The chemistry of Bodipy: A new *El Dorado* for fluorescence tools†

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In the steadily expanding field of fluorescent dyes, labels and electroluminescent materials difluoroboron-dipyrromethenes play a prominent role. The review highlights recent advances made with these boron-stabilized cyanine dyes. The chemistry at the boron atom and increase of delocalization on the organic core allows one to address the problems of Stokes' shifts, colours and emission wavelengths spanning from green to the NIR. The outcome is a diversity of molecules prepared by different strategies and exhibiting interesting and tunable spectroscopic, electrochemical and chemical properties. This perspective article describes the scope and spectroscopic attributes of this new class of fluorescent dyes amenable to applications in various disciplines.

Introduction

Among the large variety of known fluorescent dyes, the difluoro-boraindacene family (abbreviated hereafter as *F*-Bodipy) has gained recognition as being one of the most versatile reagents and has found great popularity with chemists, biochemists and physicists. Since their discovery by Treibs and co-workers in 1968,[1] the number and range of applications have blossomed and include such diverse uses as biomolecular labels,[2] chromogenic probes and cation sensors,[3] drug delivery agents,[4] fluorescent switches,[5] electroluminescent films,[6] laser dyes,[7] light-harvesters[8] and sensitizers for solar cells.[9] In more fundamental work, *F*-Bodipy has found use as an electron trap for radical pairs generated electrically[10] and for spin-polarized quartet states.[11] The excellent stability, high fluorescence yield, negligible triplet state formation, intense absorption profile, good solubility, and chemical robustness have added to the general attractiveness of these dyes. Furthermore, the field has been extended significantly by the vast number of *F*-Bodipy derivatives that can be accessed by attaching secondary units at the pyrrole,[12] *meso*,[13] and N-*ortho* positions[14] and this has been further expanded by the recent realization that the boron atom is also amenable to substitution.[15] To illustrate the way in which rational design of improved dyes has advanced in this area we consider the problem caused by the small Stokes' shift that is inherent to all *F*-Bodipy dyes. This is a particular problem for flow cytometry using fluorescence detection but has been nicely overcome by advanced prototypic dyes introduced independently by Burgess[16] and by Ziessel.[17]

Dr Raymond Ziessel gained a PhD in Organic Chemistry from the University Louis Pasteur of Strasbourg under the supervision of Professor Jean-Marie Lehn and Dr Jean-Pierre Sauvage. He is currently the Director of the Laboratoire de Recherche de Chimie Moléculaire located at the Engineer School of Chemistry (ECPM) in Strasbourg. His research interests cover many aspects of organic chemistry and applications to molecular electronics, molecular materials, catalysis and molecular detection and molecular probes for labeling of biological materials. Recent interests focus on the preparation of novel liquid crystals, metallo-polyacetylenes and lanthanide complexes for biomaterial labeling and time-resolved fluorescence imaging. He has published over 350 papers in International journals and monographs, is co-author of 10 PCT patents, and has given 260 research lectures, in over 15 countries worldwide. From his research group have emerged over 18 research chemists who have earned PhDs, and now pursue their own scientific careers. He is the recipient of the Silver Medal CNRS award in 2000.

Results and discussion

Thus, a strategy has evolved in which one or more aromatic polycycles are attached to the Bodipy nucleus. Illumination into the appended polycycle, this being anthracene in **1** and **2** and pyrene in **3** and **4** (Chart 1), is followed by rapid intramolecular excitation energy-transfer to the *F*-Bodipy. The latter unit is strongly fluorescent and the net effect is to induce a large virtual Stokes' shift; this shift can reach as high as 10 900 cm^{-1} in the case of **3**. An important feature of these systems is that the two chromophores remain electronically

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† Dedicated to the memory of Professor Guy Ourisson.

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isolated due to the orthogonal arrangement around the connecting linkage. The rate of energy-transfer depends on the structure of the dual-dye system and decreases with increasing centre-to-centre separation in line with a dipole–dipole transfer mechanism. The overall energy-transfer efficiency exceeds 90%, even in the most extended system.[17] Significantly faster energy-transfer is found when the anthracene donor is attached to the long axis of the *F*-Bodipy acceptor, as in **2**, than if the donor is coupled to the short axis, as in **1**.[16]

Surprisingly, functionalization of the boron atom in the Bodipy framework has been completely neglected until very recently.[15] Replacement of the F atoms with aryl or ethynylaryl subunits provides a library of cascade-type *C*-Bodipy (*C* for carbocycle) and *E*-Bodipy (*E* for ethynyl) dyads, **5–10** (Chart 2), in which singlet-energy-transfer is both fast and highly directional. This has led to the development of molecular dyads in which only the Bodipy unit fluoresces, even at low temperature. Tuning the rate constant for intramolecular energy-transfer becomes feasible by optimization of the spectral overlap integral between fluorescence from the appendage and absorption by the Bodipy residue. For example, the highest spectral overlap for the *E*-Bodipy **8** involves absorption by the second singlet-excited state localized on the Bodipy fragment whereas that for **9** involves absorption by the first singlet-excited state on the Bodipy chromophore.

An unusual feature noted for **6** is that non-radiative decay from the first singlet-excited state is an activated process such that the fluorescence quantum yield increases with decreasing temperature. There is no indication for population of a charge-transfer state in which the aryl substituent might act as donor and the *C*-Bodipy fragment as acceptor. It has been rationalized that, in this case, non-radiative decay involves an internal conformational change driven by the solvophobic effect. Indeed, over the series of *C*-Bodipy derivatives it is seen that the

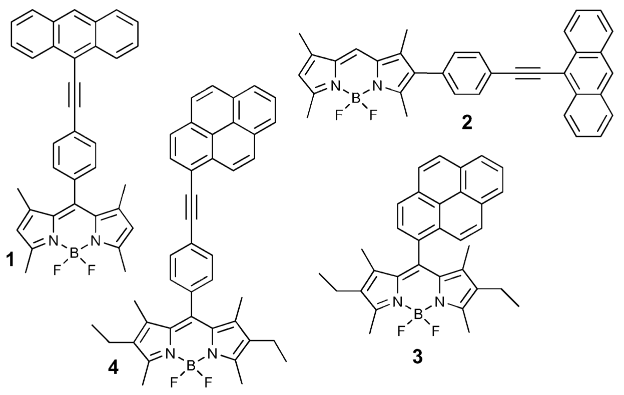

Chart 1

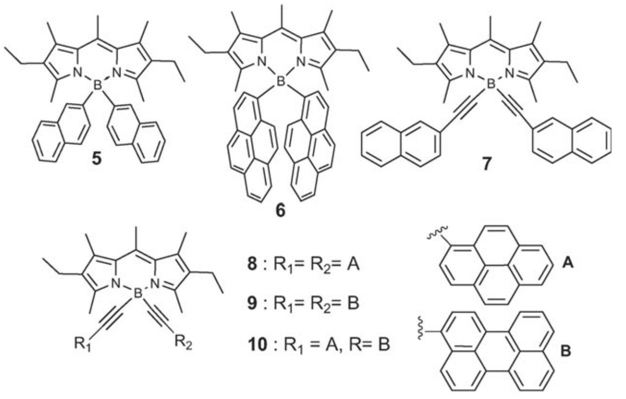

Chart 2

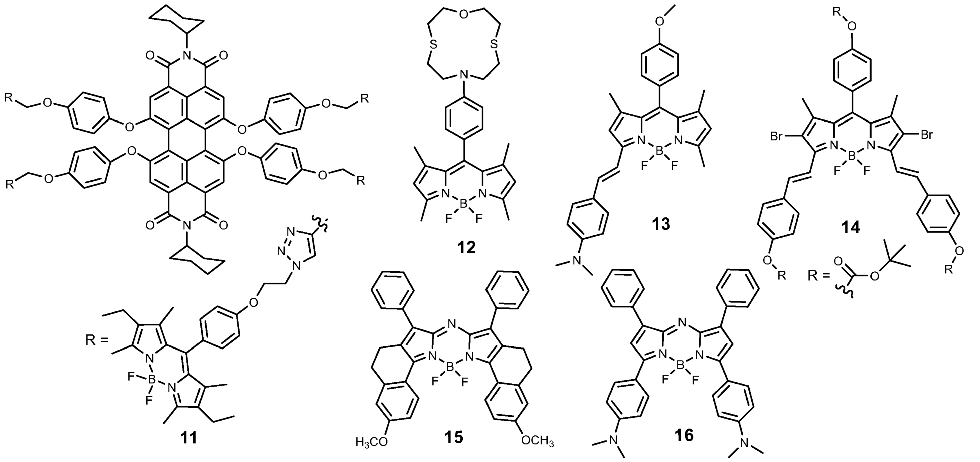

Chart 3

rate of non-radiative decay in any given solvent increases with increasing surface accessibility of the aryl substituent.[18] It might be stressed here that many Bodipy derivatives are known that do undergo intramolecular electron-transfer under visible light illumination in polar solvents.

Transforming symmetrical pyrene and perylene derivatives **8** and **9** to the asymmetric *E*-Bodipy **10**, which itself might be expected to display cascade-type multiple energy-transfer steps, has been a major synthetic challenge. The absorption spectral profile recorded for **10** contains important contributions from each subunit, but the fluorescence profile is exclusively that of the Bodipy fragment. Throughout the series **8–10** intramolecular excitation energy-transfer is extremely efficient, despite the modest spectral overlap integrals for the pyrene-based systems. The rates are rather fast, being 4.7×10^{10}, 1.7×10^{12} and 5.0×10^{10} s^{-1}, respectively, for **8**, **9** and **10**, and there is no obvious indication for competing intramolecular electron-transfer, for which there are modest thermodynamic driving forces. The actual occurrence of a cascade of energy-transfer steps in the asymmetric derivative **10**, however, is still an open question, because of limitations in the available instrumentation. On the basis of model computations, it is anticipated that photons absorbed by the pyrene residue will be channeled to perylene and Bodipy units with equal probability.[19] Additional compounds are needed to fully explore this interesting possibility and it should be emphasized that a range of polycyclic substituents are now known to undergo very efficient intramolecular energy-transfer when used in the *E*-Bodipy configuration. These include ethynylfluorene, ethynylthiophene and ethynylcarbazole.[20] In each case, only the Bodipy unit exhibits fluorescence. A collection of these dyes would absorb all incident photons over the range 290 to 500 nm wavelength region whilst retaining selective emission at 540 nm.

An important issue concerning the design of novel fluorescent labels is to address the problem of Stokes' shifts which are small in most organic dyes. Small shifts necessitate narrow-band filters for the analysis protocol and selective excitation sources. The common approach to enhancement of Stokes' shifts is to unite two chromophores in one molecule, one taking the role of energy donor (high energy absorbing chromophore) and the other being the acceptor (lower energy emitting fluorophore). In such tandem systems, a through-space energy-transfer process (*i.e.* Förster type) is believed to occur and this requires a significant overlap of the donor emission and acceptor absorption spectra, a requirement which determines the virtual Stokes' shifts. In general, readily synthesized, highly luminescent dyes showing large virtual Stokes' shifts should find numerous applications in direct multi-colour labeling experiments, obviating the need for highly sophisticated detection systems. The development of fluorescent energy-transfer devices on modified oligo-deoxynucleotides (ODNs) has provided an elegant means of enhancing detection sensitivity in DNA sequencing. One of the leaders in engineering such systems is pyrene and its analogues which provide suitable wavelengths of excitation (around 350 to 370 nm) and strong molar absorption coefficients of the same order of magnitude as the emitting dye (around 48 000 M^{-1} cm^{-1} per pyrene unity).

Modification of the fluorines in *F*-Bodipy by alcohol or phenol substitution affording *O*-Bodipy was also revealed to be a useful strategy for controlling fluorescence properties (compounds **17** to **21** in Chart 4).[21–25] In particular the validity

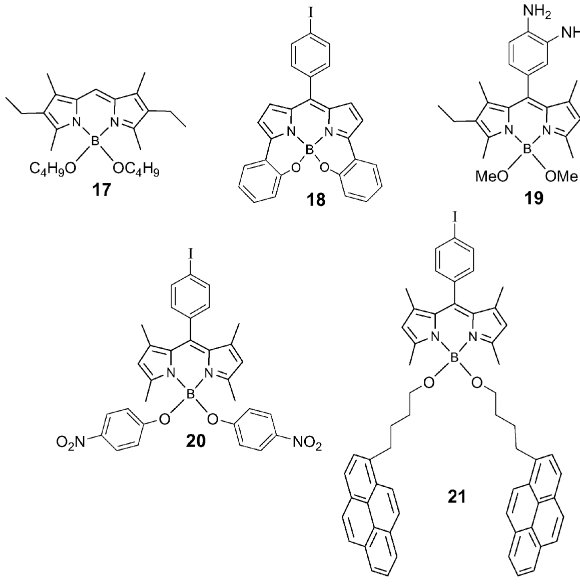

Chart 4

of this approach was confirmed by applying dye **19** as a highly sensitive fluorescent probe for nitric oxide.[23] Interestingly, controlling the position of nitrophenyl residues at the boron position such as in **20** allowed very high quantum yields to be maintained,[24] whereas in most other cases the fluorescence is heavily quenched by photoinduced electron-transfer processes.[26,27] Recent advances allow the connection of 1-pyrenebutanol to the boron centre in order to get energy-transfer from the pyrene to the appended dye. Unfortunately, due to the flexibility and the greater distance compared to dye **8** the energy-transfer is much less efficient and prone to non-radiative deactivation of the singlet excited state.[25]

Related hybrid-type *F*-Bodipy dyes, these being capable of functioning as photon concentrators, have been engineered around perylenediimide (PDI) frameworks by means of "click" chemistry.[28] The presence of four Bodipy units in **11** offers a large cross-section for light absorption in the visible region and, in this case, energy-transfer occurs from the Bodipy unit to the PDI central core, which fluoresces at 618 nm.

Fluorescence modulation/amplification has also been studied in tailor-made Bodipy dyes coupled with rationally designed fluoro-ionophores. Thus, compounds **12** and **13** (Chart 3) behave as molecular sensors and/or switches for transition metals ions and protons, respectively. The presence of a size-restricted dithia-aza-oxa macrocycle[29] in **12** provides an opportunity for Fe(III)-amplified fluorescence. Here, fluorescence from the free ligand is heavily quenched due to ultra-fast charge transfer from the electron-rich anilino receptor to the electron-affinic Bodipy. This process is switched off by coordination of the metal ion at the macrocyclic receptor. Likewise, for compound **13**, which bears a dimethylaminostyryl donor group, the fluorescence yield is strongly solvent dependent due to the occurrence of an intramolecular charge-transfer process.[30] Fluorimetric pH titrations indicate that protonation of the tertiary amine switches on fluorescence by curtailing the electron-transfer step. Interestingly, fluorescence excitation spectra reveal a bathochromic shift for the neutral amine with respect to the cationic form, thereby allowing ratiometric measurement of the pK_A.[30]

The orange/red colour of *F*-Bodipy dyes constructed from kryptopyrrole (2,4-dimethyl-3-ethyl-pyrrole) or Knorr's pyrrole (2,4-dimethyl-pyrrole) can be shifted to the blue or green regions by logical modification. This can be achieved either by replacement of the methyl group at the *ortho*-N position with vinylaryl groups, as in **14**,[12a,31] or by construction of aza-dipyrromethenes, as in **15**[32] and **16**.[33] Photophysical investigations have revealed that the blue dye **14** absorbs at 646 nm and fluoresces at 668 nm with 44% efficiency.[12a,31] Likewise, the green aza *F*-Bodipy **15**, which emits at 752 nm with 28%, and **16**, which emits at 823 nm, exhibit interesting near-IR spectral properties (see Table 1 for selected data).[12a,31,33]

Table 1 Selected spectroscopic data for the given complexes measured in various solvents (S) at rt

Cmpd (S)	λ_{abs}/nm	λ_F/nm	Φ_F[a]	τ_F/ns
1 ($CHCl_3$)	500	517	0.16	1.1
2 ($CHCl_3$)	525	569	0.75	3.7
3 (CH_2Cl_2)	528	544	0.90	7.0
4 (CH_2Cl_2)	526	544	0.60	5.0
5 (CH_2Cl_2)	516	552	0.50	5.7
6 (CH_2Cl_2)	523	577	0.25	2.0
7 (CH_2Cl_2)	517	537	0.90	9.5
8 (CH_2Cl_2)	516	535	0.86	6.2
9 (CH_2Cl_2)	516	535	0.63	7.6
10 (CH_2Cl_2)	516	535	0.86	6.8
11 ($CHCl_3$)	526	540	<0.01	—
12 (CH_3CN)	497	505	0.60	3.2
13 ($CHCl_3$)	605	656	0.82	3.5
14 (—)	646	668	0.44	—
15 ($CHCl_3$)	740	752	0.28	—
16 ($CHCl_3$)	799	823	—	—
21 (CH_2Cl_2)	673	704	0.49	14.6
22 (CH_2Cl_2)	727	780	0.20	7.2
24 (CH_2Cl_2)	667	702	0.56	14.8
25 (CH_2Cl_2)	720	754	0.33	6.5
26 (CH_2Cl_2)	525	538	0.50	7.3
27 (CH_2Cl_2)	510	539	0.25	5.1

[a] Relevant reference compounds are given in the corresponding original publications such as Rhodamine 6G, as reference Φ = 0.78 in water, λ_{exc} = 488 nm or Cresyl Violet Φ = 0.51 in EtOH, λ_{exc} = 578 nm.

Manipulation of the nature of the central core in bis-indolo frameworks offers further potential for the generation of a large array of next-generation dyes. In particular, substitution at the N-*ortho* positions of *F*-Bodipy by anisole or ethylthiophene residues substantially increases the extent of π-electron conjugation and pushes the absorption maximum to 673 and 727 nm, respectively, for **22** and **23** (Chart 5). In good accord with the exponential energy-gap law, there is a decrease in the quantum yield, from 49 to 20%, as the emission maximum moves towards lower energy. The strategy of conducting chemistry at the boron centre using ethynylaryl-Grignard reagents opens the route to produce the *cascatelle*-type dyes **24** and **25** for which the virtual Stokes' shifts exceed 13 000 cm^{-1} (see Table 1 for selected data).[34]

Clearly, the substitution patterns on the dipyrromethene core and on aza-Bodipy or diisoindolomethene platforms alter the spectroscopic features of the dyes. In some cases, the modification is just a consequence of synthetic expediency and is inconsequential but in most of the cases the substituents are introduced for specific reasons. In short, the use of kryptopyrrole or Knorr's pyrrole will shift the absorption and the emission to the red by 20 to 30 nm (case of molecules **1** to **12**). However, the chemical transformation of the 3,5 methyl groups to vinylphenyl groups with strong donor atoms induces a dramatic bathochromic shift to 650 nm (for one

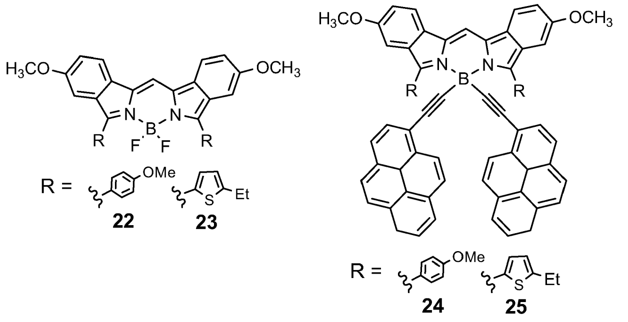

Chart 5

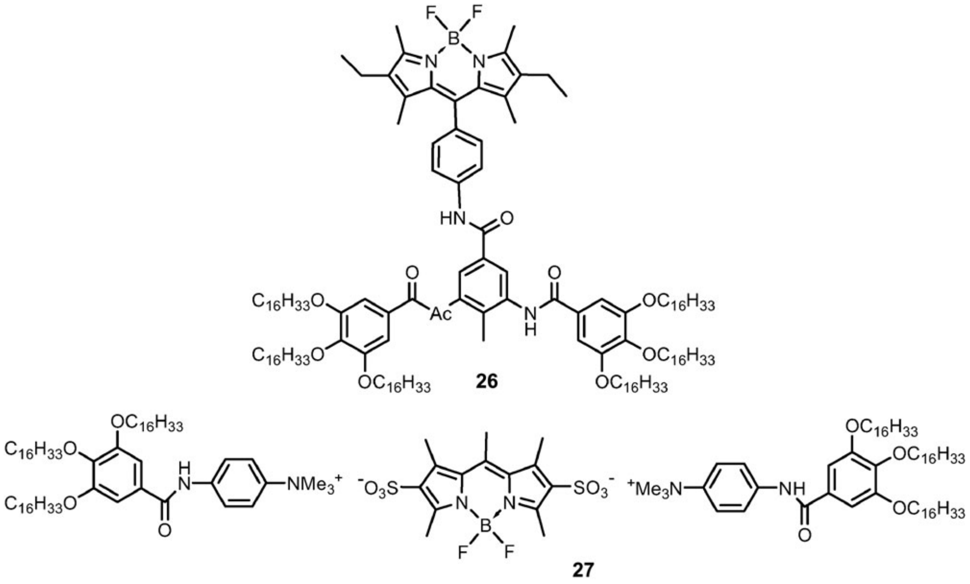

Chart 6

vinyl), to 668 nm in emission (for two vinyl groups) with respect to the previous dyes which emit around 520–540 nm. The strongest bathochromic shift is observed for aza-Bodipy's in which the central carbon (in the 8 position) is replaced by a nitrogen atom and also with conjugated π-systems tethered in the 3,5 substitution positions. Clearly, the increase of delocalization imparted by a more conjugated and planar vinyl system decreases the energy required to reach the excited state. The observed colour shifts from yellow-orange to blue and green in the most delocalized cyanine frameworks.

Substitution at the boron centre also causes modulation of the electrochemical properties. Indeed, the introduction of polycyclic substituents in place of the F atoms has serious implications for both oxidation and reduction potentials associated with the Bodipy units, despite the insulating nature of the B atom.[20] Such perturbations of the HOMO and LUMO positions are of great importance for the rational design of electro-luminescent devices by adjusting these levels in respect to the work functions of the actual electrodes. The potential use of Bodipy dyes in electroluminescent devices is being actively pursued by several industrial leaders.[35]

Consideration can also be given to modification of the Bodipy architectures so as to enable their incorporation into supramolecular assemblies, such as liquid-crystalline materials or organo-gelators.[36] To date, entangled three-dimensional networks of fibers entrapping solvent molecules have been produced by grafting paraffin chains onto pre-organized platforms carrying amido functions, as in **26** (Chart 6). Balancing the mole fractions of paraffin chains and the rigid aromatic core provides columnar mesophases, the symmetry of which depends strongly on weak intermolecular interactions.[37] Finally, the use of ionic self-assembled adducts like **27** provides a relatively easy way in which to generate liquid-crystalline materials and thin films that are stable over a wide temperature range. The flexibility caused by the ready exchange of ionic components and the use of highly fluorescent templates allows the emergent mesomorphic textures to be monitored by fluorescence microscopy without the need for cross polarizers.[38]

Future perspective

The expansive field of classical Bodipy dyes has been greatly enriched by the recent development of new types of expanded frameworks and of B-substituted dyes. The growth of new structures, being mirrored by the potential for new applications, has been astounding and has created a highly promising career for ''porphyrin's little sister'' at the frontier between chemistry (*i.e.*, the development of new dyes), physics (*i.e.*, tuning the emission and transfer properties), biology (*i.e.*, labeling, mapping and imaging), engineering (*i.e.*, device manufacture) and supramolecular science (*i.e.*, self-assembly into organogels, mesophases and thin films). The selected examples discussed here represent an important advance in these diverse areas that overcomes many of the hurdles that have constrained conventional reagents. This is especially true for the *C*-Bodipy and *E*-Bodipy dyes where radically improved properties can be accomplished by straightforward synthetic approaches. Such exciting features are a source of inspiration for chemists to design, synthesize and characterize new architectures for multi-colour imaging and energy-conversion devices.

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