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Synthesis, fluorescence and two-photon absorption properties of multichromophoric boron-dipyrromethene fluorophores for two-photon-excited fluorescence applications

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Abstract—The synthesis and the characterization of new multichromophoric boron-dipyrromethene dyes are described. Their absorption, photoluminescence as well as their two-photon absorption properties have been investigated. This work shows that assembling several dyes in conjugated multichromophoric structures is a promising strategy for improving the two-photon absorption properties of such fluorophores in the NIR region while retaining their excellent photoluminescence properties.

For more than a decade, two-photon absorption (TPA) has attracted increasing attention in relation with various applications, such as 3D microfabrication[1] and optical data storage,[2] photodynamic therapy,[3] and optical power limiting.[4] Moreover, two-photon-excited fluorescence (TPEF) has been found to be of particular interest for the biology community: two-photon laser scanning fluorescence microscopy (TPEFLSM) offers the advantages of imaging deeper in living tissues (down to 500 μm), with reduced photodamages and background fluorescence and with sharp 3D spatial resolution.[5] The advantages of TPEFLSM call for the design of new fluorophores whose TPA cross-sections are optimized in the spectral range of interest for biological imaging (700–1200 nm). Indeed designing molecular fluorophores with a much higher TPA cross-section than endogenous chromophores[6] and conventional fluorophores such as fluorescein or rhodamine,[7] would allow to reduce the concentration of fluorophores and molecular markers and/or the excitation intensity, which is highly desirable for biological imaging.[8] Key parameters for the design of new TPE fluorophores and markers for biological imaging are high fluorescence quantum yield Φ and very large TPA cross-section (σ_2). In addition, excellent photostability and low (photo)toxicity are required.

Boron-dipyrromethene dyes (Fig. 1) belong to a modern class of fluorophores showing attractive properties: tunable photoluminescence in the 500–650 nm spectral range, high fluorescence quantum yield in various media (including water in the case of water-soluble derivatives), long enough fluorescence lifetime (about 5 ns).[10–20] In addition, both hydrophilic and lipophilic derivatives can be prepared via grafting of suitable side groups on the pyrrole moieties. Boron-dipyrromethene fluorophores have been used in fluorescent probes for various applications including cation sensing,[21] ionofluorophores,[22] dosimetric reagents,[23] monitoring

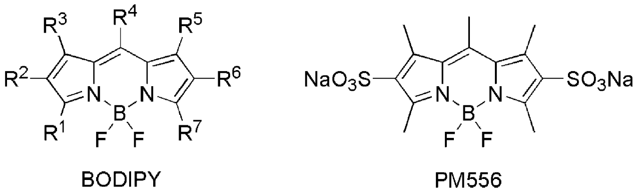

Figure 1. Left: general structure of boron-dipyrromethenes (BODIPY®). Right: structure of water-soluble 4,4-difluoro-1,3,5,7,8-pentamethyl-4-bora-3a,4a-diaza-*s*-indacene-2,6-disulfonic acid, disodium salt[27] (PM556).

Keywords: Two-photon-excited fluorescence (TPEF); Multichromophores; Photoluminescence; BODIPY®.

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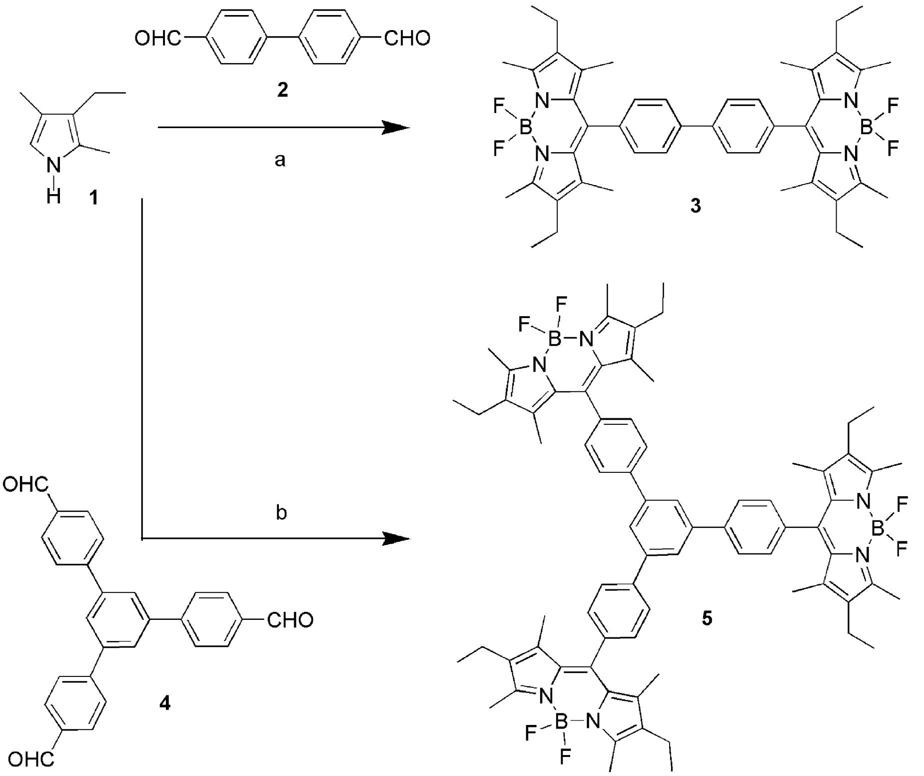
of bioactivity (NO imaging),[24] live-cell imaging[25] and even in TPEF-based fluoroimmunoassays.[26] However, these compounds have not yet been optimized for TPA and their TPEF cross-sections remain low.[7] In this letter, we describe the strategy that we have implemented towards improved TPEF.

Our approach is based on the design of multichromophoric boron-dipyrromethene assemblies, where dyes moieties are assembled in defined geometries by using conjugated rigid spacers (Scheme 1). Although much work has been carried out in the past on multichromophoric assemblies in the field of second-order nonlinear optics,[28] the mutichromophoric strategy is very recent in the field of TPA.[29,30]

Based on our earlier work on the design of nanoscale elongated quadrupolar and octupolar derivatives built from either a biphenyl[31] or a triphenylbenzene[30,32] core and displaying giant TPA cross-sections, we chose to use biphenyl and triphenylbenzene as rigid spacers connecting the boron-dipyrromethene fluorophores. However, in contrast to our previous work, we chose to focus on short derivatives to maintain compact size/volume. In addition, we did not introduce ethynylene or vinylene intermediary linkers to ensure high photostability. Hereafter, we will describe the synthesis, photoluminescence and TPA properties of such bis-chromophoric and tris-chromophoric derivatives. An important issue is to investigate how the approach implemented here affects the photoluminescence and TPA properties.

The bis-chromophoric dye **3** was synthesized from (1,1′-biphenyl)-4,4′-dicarboxaldehyde[33] (**2**) and 4 equiv of 2,4-dimethyl-3-ethylpyrrole (**1**) (Scheme 1). The synthesis proceeds in three steps: first addition of TFA to the mixture of aldehyde and pyrrole to give in situ the corresponding dipyrromethane, then conversion of the latter into dipyrromethene by oxidation with DDQ, and finally treatment with an excess of trifluoroboron-etherate in the presence of base to afford the corresponding boron complex. The tris-chromophoric dye **5** was prepared by reacting the trialdehyde **4**[34] with 6 equiv of the pyrrole **1** (Scheme 1), using a procedure similar as that for **3**. The new fluorophores **3** and **5** have been fully characterized by NMR and HRMS.[35]

The absorption and photoluminescence characteristics (including fluorescence quantum yields and fluorescence lifetimes) of the series of dyes are gathered in Table 1. As illustrated in Figure 2, chromophores **3** and **5** exhibit an intense and sharp absorption band in the visible region. Both dyes present similar photophysical properties. Both the energy absorption and emission band peaks are at the same wavelength, and absorption and emission bands show identical width and vibronic structure. In addition, the molar extinction coefficients were found to increase linearly with the number of boron-dipyrromethene chromophores while the fluorescence quantum yields and lifetimes remain the same (Table 1). This indicates that the excitation energy is localized on the boron-dipyrromethene moieties and that emission occurs from these units, thus retaining the excellent



Scheme 1. Reagents and conditions: (a) **1** (4 equiv), **2** (1 equiv), TFA, CH_2Cl_2, rt, 2 h, then DDQ (2 equiv), rt, 1 h, then *i*-Pr_2NEt, BF_3–Et_2O (excess), rt, 1 h (overall yield 42%); (b) **1** (6 equiv), **4** (1 equiv), TFA, CH_2Cl_2, rt, 2 h, then DDQ (3 equiv), rt, 1 h, then *i*-Pr_2NEt, BF_3–Et_2O (excess), rt, 1 h (overall yield 23%).

Table 1. One and two-photon photophysical data of fluorophores **3** and **5**

Compd	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Φ[d]	τ[e] (ns)	σ_2 (GM)[f]	
						at 700 nm	at 990 nm
3[a]	527	161,900	542	0.72	4.76	57	48
5[a]	527	244,300	542	0.69	4.78	82	75
PM556[b]	491[g]	98,600[g]	519[g]	0.83[g]	4.23[g]	—	9 (20[h])[i]
Fluorescein[c]	491	75,500	515	0.90		18[i]	13[i]

[a] In toluene.

[b] In water.

[c] In water, pH 11.

[d] Fluorescence quantum yield determined relative to fluorescein in 0.1 N NaOH.

[e] Experimental fluorescence lifetime using time-correlated single photon counting.

[f] TPA cross-sections; 1 GM = 10^{-50} cm^4 s $photon^{-1}$; TPEF measurements were performed using a mode-locked Ti:sapphire laser delivering 80 fs pulses at 80 MHz, calibrated with fluorescein.[7]

[g] Data from lit.[13]

[h] TPA cross-section at 920 nm.

[i] Data from lit.[7]

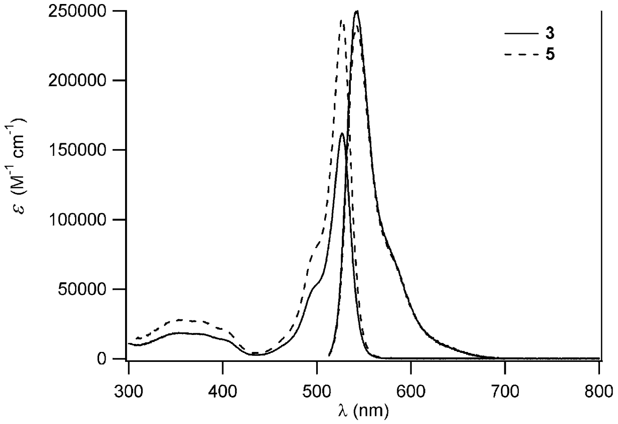


Figure 2. Absorption and fluorescence emission spectra of dyes **3** and **5** in toluene.

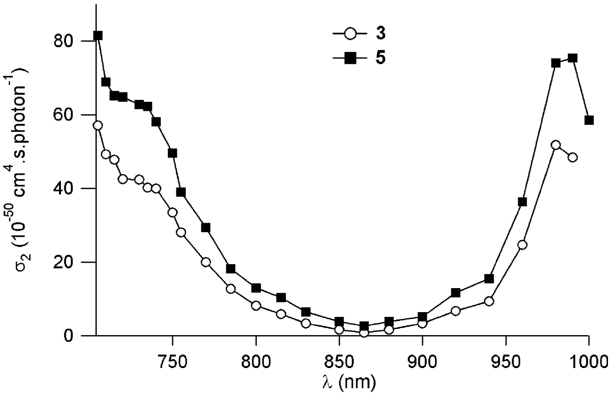


Figure 3. TPA spectra of dyes **3** and **5** in toluene.

photoluminescence properties of the boron-dipyrromethene fluorophores.

The TPA spectra of multichromophoric dyes **3** and **5** (Fig. 3) were determined in the NIR range (700–1000 nm) by investigating the two-photon-excited fluorescence (TPEF) in 10^{-4} M toluene solutions using a mode-locked Ti:sapphire laser delivering 80 fs pulses at 80 MHz, following the experimental protocol described by Xu and Webb.[7] The quadratic dependence of the fluorescence intensity on the excitation intensity was verified for every data point. TPEF measurements were calibrated relative to the absolute TPEF action cross-sections determined by Xu and Webb for fluorescein in water (pH = 11) in the 690–1000 nm range.[7,36] This procedure provides the TPEF action cross-section $\sigma_2\phi$ from which the corresponding σ_2 value is derived. Selected data are included in Table 1. Literature TPA data for PM556 and fluorescein[7] are also shown for comparison.

The TPA cross-sections of bis-chromophoric dye **3** and tris-chromophoric dye **5** were found to be of 48 and 75 GM at 990 nm, respectively, which correspond to about 2.4 and 3.7 times that of PM556 at its maximum (σ_2^{max} = 20 GM at 920 nm). This reveals a reasonable increase (20% for **3** and 25% for **5**) of the lower energy TPA maxima in the assemblies as compared to the additional contribution of two or three independent PM556 chromophores. More importantly, we observe the emergence of *a new and more intense TPA band* at lower wavelength that is not present in the TPA spectrum of the reference boron-dipyrromethene dye.[7] As a result, multichromophoric fluorophores **3** and **5** show much larger TPA cross-section at 700 nm than single boron-dipyrromethene dyes. This higher energy two-photon excitation band responsible for the marked TPA enhancement at 700 nm is most probably related to the presence of the biphenyl and triphenylbenzene linkers (in relation with the weakly one-photon allowed absorption band observed at 350 nm). It should be stressed however that the TPA cross-section of both the biphenyl or triphenyl benzene moieties and of the boron-dipyrromethene are quite low at 700 nm emphasizing that the combination of these conjugated linkers with the boron-dipyrromethene moieties leads to a cooperative enhancement of the TPA responses as compared to an additive behaviour. The modular multichromophoric strategy implemented here thus opens an interesting route for TPA enhancement and could be extended to other types of conjugated connectors, including dendrimers.

In conclusion, the multichromophoric approach based on the grafting of multiple boron-dipyrromethene fluorophores on suitable cores that act as two-photon absorption enhancers indicates that the multichromophoric approach is a valid strategy for improving the TPA properties. This novel approach towards improved TPEF labels and probes offers several advantages because it allows retaining the excellent characteristics of the boron-dipyrromethene fluorescent units while taking advantage of the connectors for TPA modulation and enhancement. This leaves space for further engineering and spectral tuning of the TPEF properties in multichromophoric assemblies. In particular, the molecular engineering routes for optimization of the TPA properties of quadrupoles[31,37] and octupoles[38] could be successfully applied for the design of optimized multichromophoric architectures. Furthermore, it would be interesting to assemble a *large* number of chromophoric units in dendritic structures where the dendritic core could serve as a TPA enhancer.

Acknowledgements

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