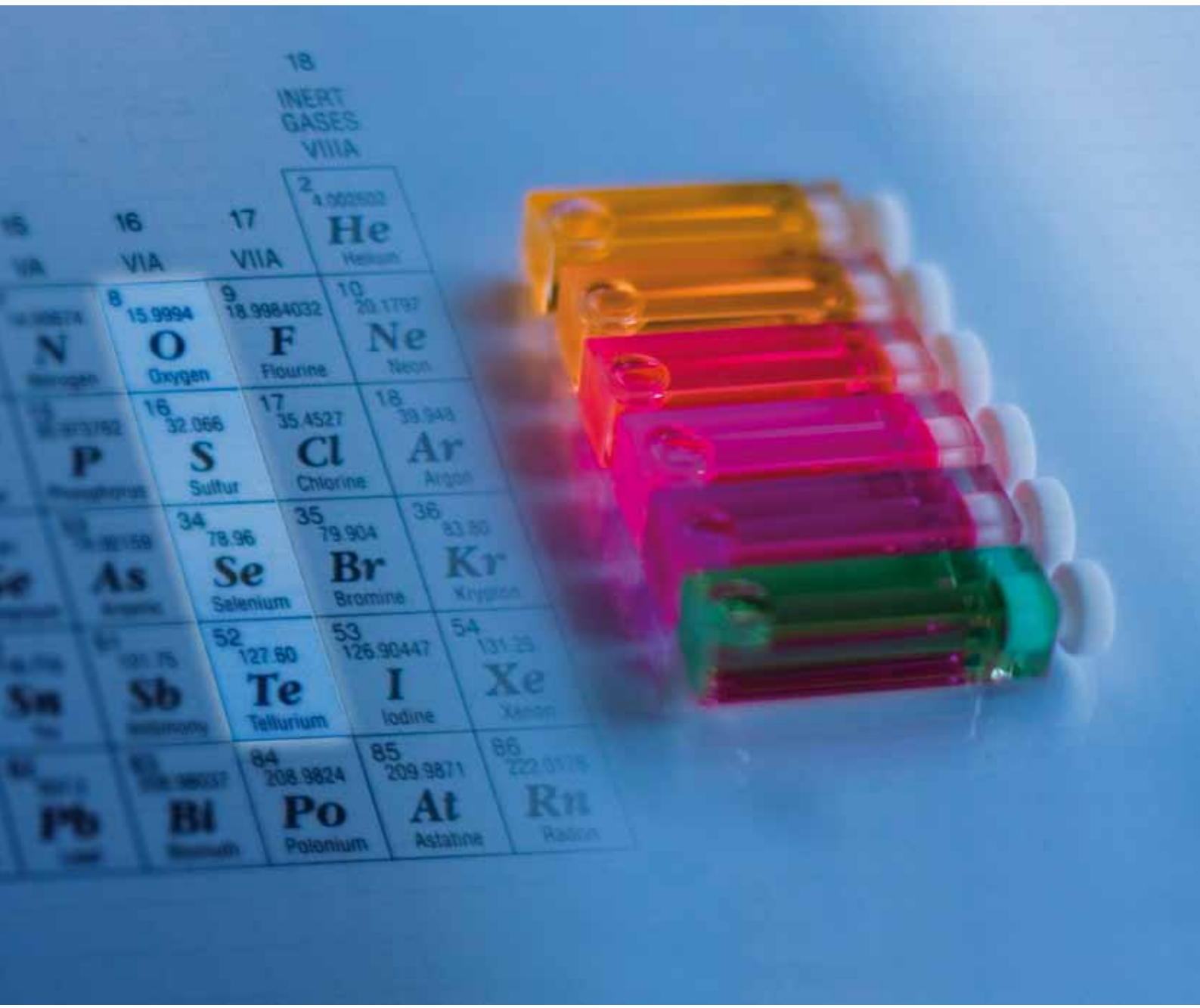
NJC

New Journal of Chemistry

An international journal of the chemical sciences

www.rsc.org/njc

Volume 33 | Number 7 | July 2009 | Pages 1441–1620



ISSN 1144-0546

RSC Publishing

PAPER

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Synthesis and photophysical characterization of chalcogen substituted BODIPY dyes

1144-0546(2009)33:7;1-X

Synthesis and photophysical characterization of chalcogen substituted BODIPY dyes†

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Received (in Montpellier, France) 15th January 2009, Accepted 9th March 2009
First published as an Advance Article on the web 14th April 2009
DOI: 10.1039/b900786e

Synthetic details and stationary and time-resolved photophysical properties of five BODIPY derivatives containing chalcogen atoms are presented. The photophysical data are compared to those of a chlorine atom containing BODIPY, acting as a reference. A strong impact in the HOMO–LUMO transition energy is achieved *via* nucleophilic substitution with chalcogen based units. Going from oxygen to tellurium a bathochromic shift in both absorption and emission spectra from the green to the near infrared region was observed. By employing fluorescence single photon timing experiments in two solvents of different polarity, the excited state dynamics and their solvent dependence indicate the presence of a mechanism involving a photoinduced charge transfer that dramatically affects the optical radiative processes of these derivatives.

Introduction

The BODIPY chromophores, first introduced in 1968,[1] have shown a phenomenal growth in applications and synthetic variants since the early nineties.[2] Currently, BODIPY derivatives are employed as tunable laser dyes,[3] chemosensors,[4] fluorescent switches[5] and biological labels.[6] Compared to other fluorescent dye families, BODIPY chromophores have absorption and emission spectra with very narrow bandwidths.[2,7–9] By exploiting the potential of small structure modifications their sharp and high fluorescence emission can be tuned to longer wavelengths, leading to probes that can be used more efficiently for *in vivo* imaging.[7,10,11]

Recently it was demonstrated that the presence of good leaving groups, such as chlorine atoms at the 3- and 5-positions of a BODIPY dye, allows the facile introduction of different groups (containing chalcogen atoms for example) at these sites by nucleophilic substitution.[8,12] An interest in chalcogen containing chromophores as photosensitizers and probes began with the observation that the absorption and emission maxima shift to longer wavelengths by varying the chalcogen atom.[13–15] Selenium containing chromophores are of interest since they can act as a model for biologically relevant organoselenium compounds,[16] for example, glutathione peroxidase (GPx) mimics.[17] GPx is a mammalian antioxidant enzyme that protects biomembranes and other cellular components from oxidative damage by catalyzing the reduction of a variety of hydroperoxides, using glutathione (GSH) as the reducing substrate.[18] The catalytically active center of glutathione peroxidase is a selenocysteine.[18] Therefore, selenium containing BODIPY derivatives could find applications as a probe for studying the catalytic cycle of redox enzymes, since the oxidation of the selenium will likely have an impact on the fluorescence, and could be used as a read-out tool.

Chalcogen containing BODIPY dyes might also find applications as probes for photo dynamic therapy (PDT). PDT uses a dye to produce a cytotoxic reagent or cytotoxic reaction in the tumor cell; typically this occurs *via* the generation of singlet oxygen ($^1O_2$) or superoxide from molecular oxygen. The generation of reactive oxygen species requires a triplet state of the dye, and as BODIPY normally shows only negligible triplet state transitions, the introduction of "heavy atoms", like selenium and tellurium, might increase the intersystem crossing yield to the triplet state.[19] As several photoactive organoselenium compounds are being used as sensitizers in PDT, with regulatory approval in several countries for lung, digestive tract, and genitourinary tract cancers, we reasoned that the introduction of selenium and tellurium in the BODIPY dye could lead to novel and improved PDT sensitizers or to probes to study the PDT mechanisms.[20–22]

The presence of chlorine atoms at the 3- and 5-positions of a BODIPY dye allows the facile introduction of new substituents through nucleophilic substitution and palladium catalyzed reactions.[23] This route could be used for fast and easy variation of the dye to optimize the spectroscopic properties. Based on this background, by using a nucleophilic substitution strategy, we have synthesized a new class of five, chalcogen atom (O, S, Se, Te) containing, BODIPY chromophores (see Scheme 1). By chemical modification of the rigid aromatic π-system platform *via* substitution with chalcogen based units, specific features are introduced and a strong impact in the HOMO–LUMO transition energy is achieved. In addition to the synthetic details, the stationary photophysical properties of each derivative are presented in two solvents of different

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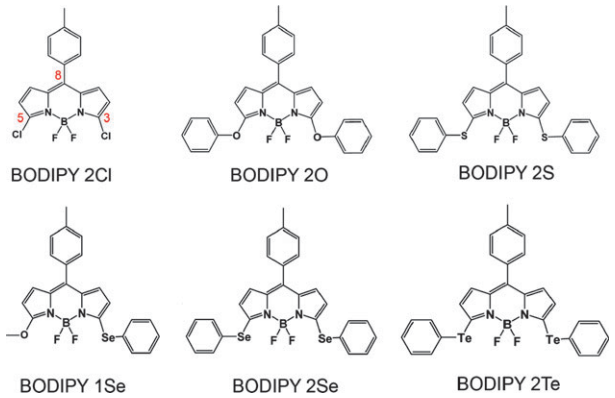
† Electronic supplementary information (ESI) available: NMR and mass spectra of the chalcogen substituted BODIPY dyes. See DOI: 10.1039/b900786e



Scheme 1 Molecular structures of the BODIPY derivatives. The positions where the chromophore is functionalized are indicated in red.

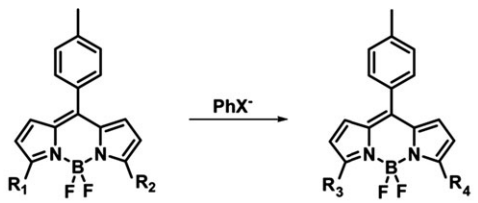
polarity. By using fluorescence single photon timing experiments the excited state dynamics and their solvent dependence are investigated in detail to elucidate the mechanisms affecting the optical radiative processes of these derivatives.

Results and discussion

Synthesis

The functionalization of 3,5-dichloro-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY 2Cl) by nucleophilic aromatic substitution reaction is a valuable method for preparing a variety of chalcogen substituted BODIPY dyes in excellent yield.

The synthetic procedures for BODIPY 2Cl and 3-methoxy-5-chloro-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY ClOMe, starting compound for the synthesis of BODIPY 1Se) were published previously.[12,24] The phenylselenide anion ($PhSe^-$, generated from PhSeSePh and $NaBH_4$) and the phenyl telluride anion ($PhTe^-$, generated from PhTeTePh and $NaBH_4$) undergo an S_NAr reaction with the BODIPY 2Cl compound to give the BODIPY 2Se and BODIPY 2Te compounds, respectively, and the S_NAr reaction of the $PhSe^-$ with the BODIPY ClOMe compound results in the BODIPY 1Se compound (see Scheme 2). The nucleophilic substitution reaction of thiophenol with the BODIPY 2Cl compound gives the BODIPY 2S compound. The synthesis and the photophysical characterization of BODIPY 2O were published previously.[12,24] An overview of the obtained synthesis yields is given in Scheme 2.



BODIPY-chalcogen	R_1	R_2	X	R_3	R_4	Yield (%)
BODIPY 2O	Cl	Cl	O	PhO	PhO	92
BODIPY 2S	Cl	Cl	S	PhS	PhS	87
BODIPY 2Se	Cl	Cl	Se	PhSe	PhSe	96
BODIPY 1Se	OMe	Cl	Se	OMe	PhSe	63
BODIPY 2Te	Cl	Cl	Te	PhTe	PhTe	91

Scheme 2 General synthetic pathway for the preparation of the BODIPY-chalcogen compounds together with the synthetic yields.

Steady state measurements

The normalized absorption and emission spectra of the BODIPY compounds dissolved in toluene and THF are displayed in Fig. 1 and the measured spectroscopic data in these solvents are compiled in Table 1. The stationary absorption and emission spectra feature a similar shape to those of the classical BODIPY dyes.[23] In absorption, the series shows narrow spectra with two maxima, a sharp peak and a shoulder corresponding to the strongly allowed $S_0 \rightarrow S_1$ transition of the delocalized π-conjugated core and its vibrational fine structure, respectively. The small bandwidth and high molar extinction coefficient ($76\,600 < \varepsilon < 117\,300\ M^{-1}\ cm^{-1}$) are characteristic of the planar aromatic skeleton of the rigid BODIPY chromophoric system with a low degree of conformational freedom. A second, less pronounced peak observed at the higher energy side of the spectrum (330–470 nm) is attributed to a transition between the ground state and a higher excited state ($S_0 \rightarrow S_2$). It is evident that the nature of the substituents in the 3- and 5-positions of the core has a large effect on the position of the absorption maxima relative to derivatives where the substituents are attached at different positions.[2] It has been previously reported that the BODIPY core consists of an extended π-system with two equivalent and symmetric delocalized structures.[25] Strong π-delocalization is observed within the central six-membered ring and both five-membered rings and is interrupted by the B–N bonds. A large bathochromic shift of 3443 cm^{-1} (105 nm) and 3635 cm^{-1} (128 nm) can be observed in absorption and emission, respectively, when comparing BODIPY 2Cl to BODIPY 2Te (see Fig. 1) upon decreasing the electron withdrawing (or increasing the electron donating) character of the substituents in the 3- and 5-positions. The BODIPY 1Se, BODIPY 2Se and BODIPY 2S have S_0–S_1 transition energies with intermediate values. This corresponds, however, to the results found upon introducing other electron donating substituents in the 3- and/or 5-position.[2,12] Note that the S_0–S_2 transition undergoes a correlated shift to lower energies (6680 cm^{-1}) as seen in Fig. 1.

Only a small hypsochromic shift of about 186 cm^{-1} (5 nm) is present in the absorption maxima on going from toluene to THF and could be attributed to the combined result of the different solvent polarizability ($n_{toluene} = 1.49$, $n_{THF} = 1.40$) and/or the decrease of the dipole moment in the excited state S_1 with respect to the ground state S_0. This shift is consistent with the general behavior of other BODIPY derivatives,[26–28] cyanine dyes[29,30] and aromatic amines.[31] The emission spectra closely resemble the mirror image of the corresponding $S_0 \rightarrow S_1$ transition showing a relative small Stokes shift, due to the rigidity of the BODIPY chromophore in BODIPY 2Cl, BODIPY 2O, BODIPY 2S and BODIPY 2Se. While this Stokes shift is the same for BODIPY 2Cl, BODIPY 2O, BODIPY 2S and BODIPY 2Se (between 579 cm^{-1} and 585 cm^{-1} in toluene) within the experimental error, it is larger in BODIPY 1Se and BODIPY 2Te. Parallel to the Stokes shift the FWHM of the absorption band is within experimental error the same for BODIPY 2Cl, BODIPY 2O, BODIPY 2S and

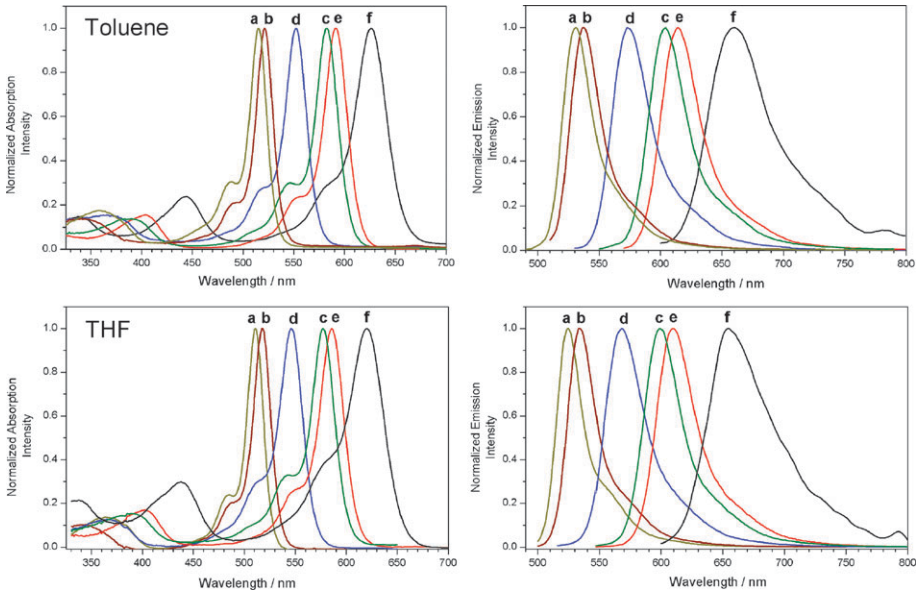


Fig. 1 Steady state absorption (left) and emission spectra (right) of the BODIPY derivatives in toluene (top) and THF (bottom). The intensities of all spectra are normalized to 1. (a) BODIPY 2Cl, (b) BODIPY 2O, (c) BODIPY 2S, (d) BODIPY 1Se, (e) BODIPY 2Se, (f) BODIPY 2Te.

BODIPY 2Se (between 558 cm^{-1} and 593 cm^{-1} in toluene). For BODIPY 2Te, a much larger FWHM of the absorption band is found in toluene. As toluene already behaves as a solvent of intermediate polarity these data indicate that, contrary to the other BODIPY derivatives, the bond lengths and the dipole moment in the excited state of BODIPY 2Te (and to a smaller extent of BODIPY 1Se) differ from those in the ground state. In THF the Stokes shift increases in a systematic way from BODIPY 2Cl to BODIPY 2Te, in accordance with the electron donating character of the substituent. This suggests that a decrease in excitation energy is accompanied by an increase in the difference between the Franck–Condon state and relaxed excited state. Also the FWHM of the absorption band is always larger in THF than in toluene and the effect becomes more pronounced with increasing electron donating character of the substituent. The spectral shape and position of the maxima (see Fig. 1) do not show any significant dependence on the solvent polarity, suggesting that the emission always occurs from the relaxed Frank–Condon state with a similar or weaker polar character than the ground state.

Time-resolved fluorescence measurements

In order to establish the influence of the substituents on the excited state properties of the BODIPY core in solution, a series of time-resolved fluorescence experiments were performed. The fluorescence decays (see Fig. 2) were recorded for each sample at four different detection wavelengths selected across the emission spectrum and the decay traces were globally analyzed.[32] The fluorescence decay properties of the BODIPY derivatives in toluene and THF are given in Table 1. In both solvents, the emission of each derivative decays mono-exponentially, yielding radiative rate constants of similar values which are consistent with the general behavior of BODIPY chromophores.[25] However, the non-radiative rate constants always have higher values in THF than in toluene, suggesting that a polar solvent favors the deactivation of the fluorescent locally excited state as observed for other BODIPY's.[2]

As seen in Table 1, k_r shows only slight variation from BODIPY 2Cl to BODIPY 2Se in the two solvents with a mean value of 0.21×10^9 s^{-1} (calculated for toluene). The value is reduced to almost half for the BODIPY 2Te. According to the k_r/ν_{emiss}^3 value, the derivatives containing S and Se in the substituents show the strongest transition dipole moments. This does not correlate directly with changes in the molar extinction coefficient or with the FWHM of the $S_0 \rightarrow S_1$ absorption for the sulfur or selenium compounds.

Following the relaxation of the Frank–Condon state, the rate constant of the non-radiative decay for the BODIPY series presented here varies substantially. As seen in Table 1, k_{nr} and the fluorescence quantum yield are strongly dependent on both the nature of the substituents and the solvent polarity, ranging from 0.84 (BODIPY 2S in toluene) to 0.01 (BODIPY 2Te in THF). As observed for other (especially donor substituted) BODIPY's the values of k_{nr} increase upon increasing the solvent polarity form toluene to THF. While the dramatic increase of k_{nr} observed for the BODIPY 2Te can be related to the increased donor strength and smaller singlet energy (as observed for other BODIPY's), there is for the moment no clue why significantly smaller values are observed for the sulfur or selenium substituted compounds compared to those with chlorine or oxygen substituents. Tentatively, for substituents in the 3- and 5-positions, one expects an increased rate of internal conversion when the S_0–S_1 energy gap is decreased by stabilizing the LUMO or destabilizing the HOMO. Another effect that one should take into account is the increasing nuclear charge of the atom bound to the BODIPY structure which can promote intersystem crossing. Both mechanisms could explain to some extent why BODIPY 2Te has the lowest fluorescence quantum yield and the smallest excitation energy. There is, however, no correlation when comparing the high fluorescence quantum yield of BODIPY 1Se and BODIPY 2Se, which have smaller S_0–S_1

Table 1 Photophysical and fluorescence time-resolved properties of BODIPY compounds in toluene and THF

		λ_{abs} (max)/nm	λ_{emiss} (max)/nm	Stokes shift/cm^{-1}	FWHM abs[a]/cm^{-1}	λ_{excit} (max)/nm	ε[b]/M^{-1} cm^{-1}	Φ_f	τ/ns	k_r (10^9)/s^{-1}	k_{nr} (10^9)/s^{-1}	$k_r/\nu_{emiss}{}^3$ (10^{-6})/ s^{-1} cm^{-3}
BODIPY 2Cl	Toluene	515	531	585	558	488	—	0.63	3.31	0.19	0.11	28.4
	THF	511	524	485	572	488	103 100	0.37	2.14	0.17	0.29	24.4
BODIPY 2O	Toluene	521	537	571	565	543	—	0.44	1.86	0.23	0.30	34.4
	THF	516	533	618	597	543	117 300	0.27	1.19	0.22	0.61	33.3
BODIPY 2S	Toluene	582	602	570	578	543	—	0.84	4.25	0.19	0.03	41.5
	THF	577	599	636	593	543	87 700	0.82	4.21	0.19	0.04	41.0
BODIPY 1Se	Toluene	552	574	724	579	543	—	0.76	3.29	0.23	0.07	43.5
	THF	546	568	709	675	543	71 070	0.53	2.59	0.20	0.18	36.7
BODIPY 2Se	Toluene	591	612	580	593	543	—	0.72	3.58	0.20	0.07	45.8
	THF	586	609	644	623	543	104 400	0.56	2.92	0.19	0.15	42.9
BODIPY 2Te	Toluene	626	658	776	680	599	—	0.03	0.23	0.13	4.2	37.0
	THF	620	659	954	744	599	76 600	0.01	0.10	0.1	9.9	23.8

[a] The full width at the half-maximum (FWHM) has been calculated taking into account only the 0–0 absorption peak from the S0–S1 transition extracted from the absorption spectrum plotted on a wavenumber scale using a multiple Gaussian fitting procedure. [b] The molar extinction coefficient was measured at the maximum of the absorption wavelength

energy gaps and heavier atoms, with that of BODIPY 2Cl or BODIPY 2O. Moreover, the change in solvent polarity from toluene to THF plays a determining role in the fluorescence properties of the series (except for BODIPY 2S) and cannot be explained under this assumption.

Chen *et al.*[33] revealed a mechanism whereby a considerable drop in fluorescence quantum yield was observed in the presence of a phenyl group at the 8-position due to free internal rotation of the phenyl ring. Although motion of the phenyl ring, when incorporated as a substituent, could increase the non-radiative rate[34] this has in our case no consistent effect when comparing the photophysical data (Table 1) of the derivatives without (BODIPY 2Cl) and with (BODIPY 2O, BODIPY 2S, ...) phenyl rings in the 3- and 5-substituent positions.

It has been reported earlier that the presence of the phenyl group at the 8-position favors the formation of a charge transfer state.[35] Depending on the oxidation potentials of the substituents relative to those of the excited states of the BODIPY core, these can act as electron donors or acceptors. When the BODIPY core is equipped with a tertiary amine on the phenyl group in the 8-position, a charge transfer is found to take place from the electron donating amine to the BODIPY unit,[25] whereas in the case of distyryl substituted BODIPY chromophore an excited state charge transfer process leads to the formation of a non-emitting charge transfer (CT) state.[36] The electron donating properties of the substituents used here (thiophenyl, selenophenyl, tellurophenyl, chloro groups)[36] and electron acceptor properties of the BODIPY core[7] suggest that an interaction with a charge transfer state could occur upon excitation. The interaction with a charged species can depopulate the relaxed excited state and lead to a reduced overall fluorescence. Furthermore, a polar solvent can stabilize the energy of the charged species and open further non-radiative decay channels from the locally excited state. This assumption could best explain the dependence of the fluorescence quantum yield on both the nature of 3- and 5-substituents (having different electron donating properties) and the solvent polarity. BODIPY 2S (and to a smaller extent BODIPY 2Se) has the smallest and solvent independent k_{nr} indicating that a CT interaction mechanism is either not involved or has a minor effect. Ongoing ultrafast femtosecond transient absorption and femtosecond fluorescence up-conversion experiments are expected to reveal the kinetic components attributed to this process and could bring additional evidences, for instance, by detecting the radical anion and/or cation absorption bands.

The presence of the external heavy atoms could promote intersystem crossing (ISC), reducing the fluorescence by populating the triplet state. Upon recording the emission of BODIPY 2Te in methyl-THF at 77 K a substantially enhanced S_1 emission is detected. The spectrum is characterized by a better defined vibronic structure (see Fig. 3A) than the one recorded at room temperature. The additional emission band observed between 820 and 1100 nm is probably due to phosphorescence. Compared to the fluorescence, the phosphorescence in BODIPY 2Te is relatively low even at 77 K. BODIPY 2Se shows even less emission at 77 K in the 800–950 nm region (see Fig. 3A), which might reflect the smaller tendency of Se (compared to Te) to enhance spin–orbit coupling. There are not many studies reporting on experimentally obtained phosphorescence spectra of BODIPY dyes. One example can be found of a dyad system comprising BODIPY and terpyridine subunits.[37] In order to confirm that triplet formation is present in BODIPY 2Te, nanosecond transient absorption measurements were performed. Fig. 3B shows transient absorption spectra of BODIPY 2Te in methyl-THF, measured at room temperature with argon bubbling through the sample in order to remove oxygen. From 500 nm to 650 nm, a ground state recovery signal can be detected. Above 650 nm and below 500 nm, a decay of the absorption of a transient species can be seen. Fig. 3C shows the ground state recovery signal at 640 nm and the decay of the absorption of the transient species at 700 nm for BODIPY 2Te in methyl-THF, bubbling the sample with either oxygen or argon gas. When bubbling argon gas through the sample, the decay of the transient species at 700 nm is substantially longer (decay time of more than 5 μs) than when bubbling the sample with oxygen (decay time of less than 100 ns). A similar effect is observed when looking at the ground state recovery at 640 nm.

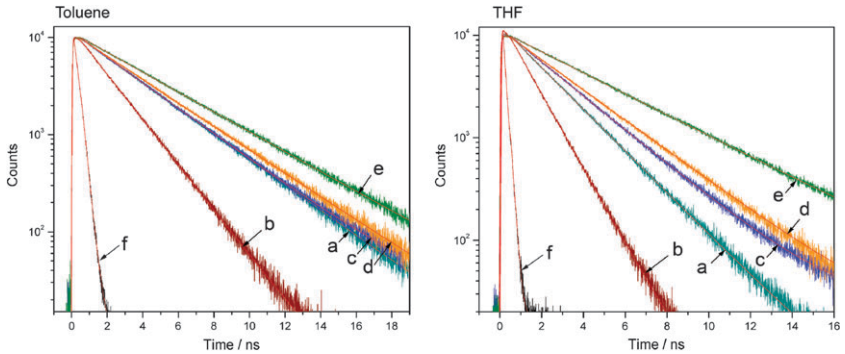


Fig. 2 Fluorescence decay traces and the corresponding fits of the BODIPY derivatives in toluene and THF recorded at the maximum of the emission wavelength. The excitation wavelengths are listed in Table 1. (a) BODIPY 2Cl, (b) BODIPY 2O, (c) BODIPY 2S, (d) BODIPY 1Se, (e) BODIPY 2Se, (f) BODIPY 2Te.

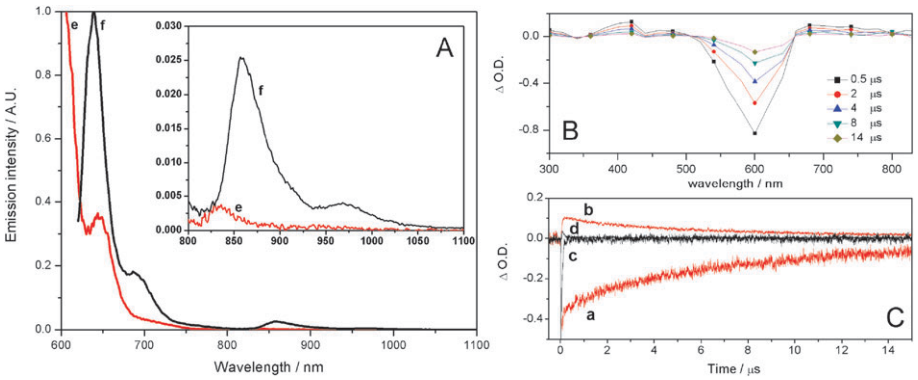


Fig. 3 (A) Normalized emission spectra of BODIPY 2Se (red) and BODIPY 2Te (black) in methyl-THF at 77 K. (e) BODIPY 2Se, (f) BODIPY 2Te. (B) Transient absorption spectra of BODIPY 2Te in methyl-THF at different time points after the excitation pulse (from 0.5 until 14 μs). (C) Transient absorption decay curves of BODIPY 2Te in methyl-THF. (a) The sample was bubbled with argon gas; detection wavelength is 640 nm. (b) The sample was bubbled with argon gas; detection wavelength is 700 nm. (c) The sample was bubbled with oxygen gas; detection wavelength is 640 nm. (d) The sample was bubbled with oxygen gas; detection wavelength is 700 nm.

The oxygen dependent decay times clearly demonstrate the triplet character of this transient species. Based on the nanosecond transient absorption data, one can conclude that the emission observed in the 820–1100 nm region is most probably phosphorescence from a triplet state.

Conclusions

The synthesis, stationary spectroscopic characteristics and excited state properties of new BODIPY derivatives bearing O, Cl, Se, S and Te based substituents attached in the 3- and 5-positions were described. The facile synthesis and high yields of a number of highly pure derivatives reported here should motivate further effort in this area. The new class of strongly absorbing and fluorescing chromophores has the advantage of being usable at wavelengths longer than for classical BODIPY structures, particularly those emitting above 600 nm.

An important outcome of this study is the strong dependence of the electron donating strength of the substituents on the excitation energy of the chromophore π-system. This proves that by simply functionalizing the core in the "sensitive" 3- and 5-positions, asymmetric (BODIPY 1Se) or symmetric (BODIPY 2Se), it is possible to tune its active spectral wavelength region.

To understand the mechanism responsible for the substantial fluorescence quenching in BODIPY 2Te, single photon timing experiments were performed in toluene and THF. Based on the experimental and literature data[8,12,38] presented here we suggest that the main pathway responsible for the increase of non-radiative processes is an ISC that leads to the formation of an intermediate species with a triplet character. The dependency of the excited state properties on the solvent polarity suggests that a charge transfer could be involved in the deactivation of the locally excited state. The charge transfer takes place from the electron rich substituents to the electron poor BODIPY core leading to an efficient depopulation of the LES. The CT is better stabilized in polar solvents like THF and the decay through non-radiative channels is further enhanced. Additional experiments using fluorescence femtosecond up-conversion, transient absorption techniques and quantum chemical calculations could improve our understanding of the excited state dynamics and allow us to design molecular systems with specific features.

Experimental

Materials and steady state spectra

The stationary measurements were recorded in toluene ($\varepsilon = 2.43$, $n = 1.49$, spectroscopic grade) and THF ($\varepsilon = 7.6$, $n = 1.40$)[39] as solvents by using a spectrophotometer (Lambda 40, Perkin Elmer) and a fluorimeter (Fluorolog FL3-11, Perkin Elmer) corrected for the wavelength dependence of

the detection system. The optical density at the absorption maximum of all solutions was kept below 0.1 in a 1 cm cuvette and for the emission spectra the excitation wavelength was set to 488 nm (BODIPY 2Cl, BODIPY 2O), 543 nm (BODIPY 1Se, BODIPY 2Se, BODIPY 2S) and 599 nm (BODIPY 2Te). The fluorescence quantum yields of the BODIPY systems were determined using rhodamine 6G in methanol and cresyl violet in ethanol as references.[40]

^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Bruker Avance 300 instrument operating at a frequency of 300 MHz for ^{1}H and 75 MHz for ^{13}C. ^{1}H NMR spectra were referenced to tetramethylsilane (0.00 ppm) as an internal standard. Chemical shift multiplicities are reported as s = singlet, d = doublet, q = quartet, and m = multiplet. ^{13}C NMR spectra were referenced to the $CDCl_3$ (77.67 ppm) signal. Mass spectra were run using a Thermo Finnigan LCQ Advantage apparatus (APCI/ESI). Melting points (not corrected) were determined using a Reichert Thermovar apparatus. For column chromatography 70–230 mesh silica 60 (E. M. Merck) was used as the stationary phase. Chemicals received from commercial sources were used without further purification. K_2CO_3 (anhydrous, granulated) was finely ground (with a mortar and pestle) prior to use.

Picosecond fluorescence time-resolved experiments

The fluorescence decay times have been determined by single photon timing (SPT) measurements described in detail previously.[41] A time-correlated single photon timing PC module (SPC 830, Becker & Hickl) was used to obtain the fluorescence decay histogram in 4096 channels. The decays were recorded with 10 000 counts in the peak channel in time windows of 25 ns and 15 ns corresponding to 6 ps/channel and 3.7 ps/channel and analyzed globally with dedicated time-resolved fluorescence analysis (TRFA) software.[42] The full width at half-maximum (FWHM) of the IRF was typically in the order of 40 ps. The quality of the fits has been judged by the fit parameters χ^2 (<1.2), Z_χ^2 (<3) and the Durbin Watson parameter (1.8 < DW < 2.2) as well as by the visual inspection of the residuals and auto-correlation function.[43] All measurements have been performed in toluene in a 1 cm optical path length cuvette at an optical density of *ca.* 0.1 at the excitation wavelength of 488 nm (BODIPY 2Cl, BODIPY 2O), 543 nm (BODIPY 1Se, BODIPY 2Se, BODIPY 2S) and 599 nm (BODIPY 2Te).

Nanosecond transient absorption spectroscopy

Nanosecond transient absorption experiments are performed using a laser flash photolysis apparatus. Excitation pulses at 355 and (7–8 ns, 1 mJ) are provided by a 20 Hz Nd:YAG laser (DIVA II, Thales laser). The probe light is provided by a Xe lamp (XBO 150W/CR OFR, OSRAM). Samples are contained in a sealable Hellma quartz cell (10 × 10 mm section) at a concentration adjusted to get an optical density (OD) value of about 1.0 at the pump excitation wavelength. The transmitted light is dispersed by a monochromator (Horiba Jobin-Yvon, iHR320) and analyzed with a photo-multiplier (R1477-06, Hamamatsu) coupled to a digitalized oscilloscope (LeCroy 454, 500 MHz). Experiments with and without oxygen are performed by bubbling oxygen and argon gas, respectively, for 30 min through the sample.

Synthetic procedures

BODIPY 2S. Benzenethiol (220 mg, 2 mmol) and potassium carbonate (276 mg, 2 mmol) were added to the DMF solution (5 mL) of BODIPY dichloride (68.3 mg, 0.2 mmol), and the reaction mixture was kept for 12 h at 50 °C under argon atmosphere. After cooling to room temperature, the solution was extracted with ethyl acetate (20 mL) and brine (3 × 15 mL), and the organic layer was dried over $MgSO_4$. The solution was dried by rotary evaporation, and the residue was purified by chromatography (silica, petroleum ether–dichloromethane = 60 : 40). The compound was thus obtained with a yield of 87%. ^{1}H NMR ($CDCl_3$): δ (ppm) = 2.35 (s, 3H), 5.80 (d, 2H, J = 4.2 Hz), 6.55 (d, 2H, J = 4.2 Hz), 7.16 (d, 2H),7.26 (d, 2H), 7.35–7.37 (m, 6H), 7.58–7.61 (m, 4H); ^{13}C NMR ($CDCl_3$): δ (ppm) = 20.4, 117.5, 128.0, 128.2, 128.5, 128.6, 129.2, 129.5, 129.9, 133.7, 135.0, 137.9, 139.2, 155.4; UV (λ_{max}, THF): 573.1 nm; ESI-mass (calc. for M + Na^+: 521.4): 521.6 (M + Na^+), 1019.3 (2M + Na^+), 1035.1 (2M + K^+). See ESI† for additional NMR data.

BODIPY 1Se. An ethanol (1 mL) solution of sodium borohydride (27 mg, 0.71 mmol) was added to the ethanol (4 mL) solution of diphenyl diselenide (100 mg, 0.32 mmol) under argon atmosphere, and the resulting solution then became colorless. The colorless solution was transferred into the THF (10 mL) solution of methoxyl-BODIPY monochloride (102.6 mg, 0.3 mmol). The reaction mixture was kept for 12 h at room temperature under argon atmosphere. The resulting solution was extracted with dichloromethane (20 mL) and brine, and the organic layer was dried over $MgSO_4$. The solution was dried by rotary evaporation, and the residue was purified by chromatography (silica, hexane–dichloromethane = 40 : 60). The compound was thus obtained with a yield of 63%. ^{1}H NMR ($CDCl_3$): δ (ppm) = 2.43 (s, 3H), 4.11 (s, 3H), 5.89 (d, 1H, J = 4.1 Hz), 6.01 (d, 1H, J = 4.1 Hz), 6.52 (d, 1H, J = 4.1 Hz), 6.83 (d, 1H, J = 4.1 Hz), 7.24 (m, 2H), 7.36 (m, 5H), 7.76 (m, 2H); ^{13}C NMR ($CDCl_3$): δ (ppm) = 21.4, 58.9, 101.8, 119.6, 127.1, 127.5, 129.0, 129.2, 129.5, 130.3, 130.7, 132.7, 136.1, 139.2, 140.0, 147.9, 152.8, 167.7; ^{77}Se NMR ($CDCl_3$): δ (ppm) = 413.4; UV (λ_{max}, THF): 542.4 nm; HRMS (calc. 468.0724): 468.0712. See ESI† for additional NMR data.

BODIPY 2Se. An ethanol (1 mL) solution of sodium borohydride (27 mg, 0.71 mmol) was added to the ethanol (4 mL) solution of diphenyl diselenide (200 mg, 0.64 mmol) under argon atmosphere, and the resulting solution then became colorless. The colorless solution was transferred into the THF (10 mL) solution of BODIPY dichloride (102.6 mg, 0.3 mmol). The reaction mixture was kept for 12 h at room temperature under argon atmosphere. The resulting solution was extracted with dichloromethane (20 mL) and brine, and the organic layer was dried over $MgSO_4$. The solution was dried by rotary evaporation, and the residue was purified by chromatography (silica, petroleum ether–dichloromethane = 50 : 50). The compound was thus obtained with a yield of 96%. ^{1}H NMR ($CDCl_3$): δ (ppm) = 2.41 (s, 3H), 5.90 (d, 2H, J = 4.1 Hz), 6.60 (d, 2H, J = 4.1 Hz), 7.23 (m, 2H), 7.32 (m, 2H), 7.36–7.45 (m, 6H), 7.72–7.80 (m, 4H); ^{13}C NMR ($CDCl_3$): δ (ppm) = 21.4, 120.5, 126.7, 129.0, 129.4, 129.7,

130.2, 130.8, 136.4, 137.2, 138.7, 140.3, 152.9; ^{77}Se NMR ($CDCl_3$): δ (ppm) = 428.6; UV (λ_{max}, THF): 581.3 nm; ESI-mass (calc. for M + Na^+: 615.2): 615.5 (M + Na^+), 1208.9 (2M + Na^+), 1224.3 (2M + K^+). See ESI† for additional NMR data.

BODIPY 2Te. The ethanol (1 mL) solution of sodium borohydride (81 mg, 2.14 mmol) was slowly added to the ethanol (4 mL) solution of diphenyl ditelluride (180 mg, 0.44 mmol) under argon atmosphere until the mixture solution became nearly colorless. The resulting solution was immediately transferred into the degassed THF (10 mL) solution of BODIPY dichloride (102.6 mg, 0.3 mmol). The reaction mixture was kept for 12 h at room temperature under argon atmosphere. The resulting solution was extracted with dichloromethane (20 mL) and brine, and the organic layer was dried over $MgSO_4$. The solution was dried by rotary evaporation, and the residue was purified by chromatography (silica, petroleum ether–dichloromethane = 50 : 50). The compound was thus obtained with a yield of 91%. ^{1}H NMR ($CDCl_3$): δ (ppm) = 2.41 (s, 3H), 6.02 (d, 2H, J = 4.1 Hz), 6.56 (d, 2H, J = 4.1 Hz), 7.22 (m, 2H), 7.34 (m, 6H), 7.45 (m, 2H), 8.00 (m, 4H); ^{13}C NMR ($CDCl_3$): δ (ppm) = 21.8, 112.9, 125.6, 129.2, 129.5, 129.9, 130.3, 130.6, 131.1, 137.9, 138.2, 139.7, 140.7, 141.7; UV (λ_{max}, THF): 615.2 nm; ESI-mass (calc. for 2M + Na^+: 1402.0): 1402.5 (2M + Na^+), 1418.5(2M + K^+). See ESI† for additional NMR data.

Acknowledgements

T.V. would like to thank the "Fonds voor Wetenschappelijk Onderzoek (F.W.O.) Vlaanderen" for a postdoctoral fellowship. Support from the F.W.O., the Flemish Ministry of Education (GOA 2001/02 and 2006/2) and the Federal Science Policy of Belgium (IAP-V-03 and IAP VI-27) is gratefully acknowledged. The 'Instituut voor de aanmoediging van innovatie door Wetenschap en Technologie in Vlaanderen' (IWT) is acknowledged for a fellowship to L.P.

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