparison with the monomers properties and with some intra- or inter-molecular BODIPY dimers reported in the literature. Potential applications of these new dyes with respect to BODIPYs are pointed out on the basis of their spectroscopic and photophysical properties.

Introduction

Difluoroboraindacene (BODIPY) dyes, a relatively new family of luminophores discovered only forty years ago,[1] are gaining increasing reputation and are used in several fields, from material science to biological applications. The photophysical characterization of their properties is crucial for their widespread applications, based on the remarkable luminescence properties. Good stability, high absorbance in the visible region of the spectrum, high luminescence quantum yield, the possibility to tune the absorption and emission wavelength by convenient substitution are some of the reasons of their success in imaging technologies, lasers application, biomolecular labels and cation sensing.[2–4] It is also worth mentioning their increasing use as photo- or electro-active components in multi-partite systems for the collection and conversion of light energy.[5–10]

In an effort to further exploit the potential of these chromophores we have recently reported on the synthesis of a series of BODIPY dimers, displayed in Chart 1 with the corresponding monomers.[11] A preliminary, basic study of their spectroscopic and photophysical properties has shown a large difference with respect to the corresponding characteristic of the monomer components. The latter, as most classical BODIPYs, are characterized by a single strong absorption transition in the visible region of the spectrum around 530 nm and by an intense, mirror image emission maximizing around 540 nm and with a nearly unity quantum yield. The dimer displayed peculiar characteristics, still preserving a remarkably high absorption in the visible range of the spectrum and a high emission quantum yield. The absorption feature is in fact characterized by two intense exciton split bands, while the luminescence is characterized by a remarkably Stokes shifted emission. We undertook this study with the aim of clarifying the nature and dynamics of the excited states in order to point out complementary photophysical properties in these dimers with respect to the well known BODIPY dyes and outline potential new applications based on their photophysical properties.

Results and discussion

Absorption in toluene

The absorption spectra of some representative cases of the dimers studied in toluene solutions are reported in Fig. 1 with

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† Dedicated to Prof. Jean-Pierre Sauvage on the occasion of his 65th birthday.

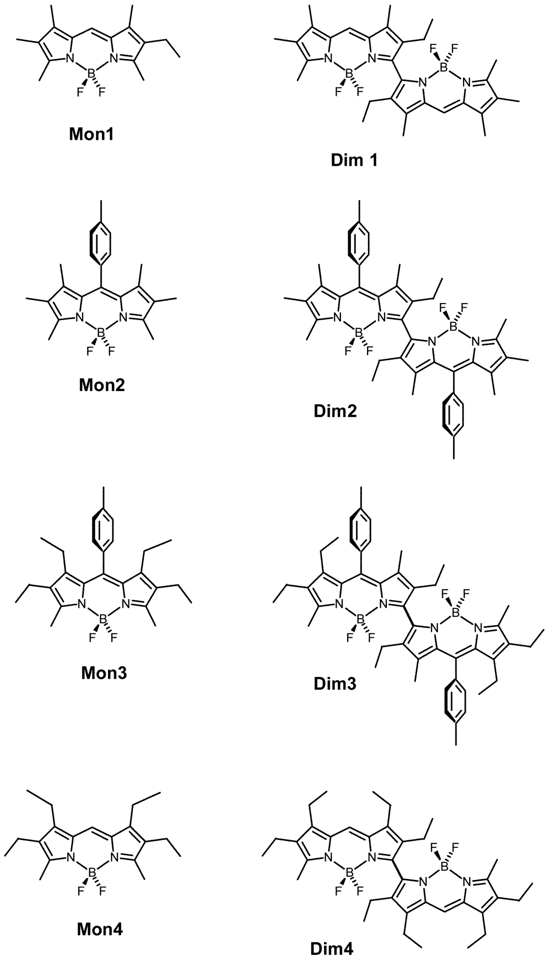

Chart 1

those of the corresponding monomers. The wavelength maxima and molar absorption coefficients of all compounds are collected in the first columns of Table 1. The absorption in the monomers display two major bands: one at *ca.* 380 nm, assigned to the $S_0 \rightarrow S_2$ transition (ε *ca.* 7000–8000 M^{-1} cm^{-1}), the other around 530 nm assigned to the $S_0 \rightarrow S_1$ transition (ε *ca.* 70 000–80 000 M^{-1} cm^{-1}). The latter band is characterized by shoulders at 500 and 520 nm for **Mon1** and **Mon4** (without substituent at the 8 position) and by a single shoulder at 495 nm for the 8-aryl monomers **Mon2** and **Mon3**. These shoulders are assigned to vibrational progressions of the transitions. All the above properties are typical of BODIPYs and have been previously reported for similar dyes.[2] The dimer absorption spectra display a slight bathochromic shift of the $S_0 \rightarrow S_2$ transition and a molar absorption coefficient which is about twice with respect to the monomer, exhibiting overall a modest effect of the dimerization on this transition. The two monomer components are in fact electronically decoupled owing to the nearly perpendicular orientation of their molecular planes.[11] On the contrary the $S_0 \rightarrow S_1$ band, appearing around 530 nm in the monomers and characterized by a very high oscillator strength, is split in two bands, one bathochromically and the other hypsochromically shifted. The molar absorption coefficients of the visible range bands are relatively high and lie in the range 65 000–83 000 M^{-1} cm^{-1}.

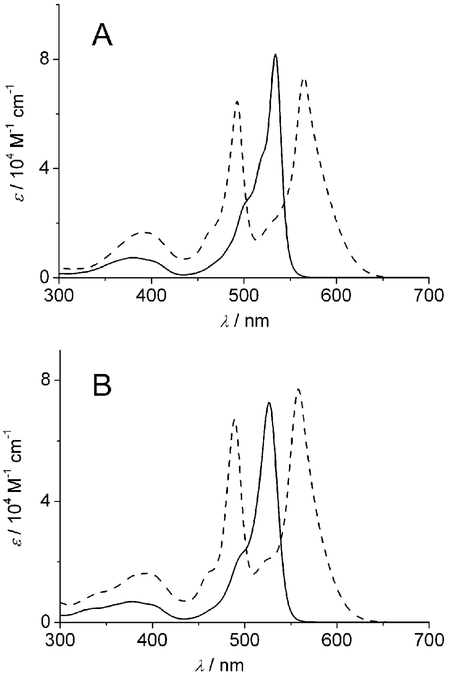

Fig. 1 Absorption spectra in toluene solutions of: (A) **Mon1** (black line) and **Dim1** (dash), (B) **Mon2** (black line) and **Dim2** (dash).

The ratio between the integrated absorption spectra of dimers and monomers is 2, as expected for cases of exciton coupling within a pair of identical chromophores.[12] The splitting ($\Delta\nu_{ES}$) is therefore assigned to exciton coupling; it is of the order of 2500–2600 cm^{-1} for all dimers (Table 1 and Fig. 1). In order to exclude the intermolecular nature of this phenomenon, which might originate from interactions in aggregated forms of the dimers, the effect of concentration on the absorption parameters (wavelength and molar absorption coefficients) is evaluated. No concentration effect could be detected in the range 10^{-6}–10^{-4} M (data not shown), indicating that there is no aggregation in this range and that the exciton splitting detected has an intramolecular origin.

Emission in toluene

The luminescence spectra in toluene of **Mon3** and **Dim3** as representative cases are reported in Fig. 2 and the data for all compounds are collected in Table 1. The luminescence of the monomers is quite similar to other BODIPYs; it is narrow, with a mirror image with respect to absorption band and is very little Stokes-shifted. The Stokes shift ($\Delta\nu_{SS}$) is *ca.* 200 cm^{-1} for un-substituted derivatives at the 8 position and *ca.* 400 cm^{-1} for aryl substituted compounds. At variance with the monomer behavior, the dimer emission is characterized by a large Stokes shift, of the order of 2200 cm^{-1} and by a broad and unstructured emission. The excitation spectra of the dimers, a representative case is reported in Fig. 3, reproduces perfectly the absorption spectrum of the species confirming that the emission is genuine and originating from an excited state which is populated irrespective of the excitation wavelength. There is no effect of concentration on the luminescence properties.

Table 1 Spectroscopic (absorption maxima, molar absorption coefficients, exciton splitting, emission maxima, Stokes shift) and photophysical parameters (fluorescence quantum yield, lifetime, radiative and non-radiative rate constants) of monomers and dimers in toluene solutions, 295 K. The dielectric constant ε, the viscosity η and the refraction index n are reported for toluene

	Toluene (ε = 2.38, η = 0.586 × 10^{-3} Pa s, n = 1.497)								
	λ_{abs}/nm	$10^{-4}\varepsilon$/M^{-1} cm^{-1}	$\Delta\nu_{ES}$/cm^{-1}	$\lambda_{em}{}^{a}$/nm	$\Delta\nu_{SS}$/cm^{-1}	$\Phi_{fl}{}^{b}$	τ^{c}/ns	k_r/s^{-1}	k_{nr}/s^{-1}
Mon1	381 534	0.74 8.20	—	540	210	1.00	5.8	1.8×10^8	0
Mon2	378 526	0.70 7.26	—	538	420	0.88	5.0	1.8×10^8	2.4×10^7
Mon3	380 529	0.71 7.75	—	538	3206	0.80	4.4	1.8×10^8	4.5×10^7
Mon4	380 535	0.78 8.89	—	540	170	1.00	5.9	1.8×10^8	0
Dim1	393 492 565	1.66 6.44 7.36	2630	648	2270	0.71	3.4	2.1×10^8	8.5×10^7
Dim2	394 489 558	1.62 6.71 7.71	2530	638	2250	0.67	3.4	2.0×10^8	9.7×10^7
Dim3	395 490 559	1.70 7.20 8.26	2520	638	2220	0.69	3.3	2.1×10^8	9.4×10^7
Dim4	393 494 567	1.55 6.46 7.15	2610	650	2250	0.76	3.4	2.2×10^8	7.1×10^7

[a] λ_{max} derived from corrected emission spectra. [b] Luminescence quantum yields in air free toluene, against N,N'-bis(1-hexylheptyl)-3,4:9,10-perylenebis(dicarboximide) in aerated dichloromethane as a standard, see Experimental section. Excitation at 490 nm. [c] Fluorescence lifetimes in air-equilibrated toluene. Excitation at 465 nm.

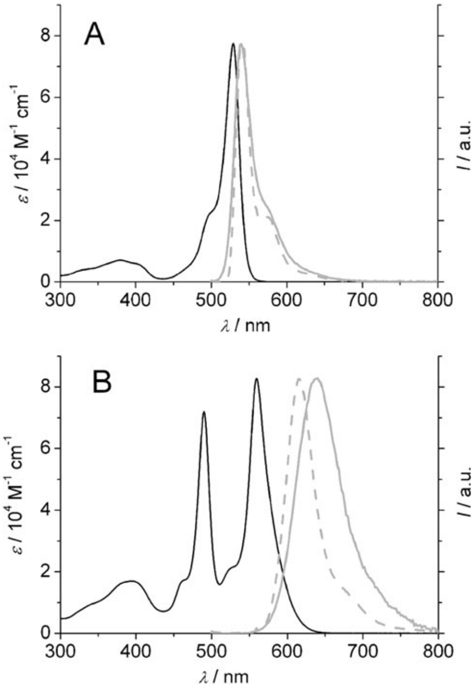

Fig. 2 (A) Absorption (black) and emission (gray) of **Mon3** at RT (line) and at 77 K (dash). (B) Absorption (black) and emission (gray) of **Dim3** at RT (line) and at 77 K (dash).

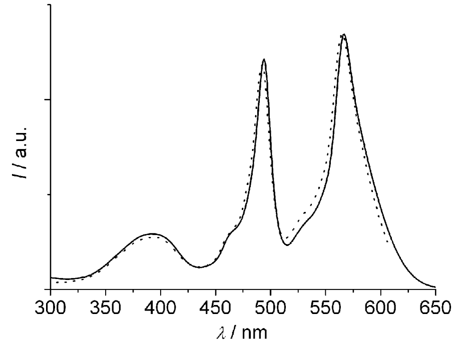

Fig. 3 Excitation spectrum (dot) registered at 640 nm and normalized absorption spectrum in toluene of **Dim4**.

The luminescence yield is unity within experimental error for **Mon1** and **Mon4** and *ca.* 0.85 for the aryl substituted BODIPYs (Table 1). The fluorescence lifetime, which is described by a single exponential, parallels the luminescence quantum yield value, with a lifetime of *ca.* 5.9 ns for **Mon1** and **Mon4** and of *ca.* 4.7 ± 0.3 ns for **Mon2** and **Mon3**. The same radiative rate constant $k_r = 1.8 \times 10^8$ s^{-1}, where $k_r = \Phi_{fl}/\tau$, can be calculated for all monomers. The observed behavior is perfectly in line with the one previously reported for similar BODIPYs.[2,13–16] For the dimers the emission quantum yield in toluene is 0.71 ± 0.05, indistinguishable within the experimental error for all samples. The lifetime is exponential and essentially identical for all dimers with a value of 3.3–3.4 ns. The radiative rate constant is the same, 2.1×10^8 s^{-1}, slightly higher than that of the monomers. It is quite evident that whereas the aryl substitution at the 8 position is important for the deactivation path of the monomer excited state, it becomes less important for the deactivation of the lowest singlet state in the dimers. A further difference between monomers and dimers is registered in the calculated non-radiative rate constant k_{nr}, where $k_{nr} = (1 - \Phi_{fl})/\tau$. The non-radiative rate constants of the dimers are of the order of 10^8 s^{-1}, whereas for monomers they vary from 0 to 4×10^7 (Table 1). The dimers are therefore characterized both by a radiative and by a non-radiative rate constant higher than those of the monomers.

Absorption and luminescence properties in different solvents and in glassy matrix

In order to get a further insight on the spectroscopic and photophysical properties, we run experiments on the dimers **Dim1**–**Dim4** in different solvents and in solvent glassy matrices at 77 K. For comparison purposes parallel experiments were also run on a couple of monomers, **Mon1** and **Mon2** each one representative of the two classes of unsubstituted or aryl substituted at the 8 position, which have been shown to have slightly different properties.

The data for the monomer models are collected in Table 2, and the luminescence spectra of optically matched solutions of **Mon2** in different solvents are reported in Fig. 4. The emission yield in dichloromethane is essentially identical to that in toluene, it decreases slightly (*ca.* 10%) in acetonitrile, but it is higher in polar ethylene glycol. Overall, the luminescence yield is very little affected by the solvent whereas the lifetime increases slightly compared to toluene. This leads to a slight reduction of the radiative rate constant, more evident in acetonitrile where k_r is of the order of 1.5×10^8 s^{-1}, lower by 15% with respect to the toluene solutions. A small increase in the non-radiative rate constants k_{nr} is also registered in acetonitrile, as previously observed for similar BODIPYs.[13,17] In agreement with previous reports, the shift in absorption maxima can be accounted for by the polarizability of the solvent, which follows the order: stabilization in toluene > ethylene glycol ≈ dichloromethane > acetonitrile. Polarity, which is in the order toluene < dichloromethane < acetonitrile ≈ ethylene glycol does not play any role. A similar trend to absorption is displayed by luminescence maxima, and this led to assume that there is no change in dipole moment from the ground to the excited state.

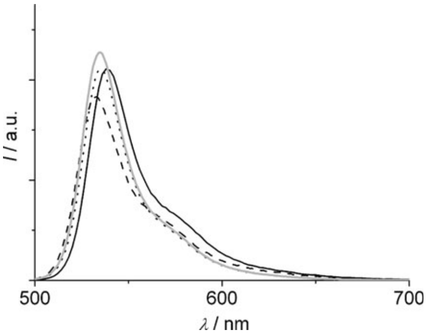

Fig. 4 Emission spectra of **Mon2** in optically matched solutions, excitation at 490 nm (A_{490} = 0.12): toluene (black line) dichloromethane (dot) acetonitrile (dash) ethylene glycol (grey).

As far as dimers are concerned, the data are collected in Table 3 and the change in emission maxima and yield upon change of solvents for a representative case—they all behave similarly—is reported in Fig. 5. It should be stressed that the ethylene glycol data for **Dim1** and **Dim4** reported in Table 3 are liable to larger errors than usual ones (see Experimental section for details) due to the extremely low solubility of the dyes in ethylene glycol. A slight blue-shift of the band maxima in passing from toluene to dichloromethane to acetonitrile can be noticed. The maxima of the bands in ethylene glycol appear almost at the same wavelengths as in dichloromethane indicating that also for this transition the polarizability is determining. The shift of the luminescence maxima of the dimers with the solvents is very small, somehow erratic and difficult to analyze. A slight dependence on the solvent polarity can be noticed in the Stokes shift which shows a slight increase from toluene (*ca.* 2200 cm^{-1}) to dichloromethane, acetonitrile and ethylene glycol where it can be approximated to

Table 2 Spectroscopic (absorption, emission, Stokes shift) and photophysical parameters (emission quantum yield, lifetime, radiative and non-radiative rate constants) of a couple of representative monomers in different solvents at 295 K. The dielectric constant ε, the viscosity η and the refraction index *n* are also reported for the solvents

	λ_{abs}/nm	$10^{-4}\varepsilon$/M^{-1} cm^{-1}	$\lambda_{em}{}^{a}$/nm	$\Delta\nu_{SS}$/cm^{-1}	$\Phi_{fl}{}^{b}$	τ^{c}/ns	k_r/s^{-1}	k_{nr}/s^{-1}
			Dichloromethane (ε = 8.93, η = 0.449 × 10^{-3} Pa s, n = 1.424)					
Mon1	379	0.88	537	210	1.00	6.7	1.6×10^8	0
	531	8.20						
Mon2	377	0.79	536	430	0.88	5.7	1.5×10^8	2.1×10^7
	524	7.19						
			Acetonitrile (ε = 35.9, η = 0.345 × 10^{-3} Pa s, n = 1.344)					
Mon1	379	0.87	532	250	0.98	6.6	1.5×10^8	3.0×10^6
	525	7.48						
Mon2	374	0.83	532	430	0.77	5.6	1.4×10^8	4.1×10^7
	520	7.46						
			Ethylene glycol (ε = 37.7, η = 19.9 × 10^{-3} Pa s, n = 1.432)					
Mon1	380	0.79	536	250	1.00	6.6	1.7×10^8	0
	529	6.68						
Mon2	376	0.72	536	430	0.95	6.4	1.5×10^8	7.8×10^6
	524	5.46						

[a] λ_{max} derived from corrected emission spectra. [b] Luminescence quantum yields in air free toluene, against *N*,*N*′-bis(1-hexylheptyl)-3,4:9,10-perylenebis(dicarboximide) in aerated dichloromethane, see Experimental section. Excitation at 490 nm. [c] Fluorescence lifetimes in air-equilibrated toluene. Excitation at 465 nm.

ca. 2600–2700 cm^{-1}. This shift indicates a slight stabilization of the emitting state with respect to the ground one in the more polar solvents, suggesting a slight increase in the dipole moment of the excited state. Given that for the absorption transition different indications have been derived, this might indicate that the relaxed emitting excited state is different from the Frank–Condon state reached by excitation.

More remarkable is the effect of polarity on other luminescence parameters. A decrease of the luminescence quantum yield is registered in passing from toluene (0.7) to dichloromethane (0.6) and much more to acetonitrile, where the yield is strongly reduced, mainly in dimers without substituent at the 8 position. In this solvent, in fact, Φ_{fl} is <0.1 in **Dim1** and **Dim4** and of the order of 0.2 in the aryl substituted dimers. In the viscous ethylene glycol, having a similar dielectric constant

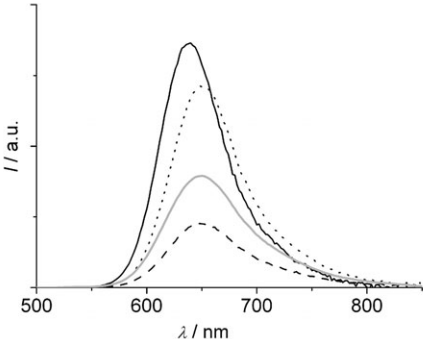

Fig. 5 Emission spectra of **Dim3** in optically matched solutions, excitation at 490 nm (A_{490} = 0.11): toluene (black line) dichloromethane (dot) acetonitrile (dash) ethylene glycol (grey).

Table 3 Spectroscopic (absorption maxima, molar absorption coefficients, exciton splitting, emission maxima, Stokes shift) and photophysical parameters (fluorescence quantum yield, lifetime, radiative and non-radiative rate constants) of dimers in several solvents, 295 K

	λ_{abs}/nm	$10^{-4}\varepsilon$/M^{-1} cm^{-1}	$\Delta\nu_{ES}$/cm^{-1}	$\lambda_{em}{}^{a}$/nm	$\Delta\nu_{SS}$/cm^{-1}	$\Phi_{fl}{}^{b}$	τ/ns	k_r/s^{-1}	k_{nr}/s^{-1}
Dichloromethane (ε = 8.93, η = 0.449 × 10^{-3} Pa s, n = 1.424)									
Dim1	389	1.84	2560	651	2530	0.56	3.2	1.8×10^8	1.4×10^8
	489	5.63							
	559	7.01							
Dim2	390	1.85	2520	650	2630	0.60	3.4	1.8×10^8	1.2×10^8
	487	6.15							
	555	7.39							
Dim3	392	1.92	2540	650	2570	0.62	3.3	1.9×10^8	1.2×10^8
	488	6.49							
	557	7.85							
Dim4	390	1.74	2570	652	2460	0.63	3.3	1.9×10^8	1.1×10^8
	491	5.80							
	562	6.95							
Acetonitrile (ε = 35.9, η = 0.345 × 10^{-3} Pa s, n = 1.344)									
Dim1	386	1.95	2580	648	2650	0.036	0.37	1.0×10^8	2.6×10^9
	484	5.58							
	553	7.17							
Dim2	388	1.83	2520	646	2700	0.15	1.1	1.4×10^8	7.7×10^8
	483	5.81							
	550	7.27							
Dim3	389	1.92	2540	650	2700	0.24	1.6	1.5×10^8	4.7×10^8
	485	6.37							
	553	7.95							
Dim4	388	1.81	2620	652	2620	0.086	0.72	1.2×10^8	1.3×10^9
	486	5.77							
	557	7.09							
Ethylene glycol (ε = 37.7, η = 19.9 × 10^{-3} Pa s, n = 1.432)									
Dim1[e]	388	—[d]	2550	640	2360	0.10	0.36	2.8×10^8	2.5×10^9
	487								
	556								
Dim2	390	—[d]	2500	648	2650	0.23	1.2	1.9×10^8	6.4×10^8
	486								
	553								
Dim3	390	—[d]	2550	650	2600	0.31	1.8	1.7×10^8	3.8×10^8
	487								
	556								
Dim4[e]	390	—[d]	2590	653	2510	0.20	0.65	3.1×10^8	1.2×10^9
	490								
	561								

[a] λ_{max} derived from corrected emission spectra. [b] Luminescence quantum yields in air-free toluene, against *N*,*N*′-bis(1-hexylheptyl)-3,4:9,10-perylenebis(dicarboximide) in aerated dichloromethane as a standard, see Experimental section. Excitation at 490 nm. [c] Fluorescence lifetimes in air-equilibrated toluene. Excitation at 465 nm for lifetimes >1 ns and at 532 nm for lifetimes <1 ns. [d] The solubility is too low to allow reliable values to be derived. [e] Large errors due to an extremely low solubility.

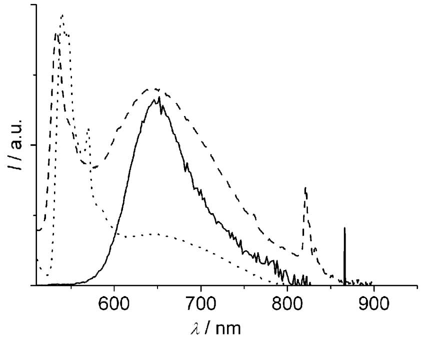

Fig. 6 Emission spectra of **Mon1** after excitation at 490 nm in different solvents at 77 K: dichloromethane (dot) acetonitrile (dash). For comparison purposes the emission spectrum of **Dim1** in acetonitrile at RT is also reported (black line).

with respect to acetonitrile, the yield tends to increase with respect to acetonitrile but it is still well lower than that in dichloromethane (ethylene glycol and dichloromethane have similar polarizabilities). So it can be derived that polarizability is not an important factor in these variations of parameters.

In all cases the fluorescence lifetime could be described by a single exponential, identical over the whole emission spectral region. The lifetime in dichloromethane is essentially identical to that in toluene, 3.3 ± 0.1 ns, but it decreases abruptly especially for **Dim1** and **Dim4** in acetonitrile. In ethylene glycol the lifetime remains essentially the same as in acetonitrile. The radiative rate constants decrease slightly from toluene to dichloromethane, from this to acetonitrile and in ethylene glycol are very similar to acetonitrile. The non-radiative rate constants increase from toluene to dichloromethane and to acetonitrile, mainly for **Dim1** and **Dim4** and tend to be the same as acetonitrile in ethylene glycol. Quite clearly the non-radiative processes are enhanced by increasing dielectric constants (toluene < dichloromethane < acetonitrile ≈ ethylene glycol) whereas there is no large effect of viscosity on these parameters, see *e.g.* acetonitrile ($\eta = 0.345 \times 10^{-3}$ Pa s) and ethylene glycol ($\eta = 19.9 \times 10^{-3}$ Pa s).

At 77 K in a rigid solvent, the luminescence behavior of the monomers **Mon1** and **Mon2** in toluene is very similar to that at RT, except for a slightly longer lifetime. In polar solvents, dichloromethane and even more acetonitrile, the spectra of **Mon2** appears broad and bathochromically shifted, whereas for **Mon1** a new band with a maximum around 650 nm clearly appears in both polar solvents (Fig. 6). The monomer decays in polar solvents can be fitted by two exponentials with a short component of *ca.* 4.5 ns for **Mon1** and **Mon2** and a longer component which is *ca.* 40 ns for **Mon1** and *ca.* 50 ns for **Mon2**. The position, the shape and the lifetime of the new bands, appearing only as a broadening in dichloromethane, are typical of an excimeric or dimeric species. Quite obviously the decrease in temperature favors dimerization and/or formation of higher degree aggregates in polar solvents which result into the formation of a new emitting species. It is not our aim to look with much detail into the behavior of monomers, but it is interesting to note that the position of the excimeric luminescence band is reminiscent of that of the covalent dimers under examination, reported for comparison purposes for the case of **Dim1** in Fig. 6.

The luminescence of the dimers in solid solvent matrices at 77 K exhibit an hypsochromic shift which leads to very similar emission spectra in all solvents (Table 4). Also the effect of the solvents on lifetime vanishes, and the lifetimes are the same in all solvents, respectively 3.8 ± 0.1 for **Dim1**, 3.5 ± 0.2 for **Dim2** and **Dim3** and 4.0 ± 0.3 for **Dim4**. Therefore in frozen solvents, where the molecular motion is reduced, all the solvents behave similarly. The shift to higher energies upon rigidification of the solvent in the dimer would suggest some charge transfer character and contrast the behavior of the monomers (see in toluene, where no dimer is formed) which slightly red-shift.

Absorption of excited states

A series of experiments for the determination of the singlet and triplet excited state properties based on transient absorbance was designed. The representative monomers **Mon1** and **Mon2** and all dimers were studied in the two extreme cases of toluene and acetonitrile as solvents. The singlet excited state absorption spectra were determined with a pump and probe system with 20 ps resolution and excitation at 532 nm. The transient absorption spectrum of the monomers in both solvents shows a negative band around 530 nm (at the limit of the instrumental resolution) due to the bleaching and stimulated emission, but no other feature in the explored range (530–1000 nm). On the contrary the absorption spectrum of all dimers in toluene is characterized by a bleaching band around 550 nm, a stimulated emission band around 650 nm and a broad, intense absorption band with a maximum around 850 nm. A representative case for monomers and dimers in the two solvents is reported in Fig. 7. The detected spectrum in dimers is assigned to the singlet excited state on

Table 4 Fluorescence data of representative monomers and dimers in air-equilibrated solid matrix at 77 K

	Toluene			Dichloromethane		Acetonitrile	
	λ_{max}/nm	τ^a/ns	E^b/eV	λ_{max}/nm	τ^a/ns	λ_{max}/nm	τ^a/ns
Mon1	539	6.2	2.30	539, 652	4.6; 37^c	533, 647	4.6; 40^c
Mon2	534	5.4	2.32	548	4.3; 52^c	567	4.7; 50^c
Dim1	623	3.7	1.99	623	3.8	621	3.9
Dim2	614	3.4	2.02	616	3.6	624	3.6
Dim3	616	3.5	2.01	619	3.3	618	3.7
Dim4	627	3.9	1.98	623	3.8	621	4.3

[a] Excitation at 465 nm for lifetimes. [b] Energy of the excited singlet state in toluene, derived from the fluorescence maximum. [c] The decay fitting indicates a double exponential for **Mon1** and **Mon2**, see text.

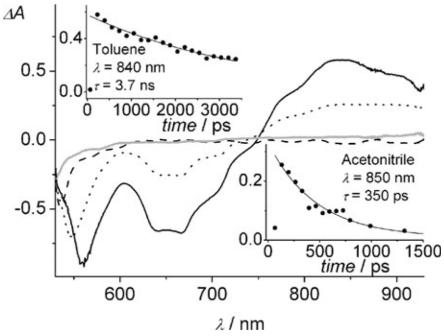

Fig. 7 Transient absorption spectra registered at the end of a laser pulse (532 nm, 35 ps, 3.3 mJ pulse^{-1}) in solution of **Mon1** in acetonitrile (grey) and toluene (dash) and **Dim1** in acetonitrile (dot) and toluene (black line). In the insets the time decays of the absorbance and the fitted exponentials for **Dim1** in the two solvents are shown. The absorbance of the solutions at 532 nm was A_{532} = 0.6 in all cases.

the basis of the time evolution. The lifetimes (Table 5) are in fact the same within experimental errors, as those determined by luminescence. The singlet excited state spectrum of the dimers in acetonitrile is essentially identical, just with a slightly broader near IR absorption band, but with an absorbance reduced to *ca.* 50% with respect to toluene (Fig. 7). In the reasonable assumption that the molar absorption coefficient of the singlet excited state is not affected by the solvent, this result indicates that the singlet formed in acetonitrile is about half the one formed in toluene. It can therefore be inferred that the conversion from the Frank–Condon state to the emitting state has in acetonitrile a yield which is 50% efficient with respect to toluene.

The properties of the triplet excited state were determined in air-free solutions by a flash photolysis apparatus with 20 ns resolution and excitation at 532 nm. The absorption spectra of **Mon1** and **Mon2** in toluene display a very low absorbance at 430 nm and the bleaching of the ground state band at 530 nm, Fig. 8. In acetonitrile the absorbance increases by a factor of *ca.* 2 in the 430 nm band and furthermore a sizeable absorbance from 550 nm to 700 nm can be detected. The lifetimes in air-free solutions are quite long in toluene, 0.7 and 0.6 milliseconds and shorter in acetonitrile, of the order of 120 microseconds (Table 5). These features are in reasonable agreement with previous reports for similar BODIPYs.[6,18] Assuming a molar absorption coefficient of the triplet independent on the solvent, one can derive a concentration of triplets of the monomers in acetonitrile about twice with respect to toluene solutions. This can be assigned to an increased intersystem crossing in agreement with an higher k_{nr} (Table 1 and Table 2). In air-equilibrated solutions the triplet lifetime is quenched and the reaction with oxygen is quite effective, only one order of magnitude lower than the diffusion controlled rate constants (1.9 × 10^{10} s^{-1} in acetonitrile and 1.2 × 10^{10} s^{-1} in toluene).[19]

The dimers display in air-free solutions a spectrum similar for all compounds, with a broad absorption band around 300 nm and an absorption peak at 420–440 nm, bleaching bands reproducing the exciton split bands of the ground state and a broad absorption in the 800–900 nm. Overall, the triplet absorption spectra of the dimers is much more intense than that of the monomers as already noticed for the absorption of the excited singlet. This might be due to the different molar absorption coefficient of the excited states in the monomers and the dimers but also to an enhanced intersystem crossing in dimers, in agreement with an increased k_{nr}. In general, since exciton coupling splits the singlet excited state in a high and a low energy state, it leads to a situation where the lowest exciton state is closer in energy to the triplet. The latter state in fact is not affected by exciton coupling. The decrease in energy separation between the lowest exciton singlet and the triplet can therefore increase the intersystem crossing. Increase in the triplet yield has been shown to be important in cases where the low exciton state is forbidden.[20] This is not the case here, where the low energy exciton state is allowed, as can be derived from the high molar absorption coefficient of the transition but the increase in triplet yield could still be explained by the decreased singlet–triplet energy gap. The effect of solvent on the triplet excited state of dimers is evident in the yield, which is lower in acetonitrile than in toluene. This has to be ascribed to the decreased yield of the corresponding singlet excited state (reduced to about 50%, see above) but in the case of **Dim1**, displaying a signal in acetonitrile *ca.* 30% of the signal in toluene, a further reduction in the intersystem crossing efficiency might be operative. Other differences in the triplet excited state behavior of the dimers in the two solvents are not detected, the order of magnitude of the lifetime is similar, as well as the reaction rate with oxygen. In conclusion, the triplet excited state is apparently less affected than the singlet excited state by the nature of the solvent.

Singlet oxygen generation

This experiment was designed in order to test a possible use of these dyes as singlet oxygen photosensitizers. The topic has in

Table 5 Singlet and triplet excited state absorption lifetimes and oxygen quenching rate constants in toluene and acetonitrile solutions at 295 K

	Toluene				Acetonitrile			
	Singlet	Triplet			Singlet	Triplet		
	τ/ns	τ^a/μs	τ^b/ns	k_q/M^{-1} s^{-1}	τ/ns	τ^a/μs	τ^b/ns	k_q /M^{-1} s^{-1}
Mon1	—	700	390	1.3 × 10^9	—	119	240	2.2 × 10^9
Mon2	—	600	370	1.4 × 10^9	—	130	340	1.5 × 10^9
Dim1	3.7	122	334	1.6 × 10^9	0.35	100	284	1.8 × 10^9
Dim2	3.5	118	515	1.0 × 10^9	1.2	72	337	1.6 × 10^9

[a] Air-free solutions. [b] Air-equilibrated solutions.

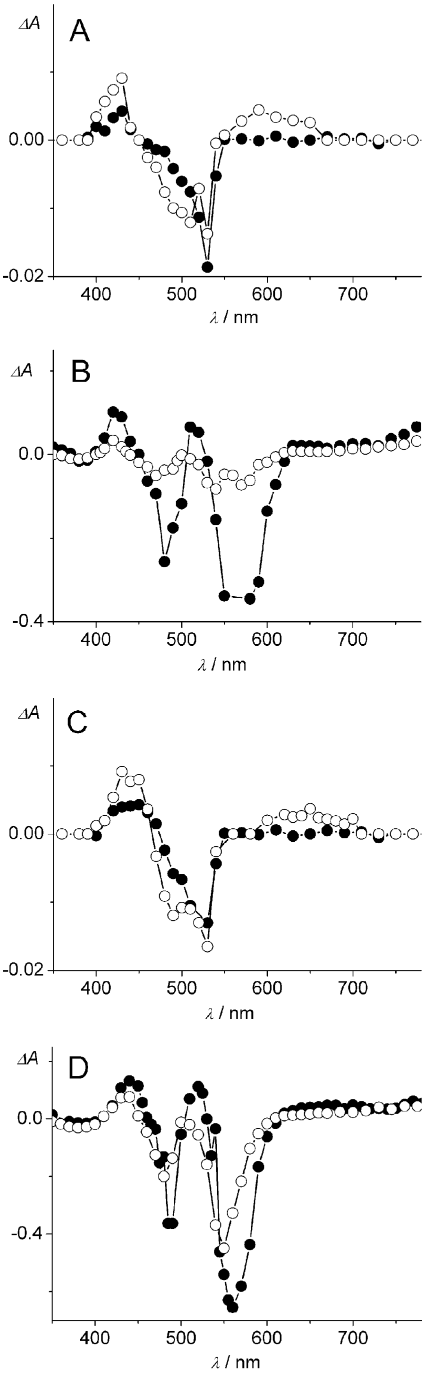

Fig. 8 Transient absorption spectra registered at the end of a laser pulse (532 nm, 20 ns, 3.3 mJ pulse^{-1}) (A) **Mon1** in acetonitrile (open circles) and toluene (full circles) and (B) **Dim1** in acetonitrile (open circles) and toluene (full circles). (C) **Mon2** in acetonitrile (open circles) and toluene (full circles) and (D) **Dim2** in acetonitrile (open circles) and toluene (full circles). The absorbance of the solutions at 532 nm was A_{532} = 1 in all cases.

fact a large impact both on photocatalysis and on photobiological applications. The energy of the triplet excited state, which is *ca.* 1.6 eV[6,21] in the monomers and very likely lower in the dimers, is sufficient to transfer energy to the ground state oxygen to generate singlet oxygen $^1\Delta_g$ which has a E_{0-0} = 0.98 eV.

As discussed in the section above, the triplet of both monomers and dimers reacts efficiently with ground state oxygen, the reaction rate in toluene is of the order of 1.4 × 10^9 s^{-1}, about half that of oxygen with tetrapyrroles, considered good singlet oxygen photosensitizers.[22,23] Singlet oxygen $^1\Delta_g$ was detected by the typical NIR luminescence band with maximum at 1268 nm. The data in toluene, dichloromethane and acetonitrile solutions of monomers and dimers after excitation at λ = 490 nm are collected in Table 6 and the sensitized singlet oxygen luminescence spectra for a representative case (**Dim1** and **Mon1**) is displayed in Fig. 9. The low solubility of dimers in ethylene glycol prevents experiments in this solvent. The quantum yield of production of singlet oxygen in monomers is ≤0.1, with no apparent differences in the solvents examined. Very likely the absolute yield of triplet for monomers is so low in all solvents to prevent any meaningful difference in the singlet oxygen luminescence yield. In dimers the singlet oxygen yield is *ca.* 0.4 in toluene and 0.5 in dichloromethane, pointing to an high value of triplet yield in these solvents. The results in acetonitrile indicate that the singlet oxygen sensitization has essentially no yield, with an emission quantum yield ≪0.1. in spite of the higher lifetime of $^1\Delta_g$ in this solvent with respect to toluene.[24] These data indicate that with a convenient choice of solvent, these dimers can also play a role as singlet oxygen photosensitizers.

Table 6 Singlet oxygen ($^1\Delta_g$) luminescence yields of dimers and representative monomers at 295 K

	Toluene $\Phi_\Delta{}^a$	Dichloromethane $\Phi_\Delta{}^a$	Acetonitrile $\Phi_\Delta{}^a$
Mon1	≤0.1	—	≤0.1
Mon2	≤0.1	—	≤0.1
Dim1	0.4	0.5	≪0.1
Dim2	0.4	0.5	≪0.1
Dim3	0.3	0.5	≪0.1
Dim4	0.3	0.5	≪0.1

[a] $^1\Delta_g$ luminescence, the standard used is **TPP** in aerated toluene at room temperature (Φ_Δ = 0.70[34]), Excitation at 490 nm.

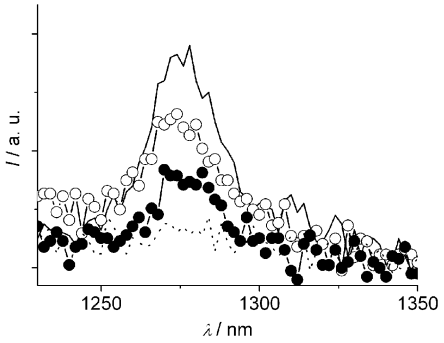

Fig. 9 Singlet oxygen luminescence from solutions of **Dim1** in toluene (full circles) and dichloromethane (open circles) compared to the standard TPP (line), see text. The singlet oxygen luminescence of **Mon1** in acetonitrile is reported (dot) and is indistinguishable from that in toluene. Excitation performed at 490 nm on optically matched solutions, A_{490} = 0.70.

Comparison with other dimeric BODIPY species

BODIPYs have gained importance in the biological field for their valuable spectroscopic properties independent on pH and polarity and have been used for the elucidation of the protein structure. In the protein micro-environment, a locally high concentration of BODIPYs is present, allowing the formation of dimers. The first observation of excited dimers was reported by Johansson *et al.* and was obtained either from different BODIPY labeled mutant forms of plasminogen activator inhibitor type 1 and from BODIPY labeled lipids.[25] The authors of this study pointed out that the species formed is an excited dimer, rather than an exciplex as previously suggested,[26] due to the fact that specific absorption bands of the dimeric species are identified in the ground state. In the two systems, either H-type non-luminescent dimers or J-type luminescent dimers were obtained in the presence of monomeric forms of BODIPY. The H type dimer was further characterized as the only excited species after preparation of samples of monomeric BODIPY in a confined environment of sodium silicate derived glass.[27] This allowed to derive precise photophysical parameters for this dimer which exhibit an absorption band at 468 nm (477 nm in a different medium[28]), is non emissive, has a sandwich structure with a separation of 7.6 Å between the planes (4.9 Å according to other studies[28]) and has parallel transition dipoles but anti-parallel electric dipole moments.[27,28] The electric dipole moments are in the direction of the C_{2v} symmetry axis (and oriented from the boron to the 8 position) whereas the transition moments are perpendicular to it. Confirmation of H type dimer comes from another report where two BODIPY units were connected through the 8 position to a rigid xanthene scaffold; in this case an absorption band at 478 nm and a very weak, broad luminescence maximizing at 590 nm was evidenced. The geometry of the bond allows a nearly sandwich structure, with parallel transition dipoles *and* parallel electric dipole moments.[29] Further characterization of the other, J-type, luminescent dimer was carried out in mono-BODIPY labeled oleoyl glyceride in lipid vesicles.[28] This dimer has: (i) a bathochromically shifted absorption band at 577 nm with respect to the monomer (505 nm) but a further band at 455 nm concealed by the monomer band was hypothesized; (ii) a broad emission maximizing at 630 nm; (iii) a biphasic lifetime with an average τ of 3.4 ns. The double exponential decay is very likely due to the micro-heterogeneity of the environment and is quite usual in the decay of dyes in non-homogeneous media. The transition moments of the two components, as calculated from the exciton coupling theory, formed an angle of 55°. However a unique definition of the geometry was difficult because of the number of variables. The data of the Johansson's J dimer are very similar to those for the covalently connected dimers here reported, with the exception of the exciton splitting which would be for the Johansson dimer nearly twice (*ca.* 4600 cm^{-1}) than that measured here. Obviously a slightly different geometry, a different environment and some unavoidable imprecision associated with the determination of the dimer spectroscopic properties in presence of monomer for Johansson J dimer, can explain these differences and we can consider the two cases reasonably similar.

Nature and dynamics of excited state in the dimmers

There are few analogies between the dimers and monomers both from a spectroscopic and from a photophysical point of view, except for the strong fluorescence of monomers and dimers in apolar solvents. The high intensity absorption band in the visible region is split in the dimers due to an exciton coupling interaction which leads to a loss of degeneracy in the S_1 state; the absorption spectra dependence on solvents is similar for monomers and dimers, indicating a similar nature of the Franck–Condon state for the two species. On the other hand, the emissive properties of the dimers, prominently the large Stokes shift, point to molecular rearrangements in the emitting species, contrary to the case of the monomers. A hint on the different geometry assumed by the emitting state with respect to the absorbing one can be given by the electronic distribution of the vertical excited singlet. The results of simple singly excited configuration calculation (MNDO + SECI[30]) on **Dim1** show that S_1 (calculated at 583 nm with $f = 0.33$) derives mainly by the HOMO−1 → LUMO molecular orbital promotion, with effective delocalization of electronic cloud from one moiety to the other of the dimer (see Fig. 10). This might induce a geometrical change leading to the relaxed emitting state along a coordinate different from that involving the dihedral angle between the two BODIPY units. Rotation about the bond connecting the two units would in fact imply a large effect of viscosity on the deactivation parameters which indeed is not observed. On the other hand the small difference calculated for the permanent dipole moment going from S_0 to S_1 (0.35 D), is in agreement with the small dependence of the first absorption band with the polarity of solvent. The dimers emit in the red region of the spectrum with a radiative rate constant in toluene even higher than that of the monomers, they also display an higher non-radiative rate constant and a detectable triplet yield. As discussed above this is a consequence of the reduced singlet–triplet splitting caused by exciton coupling. The triplet excited state sensitize singlet oxygen with a reasonable yield in toluene and dichloromethane. The dimers luminescence properties are affected by solvent polarity and by the solid or fluid physical status of the solutions, at variance with the behavior of the monomers.

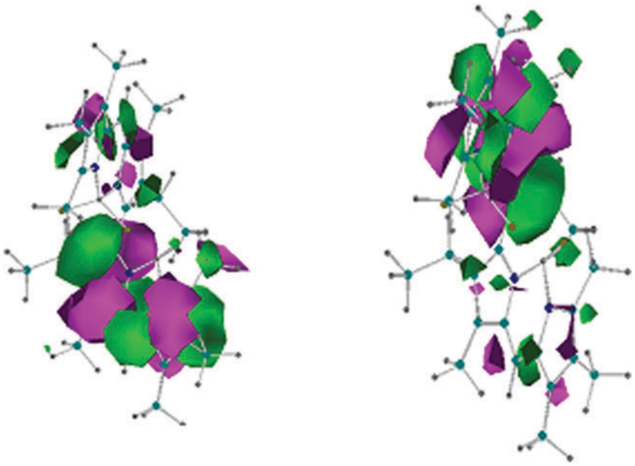

Fig. 10 Gouraud shaded surfaces of HOMO−1 (left) and LUMO (right).

Whereas the energy level is poorly stabilized in polar solvents (see $\Delta\nu_{SS}$), the luminescence quantum yield is strongly reduced, from a factor of *ca.* 3 up to a factor of 20 in passing from toluene to acetonitrile, depending on the specific dimer. For this property these bis-BODIPYs, in particular the one missing the aryl at the 8 position, can be used as polarity probes. The reduction in luminescence quantum yield is due to an increase in non-radiative rate constants to be assigned to an increased internal conversions to the ground state. Energy gap law could in part account for this observation, as an increased energy of the S_1 state leads to lower internal conversion rates. In addition, solvent polarity might affect the small distance between the fluorine of two different boron difluoride groups (their distance is < 3 Å measured by X-rays[11]) affecting the internal conversion rate, which is well known to be very sensitive to small geometrical changes.[31] This could represent an enhanced polarity-dependent deactivation path, in agreement with the observations. The viscosity is shown, see data in ethyl glycol, to play a very minor role. This might not have been so, given the high conformational mobility of the dimer and indicates that deactivation through the rotational coordinate is not important.

It should also be noticed that the emission from the dimer is very closely matching the emission from a dimeric state observed for **Mon1** in a glassy polar solvent at 77 K, Fig. 6, and the emission parameters reported for an intramolecular J dimer discussed above. The emitting excited state is doubtlessly a dimeric excited state, formed by slight rearrangement of the Frank–Condon state. In the ground state the two units are in planes forming a nearly perpendicular angle, from X-ray crystal data, and after excitation into the vertical state a relaxation to a more convenient geometry for the delocalization of the excitation can occur and be very fast. The reorganization has however to be modest, in consideration of the scarce effect of viscosity on the luminescent singlet parameters. It is worth mentioning that we were unable to identify, with a resolution of 10 ps, signatures of the original Frank–Condon state. In fact the luminescence time-resolved spectrum of all dimers in a time window of 10 ps after its formation is identical, within experimental error, to the steady-state spectrum and no evidence of a decay with a lifetime $\geq$10 ps could be detected. This is not surprising since an internal conversion or relaxation faster than 10 ps is rather usual. No other intermediates were detected in addition to the singlet and triplet excited sates.

In the case of acetonitrile solutions there is an inefficient (lower than 50%, if we assume 100% for toluene solutions) internal conversion from the Frank–Condon excited state to the emitting state, judging from the singlet excited state yield as detected from transient picosecond absorption. This also leads to a lower triplet yield in acetonitrile and to the inability of the dimers to act as singlet oxygen photosensitizer in this solvent.

Conclusions

The luminescence properties and the excited states dynamics of a series of preformed BODIPY dimers have been investigated. Comparison with the properties of the corresponding monomers and of other intra- or inter-molecular dimers reported in the literature has allowed to shed some light on the nature of the excited state and on the deactivation dynamics. In toluene, radiative rate constants increase slightly with respect to the monomers whereas non-radiative rate constants are higher by a factor of *ca.* 3 and lead to a significant amount of triplet excited state with a fair ability to sensitize singlet oxygen. Non-radiative rate constants display an important solvent dependence which has to be ascribed mainly to an enhanced internal conversion path and makes these dyes good probes of solvent polarity, at variance with the behavior of monomers. Solvent polarity is postulated to influence the internal conversion by affecting the distance between two closely spaced fluoride atoms of different boron difluoride groups. In fact, stabilization of the excited state energy by increasing solvent polarity is small to rationalize the detected increase in internal conversion rate. The luminescence of the dimers is characterized by a large Stokes shift, indicative of a molecular rearrangement in the emitting species. The absence of viscosity effect indicate that large rearrangements (*e.g.* large angle rotation of the two parts) should be ruled out. At variance with monomers behavior, singlet and triplet excited states in dimers display intense spectroscopic signals. The possibility to use transient absorption spectroscopy techniques to detect these intermediates can help in the elucidation of the elementary steps of light conversion in complex architectures. This makes these dimers valuable components of complex molecular structures for light energy conversion. Finally the well established geometry of these dimers allows to use them as models of dimers formed in microheterogeneous biological media by comparison of their spectroscopic parameters.

Experimental

Spectrophotometric grade toluene, dichloromethane, acetonitrile and ethylene glycol (Merck, pro-analysi) were used without further purification. Standard 10 mm fluorescence cells were used at 295 K whereas experiments at 77 K made use of capillary tubes dipped in an home-made quartz Dewar filled with liquid nitrogen. If not otherwise specified, solutions were air-equilibrated. The solubility of oxygen in acetonitrile and toluene was taken as 1.9×10^{-3} M.[32] Air-free solutions were bubbled for 10 min with a stream of argon in home-modified 10 mm fluorescence cells. A Perkin-Elmer Lambda 9 UV/Vis spectrophotometer and a Spex Fluorolog II spectrofluorimeter were used to acquire absorption and emission spectra. Reported luminescence spectra are corrected for the photomultiplier response. Emission quantum yields were determined after correction for the photomultiplier response, with reference to an air-equilibrated toluene solution of *N*,*N'*-bis(1-hexylheptyl)-3,4:9,10-perylenebis(dicarboximide) in aerated dichloromethane as a standard ($\Phi_{fl} = 0.99$).[33]

Singlet oxygen luminescence was determined by an FLS920 spectrofluorimeter (Edinburgh) equipped with an Hamamatsu R5509-72 supercooled photomultiplier tube at 193 K and a TM300 emission monochromator with a NIR grating blazed at 1000 nm and 5,10,15,20-tetraphenylporphyrin (TPP) in aerated toluene was used as a standard with $\Phi_{\Delta} = 0.70$.[34]

Luminescence lifetimes in the nanosecond range were obtained with an IBH single photon counting equipment with excitation at 465 nm from pulsed diode sources (resolution 0.3 ns). Emission lifetimes in the picosecond range used an apparatus based on a Nd:YAG laser (35 ps pulse duration, 532 nm, 1.5 mJ) and a Streak Camera with overall resolution of 10 ps was used.[23,35] Transient absorbance in the picosecond range made use of a pump and probe system based on a Nd-YAG laser (Continuum PY62/10, 35 ps pulse). Details are reported elsewhere.[36] Nanosecond laser flash photolysis experiments were performed by a system based on a Nd-YAG laser (JK Lasers, 532 nm, 3.5 mJ, 18 ns pulse) using a right-angle analysis on the excited sample, previously described.[37,38] Experimental uncertainties are estimated to be within 10% for lifetime determination, 15% for quantum yields, 20% for molar absorption coefficients and 3 nm for emission and absorption peaks. The temperature of operation was 295 K except otherwise stated.

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