We are IntechOpen,
the world's leading publisher of Open Access books
Built by scientists, for scientists

6,900
Open access books available

186,000
International authors and editors

200M
Downloads

154
Countries delivered to

Our authors are among the

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

BOOK CITATION INDEX
CLARIVATE ANALYTICS
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Chapter

Photophysics of BODIPY Dyes: Recent Advances

Seda Çetindere

Abstract

BODIPY dyes are unique fluorophores that can be used in numerous application areas because of their interesting photophysical properties such as high molar absorptivity, tunable absorption and emission energies, and high fluorescence quantum yields. They show impressive photophysical property changes upon substitution of functional groups on the main core structure. Exchange of the meso-carbon on dipyrrin core with nitrogen produces an analog class of BODIPY called aza-BODIPY. Up to now, various kinds of BODIPY and aza-BODIPY derivatives have been developed and applied in science and industry. In this chapter, recent studies on photophysical properties of BODIPY derivatives are summarized.

Keywords: BODIPY, aza-BODIPY, fluorescence, fluorophore, photophysical property

1. Introduction

In the constantly expanding multi-disciplinary science world, fluorescent dyes attract the attention of researchers. 4,4-Difluoro-4-bora-3a,4a-diaza-s-indacene (abridged as BODIPY) dyes are compounds that are rapidly increasing in importance among fluorescent organic dyes [1]. BODIPY core is formed from the complexation of a dipyrromethene ligand with a disubstituted boron moiety, typically in the form of BF_2 [1–4]. The first BODIPY was synthesized by Treibs and Kreuzer in 1968 by accident through the combining of 2,4-dimethylpyrrole and acetic anhydride in the presence of $BF_3.OEt_2$ [5]. Although the basic procedure for the synthesis of BODIPY core usually starts from a simple pyrrole condensation with a highly electrophilic carbonyl compound (e.g., aldehyde, acid anhydride, and acyl chloride), the three major routes of BODIPY synthesis are from pyrroles and acid chlorides or pyrroles and aldehydes or ketopyrroles [1]. BODIPY derivatives absorb strongly visible region, have relatively sharp emission peaks, possess high fluorescence quantum efficiencies (Φ ca. 0.5–0.8), high molar absorption coefficients ($\varepsilon > 7 \times 10^4\,M^{-1}\,cm^{-1}$), and have relatively small Stokes' shift (around 10 nm) [1–4]. Besides, most BODIPY dyes indicate thermal and photostability in solid and solution phases are highly soluble in most organic solvents and are insensible to solvent polarity and pH [6, 7]. The BODIPY core (see the core structure and numbering in **Figure 1**) can be easily modified to bear desired functionalities at α-, β-, and meso-positions as well as through substitution of the fluorine. The addition of functional groups to the BODIPY core can have varying effects depending upon the placement and symmetry of the substituent [8, 9]. Symmetrical BODIPYs (substitution from 1,7- or 3,5-positions) appear to produce more red-shifted absorptions compared
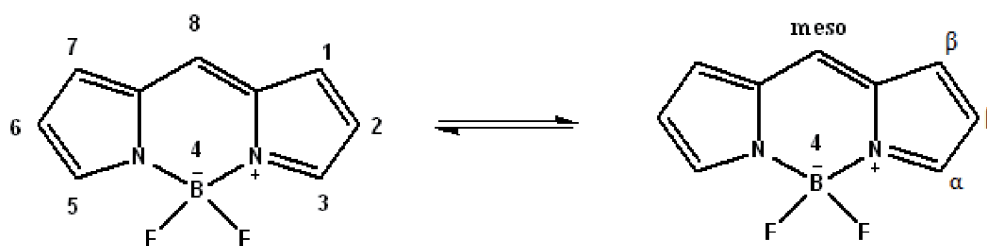
Figure 1.
Chemical structure and numbering of BODIPY core.

to either equally substituted asymmetric counterpart (substitution from 1,3- or 5,7-positions). However, the greater substitution of the BODIPY core does not necessarily produce a larger bathochromic shift, as depicted upon the comparison of the penta-substituted BODIPY (substitution from 1,3,5,7- and 8-positions) to the tetra-substituted BODIPY (substitution from 1,3,5,7-positions) [8, 9]. Red to near infrared (NIR) shifts are generally attained owing to the straightforward modification to the BODIPY core with the extension of the degree of π-delocalization. Also, the emissive behavior of BODIPY fluorophores is much affected by steric and electronic interactions of substituent moieties. Rotation of pendant components as well as their electron-donating or withdrawing effects on the conjugated core greatly influences both the brightness and absorptive and emissive properties of BODIPY [10].

Due to these excellent photophysical characteristics, BODIPY dyes increase their potential using in different applications such as fluorescent labels for biomolecules and cellular imaging [11–15], light-emitting devices [16–18], drug delivery agents [19–21], photosensitizers [22–24], fluorescent switches [25], chemosensors [26–29], energy transfer cassettes [30–33], and solar cells [34–37]. In this chapter, general photophysical properties of BODIPY and aza-BODIPY derivatives and recent studies on the photophysical properties of these dyes are presented.

2. Photophysical properties of BODIPY dyes

BODIPY dyes possess interesting photophysical properties such as high fluorescence quantum yields and narrow emission bandwidths with high peak intensities, elevated photostability, relatively high absorption coefficients, and the extra feature of excitation/emission wavelengths in the visible region. The absorption and fluorescence properties of BODIPY dyes are highly influenced by the extent of electron delocalization around the core and through conjugated substituents, and as such, may be tuned to have photophysical characteristics. BODIPY dyes show a strong, narrow absorption band in the visible region signifying the S_0-S_1 (π-π*) transition with a shoulder of high energy around 480 nm assigned to the 0–1 vibrational translation. A broad, much weaker band around 350 nm denotes the S_0-S_2 (π-π*) transition [38]. Upon excitation to either the S1 or S2 states, an equally narrow emission band of mirror image to the absorption spectra is observed from the S1 state. Most of the BODIPY dyes emit at wavelengths less than 600 nm, routinely providing yellow to green emissions (500–590 nm) [2, 39]. The fluorescence emission wavelength of BODIPY can be controlled by suitable substitution of chemical fragments such as aliphatic carbon, aromatic ring, pi-bond conjugation, halogens, and electron-withdrawing or donating groups. The pi-bond prolongation on 3 and 5 positions of BODIPY core gives the red-shifted fluorescence emission wavelength [1]. On the other hand, the substitution of electron-donating groups such as amine or alkoxy groups on the 8-position (so-called meso-position) of BODIPY gives

the blue-shifted fluorescence emission wavelength [1]. Unsubstituted BODIPY typically absorbs near 500 nm and emits around 510 nm. Small Stokes' shifts are routinely seen and indicate a modest change in the core structure following S_0-S_1 transition and vibrational relaxation [40].

The groups that substituted onto the BODIPY scaffold can adjust the photophysical properties of BODIPYs [1]. The addition of functionality at any position of the aromatic core alters the photochemical profile to varying degrees, dependent upon the groups added. BODIPY based dyes containing methyl groups at positions 3- and 5- can be functionalized with aromatic compounds with the help of the Knoevenagel reaction [41]. The 2,6-positions of the BODIPY core tend to give an electrophilic substitution reaction. Decorating the BODIPY skeleton from 3,5-positions generally produces a greater bathochromic shift (ca. 50–100 nm) than adding conjugation through the 2,6-positions, displaying the greatest shift when all four methyls have converted to styryl groups [42]. Although the tetra-styryl BODIPY has been synthesized by activation and subsequent condensation of the 1,3,5,7-methyls [43], an extension of π-conjugation and addition of functionality is most frequently accomplished through the 3,5-methyls. Thus, the visible region of different BODIPY derivatives can be largely scanned, resulting in a wider range of use.

From past to present, many research groups have been studying BODIPY and its derivatives. Consequently, there are many reported papers about the photophysical properties of BODIPY derivatives, especially in recent years. In 2014, Majumdar et al. [44] reported the synthesis of four styryl-BODIPY-containing Ir(III) complexes which show strong NIR absorption (644–729 nm), strong NIR fluorescence (700–800 nm), and long-lived triplet excited states (92.5–156.5 μs). Investigations of the photophysical properties of these complexes showed that they were strongly fluorescent, although the p-conjugation is present between the BODIPY ligands and the Ir(III) coordination center. Moderate intersystem crossing (ISC) was observed for the complexes, proved by the population of the long-lived intraligand triplet excited state (^{3}IL) and the singlet oxygen (^{1}O$_2$) photosensitizing property. Based on the property of NIR absorption/fluorescence and the reasonable ^{1}O$_2$ quantum efficiency, the complexes were used as multi-functional materials as luminescent bioimaging reagents and in intracellular photodynamic studies. Also, they reported that their results are useful for the preparation of NIR absorbing cyclometalated Ir(III) complexes, and the relevant application of these complexes as multifunctional materials such as a luminescent bioimaging reagent, in photodynamic therapy (PDT) and photocatalysis. At the same year, a 2,6-distyryl-substituted BODIPY dye and a new series of 2,6-p-dimethylaminostyrene isomers containing both α- and β-position styryl substituents were reported by Gai et al. [45]. They used styrene and p-dimethylaminostyrene with an electron-rich diiodo-BODIPY in the synthesis of these compounds. They indicated that the absorption spectra contain red-shifted absorbance bands due to conjugation between the styryl moieties and the main BODIPY fluorophore. Besides, very low fluorescence quantum yields, and significant Stokes shifts were observed for 2,6-distyryl-substituted BODIPYs, concerning like 3,5-distyryl- and 1,7-distyryl-substituted BODIPYs. In spite of the fluorescence of the compound with β-position styryl substituents on both pyrrole fragments and one with both β- and α-position substituents was fully quenched, the compound with only α-position substituents displays weak emission in polar solvents, but strong emission with a quantum yield of 0.49 in hexane. They enounced that 2,6-p-dimethylaminostyrene isomers can be used as sensors for changes in pH. Two novel azomethine-BODIPY dyads were reported by Pan et al. [46]. These two dyads have been synthesized by covalent tethering of tautomeric ortho-hydroxy aromatic azomethine moieties including N-salicylideneaniline (SA) and N-naphthlideneaniline (NA) to a BODIPY fluorophore. Both two dyads showed

enol-imine (OH) structures dominating in the crystalline state. For the first dyad, in the enol state is the most stable form at room temperature in most environments, while enol-keto prototropic tautomerism of the NA fragment in solution is maintained in the second dyad, which can be reversibly modified between enol and keto forms in the environment's polarity. Visible lighting of the second dyad in the enol case excites selectively the BODIPY moiety and then counteracts radiatively by emitting green light in the form of fluorescence, while the emission intensity of the second dyad in the keto case is quenched based on the proton-coupled photo-induced electron transfer (PCPET) mechanism. This permits to large fluorescence modulation among the two states of the second dyad and creates a new tautomerisable fluorescent switch. Photophysical properties of a pyrene-based tetramethyl difluoroborondipyrromethane (PYBDP) were investigated by Yang et al. [47]. The PYBDP showed a higher fluorescence quantum efficiency and Stokes shift than other phenyl-substituted laser dyes in the green region. Under transversal pumping conditions, this new dye exhibited highly effective and stable emissions centering at 531 nm. The PYBDP dye exhibited a maximum narrow band amplified spontaneous emission (ASE) lasing yield of 10.86% with an extensive adjustable range (525–560 nm) under demanding transversal pumping at 355 nm in toluene. The lasing efficiency remains unaffected in 1 h but a dramatic decrease or even the loss of the laser action is observed in intermediate or highly polar solvents. The combination of excellent photostability and tunability of ASE makes PYBDP a potentially green-emitting laser dye in the green-orange region. In a reported study from our working group [48] was about the treatment of boron (III) subphthalocyanine chloride with borondipyrromethene derivatives containing either one or two [4-(N,N-dimethylamino)phenyl]ethenyl groups in toluene gave the corresponding axially substituted boron(III) subphthalocyanine dyes (**Figure 2**). Methyl groups on 3- and 5-positions have acidic hydrogens due to electron-withdrawing property of heterocyclic BODIPY ring. This acidic property can be taken advantage of, in the synthesis of other BODIPY fluorophores for example with aromatic aldehydes. For this reason, N,N-dimethyl-4-aminobenzaldehyde was reacted with BODIPY, resulting in extension of conjugation in our study. This extension of conjugation allowed us to shift the absorption and emission spectra to longer wavelengths. The reaction was performed in a solution containing acetic acid and piperidine. The solvent was toluene because any water forming in the reaction should be removed. Dean-Stark apparatus is a good choice because water can be removed azeotropically during reflux. The photophysical properties of these compounds were examined utilizing absorption and fluorescence spectroscopy in dilute benzene solutions. They
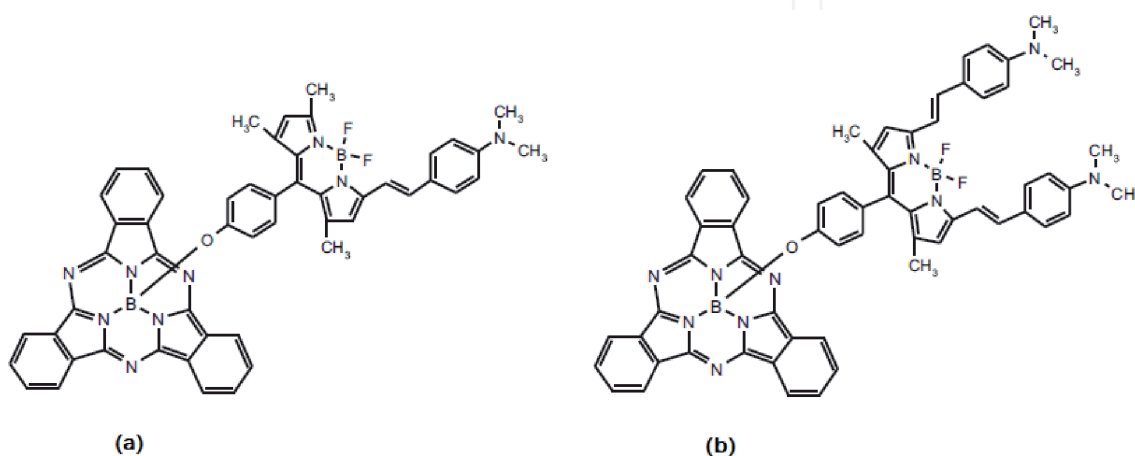

(a)   (b)

Figure 2.
Chemical structure of (a) mono-styryl and (b) distyryl-BODIPY substituted subphthalocyanines.

exhibited a highly efficient energy transfer process from the excited subphtha-locyanine (SubPc) unit to the BODIPY unit. Increased $^1O_2$ production was noted for BODIPY substituted SubPc compounds relative to their BODIPY precursors; a feature that may be useful for PDT application of these dyes.

The effect of the substituent side groups like phenyl (Ph), phenylethynyl (Ethyn) and styryl moiety at the 2-, 3- or 8- position of the BODIPY scaffold was reported by Orte et al. [49]. A large number of solvents (methanol, acetonitrile, diethyl ether, acetone, ethyl acetate, 2-propanol, isobutyronitrile, dibutyl ether, tet-rahydrofuran, 1-pentanol, 1,4-dioxane, dichloromethane, cyclohexane, 1-octanol, chloroform, cyclohexanone, toluene, chlorobenzene) were used for investigation of the photophysical properties of these compounds. A substitution from 3-position is beneficial for producing BODIPYs with sharp absorption bands and high fluores-cence quantum yields. Contrarily, substitution at the 2-position yielded BODIPY dyes with large Stokes shifts and broad bands. Substitution at the meso-position produced dyes with features like the 3-substituted ones, except for meso-phenyl BODIPY (8-Ph). Between the phenyl-substituted BODIPY dyes, some differences in absorption behavior were observed. The presence of the p-tert-butylphenyl moiety shifts the absorption maximum, λ_{abs}(max) from 516 to 530 nm when this group is at the 2-position (2-Ph) to 513–527 nm and when it is at the 3-position (3-Ph). In these two statuses, λ_{abs}(max) is more red-shifted in the more polarizable solvents toluene and chlorobenzene. Conversely, the values of λ_{abs}(max) of 8-Ph are blue-shifted concerning those of 2-Ph and 3-Ph and are close to those of unsubstituted BODIPY [50, 51], ranging from 489 nm in acetonitrile to 497 nm in toluene and chloro-benzene. This absorption energy range is in good agreement with that of other BODIPYs substituted at the meso-position with a weak electron acceptor or donor [52, 53]. For the phenylethynyl BODIPYs, the absorption spectra show also the characteristic properties of typical BODIPYs. 2-Ethyn possessed an absorption max-imum between 503 and 525 nm, whereas the λ_{abs} (max) of 3-Ethyn changes between 525 and 545 nm. For the two dyes, the lowest λ_{abs} (max) value was founded in ace-tonitrile and the highest in cyclohexane. The influence of the substitution positions (2 vs. 3) on λ_{abs}(max) is much higher for the phenylethynyl fragment than for the phenyl moiety and moving the p-tert-butylphenyl substituent from the 2-Ph to the 3-Ph causes a 3 nm blue shift of λ_{abs}(max), while the similar change from 2-Ethyn to 3-Ethyn results in a ca. 20 nm red shift of λ_{abs}(max). 8-Ethyn is bathochromically shifted for 2-Ethyn and 3-Ethyn, with λ_{abs}(max) ranging from 537 to 547 mm which is parallel with an increasing refractive index [54]. Styryl-substituted BODIPYs (2-Styryl, 3-Styryl and 8-Styryl) displayed different absorption properties. The λ_{abs}(max) values range from 549 to 561 nm, with a typical redshift from acetonitrile to chlorobenzene. The extended conjugation ensured by the styryl functional group reasons an extra bathochromic shift of around 20 nm for 3-Ethyn, and ca. 30 nm for 3-Ph. Conversely, 2-Styryl and 8-Styryl show clear dual-band absorption and emission behavior. The photophysical reaction of two BODIPY-based D−A and A−D−A molecules, where D is the donor and A is the acceptor was reported by Hendel et al. [55]. A BODIPY fragment was given as the A component and was attached through the meso position using a 3-hexylthiophene linker to an N-(2-ethylhexyl) dithieno[3,2-b:2′,3′-d] pyrrole (DTP), which was given as the D component. An A−D−A molecule was compared to its corresponding D − A dyad counterpart. This showed a potential advantage to the A−D−A molecule over the D−A dyad in creating longer-lived excited states. A−D−A possess slightly longer excited-state lifetimes, 42 ps nonradiative decay, and 4.64 ns radiative decay compared to those of D−A, 24 ps nonradiative decay, and 3.95 ns radiative decay. These results show a full picture of the electronic and photophysical properties of D−A and A−D−A that provide contextualization for structure-function relationships between molecules

and organic photovoltaic (OPV) devices. A type of fluorescent chemosensor based on tethered hexa-borondipyrromethene cyclotriphosphazene platform (HBTC) (**Figure 3**) linked via triazole groups reported by our working group [56]. Its sensing behavior toward metal ions was investigated. Addition of a Fe^{2+} ion to a tetrahydrofuran (THF) solution of HBTC gave a visual color change as well as a significantly quenched fluorescence emission, while other tested 19 metal ions (Fe^{2+}, Al^{3+}, Ba^{2+}, Ca^{2+}, Co^{2+}, Ag^+, Cd^{2+}, Cr^{3+}, Cs^+, Cu^{2+}, Fe^{3+}, Hg^{2+}, K^+, Li^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+}, and Zn^{2+}) induced no color or spectral changes. This compound was found to be highly selective and sensitive for Fe^{2+} with a low limit of detection (2.03 μM). HBTC is a potential selective and sensitive fluorescence chemosensor for imaging Fe^{2+} in the living cells.

A synthetic approach for palladium-catalyzed direct $C(sp^3)$-H arylation of the methyl group at the 8-position of BODIPY reported by Chong et al. [57]. This approach permitted attaching electron-donating/withdrawing, halogen-substituted aryls and a heteroaryl with a yield running from 55 to 99%. Novel pH sensors, which in the lack of acid demonstrated the photoinduced electron transfer (PET), were synthesized by linking dimethylaniline to the methyl at the C8-position of BODIPY. The reference compounds with dimethylaniline directly linked to the C8-position were also synthesized and PET showed a charge-transfer emission. Addition of trifluoroacetic acid (TFA) onto toluene and ethanol, the fluorescence intensity was at least an order of magnitude more effective with the synthesized sensors compared to the traditional reference sensors. The developed sensibility of these BODIPY-based pH sensors was connected to less effective proton-coupled electron transfer of the protonated types. This approach could pave a new way for the convenient syntheses of functional BODIPY molecules. Two
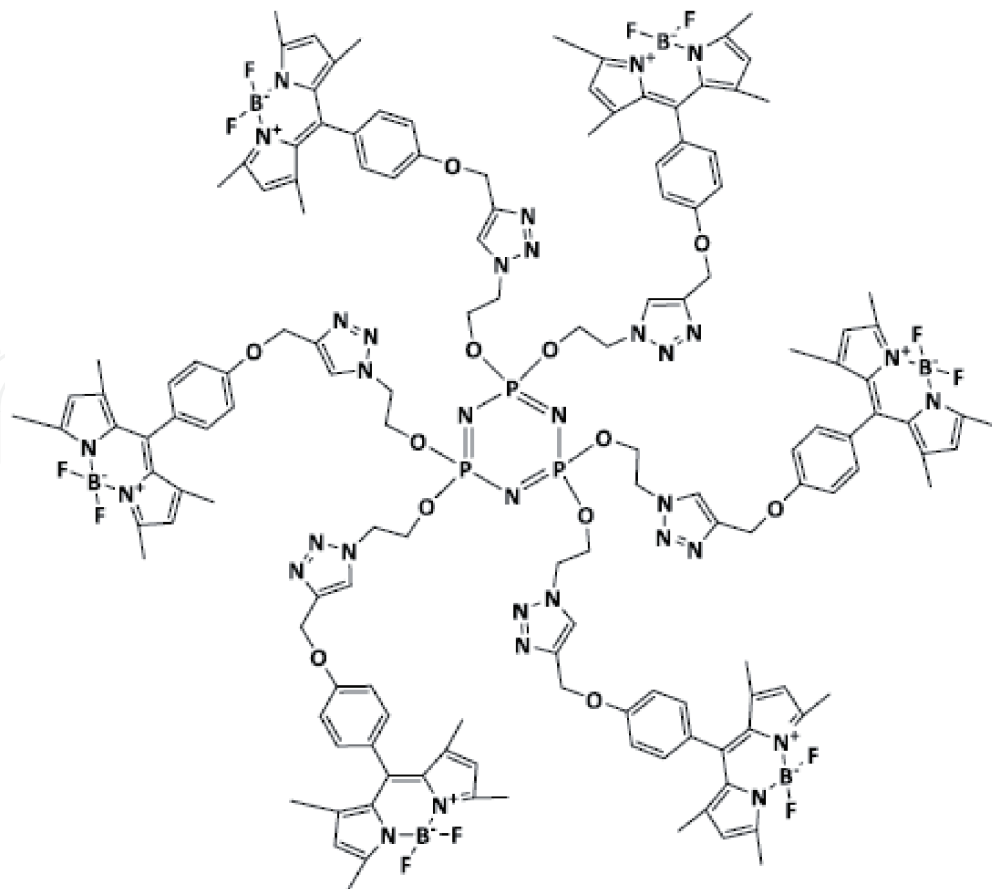

Figure 3.
Chemical structure of HBTC.

cyclotriphosphazene compounds bearing mono- and distyryl BODIPY substituents reported in 2017 (**Figure 4**) [58]. The photophysical properties of these cyclotriphosphazene compounds were examined in THF solutions. All these heavy atom free compounds indicated very limited fluorescence emission and $^1O_2$ generation owing to the internal charge transfer (ICT) that occurred between BODIPY core and dimethylaminobenzyl groups. These properties were also investigated by the protonation of the studied compounds. Fluorescence emission and $^1O_2$ generation attitudes of these compounds were dramatically increased after the addition of acid because the ICT effect was blocked owing to the protonation of the nitrogen atoms on the dimethylamine groups. These compounds can be used as potential photosensitizers that can be used as efficient singlet oxygen generators.

Six different molecules including 3,5-distyryl-BODIPY backbones were reported by Kang et al. [59] and the $^1O_2$ photosensitizing experiments of dibromo substituted BODIPY compounds and two boronic acid ester substituted BODIPY compounds were investigated. The $^1O_2$ quantum yields of dibromo substituted BODIPYs were calculated as 0.075 and 0.44 and the $^1O_2$ quantum yields of boronic acid ester substituted BODIPYs were not more than 0.07. It was indicating that halogenation on the benzene rings of 3,5 distyryl-BODIPYs or boronate esterification of BODIPY had no positive effect on $^1O_2$ production, while halogenation on the 2/6 position resulted in seemingly increased $^1O_2$ efficiencies. The results would enrich the research of BODIPYs and would provide a useful envision for the preparation of powerful BODIPYs drugs for the PDT process. An excited-state intramolecular proton transfer (ESIPT) meso linked BODIPY dyad (Bn-OH-BDY) was reported by Mallah et al. [60]. The fluorescence lifetime of Bn-OH-BDY dyad was recorded 5.71 ns. A large shift of 255 nm has been monitored between excitation and emitted light. Excitation (λ_{exc} = 290 nm) of the Bn-OH-BDY dyad leads to emission (λ_{emi} = 545 nm) directed by the BODIPY subunits pointing to excitation energy transfer (EET) from the ESIPT to BODIPY core. Two cyclotriphosphazene (Cpz) compounds bearing mono- and distyryl(pyrene) BODIPY dyes (**Figure 5**) reported in 2019 [61]. These compounds indicated intense fluorescence emission even at very low concentrations. In accordance with absorption and emission spectra of Cpz compounds, di-styryl pyrene BODIPY containing Cpz indicated redshift more than
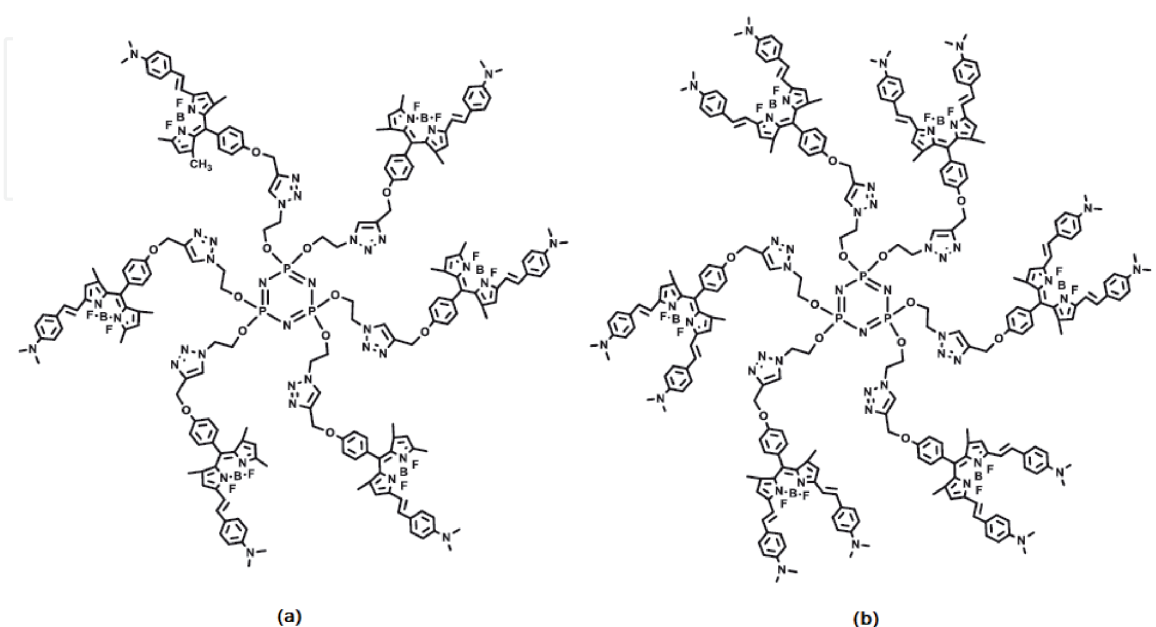

(a)   (b)

Figure 4.
Chemical structures of (a) mono-styryl and (b) distyryl-BODIPY substituted cyclophosphazenes.

mono-styryl pyrene BODIPY containing Cpz because of mono- and di-styryl bonding positions of pyrene molecules. These Cpz compounds revealed different color and spectral changes throughout reduction and oxidation reactions as compared to BODIPY derivatives and newly synthesized BODIPY molecules, which might have potential applications for electrochromic materials. Extreme properties of these compounds also illustrated probable utilization of these as functional materials for use in electrochemical and photovoltaic applications.
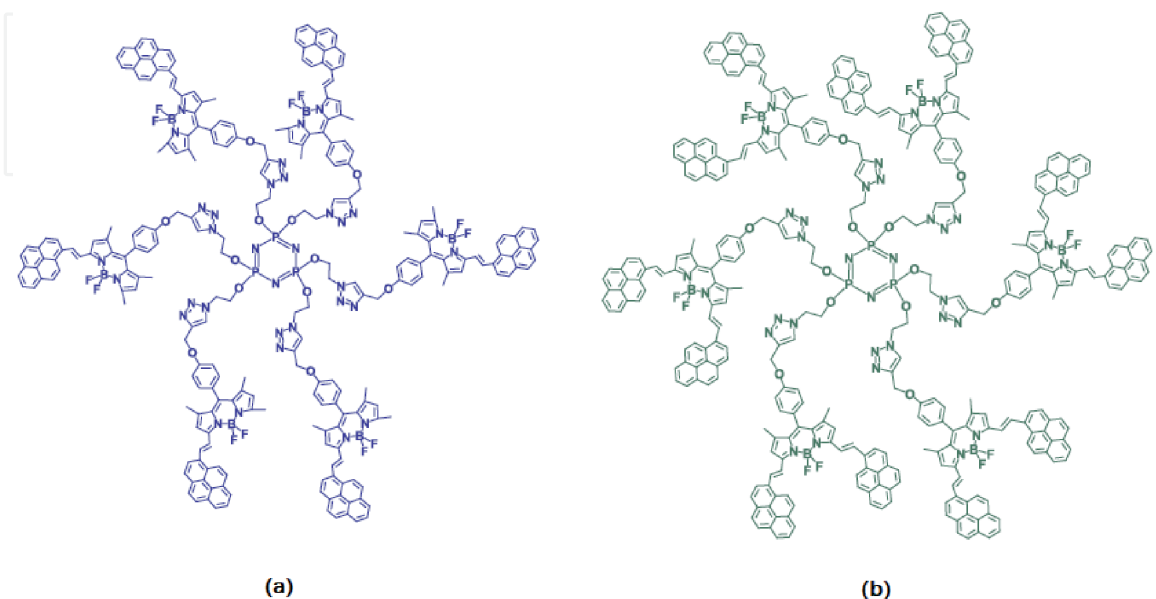

(a) (b)

Figure 5.
Chemical structures of (a) mono-styryl and (b) distyryl-pyrene BODIPY substituted cyclophosphazenes.
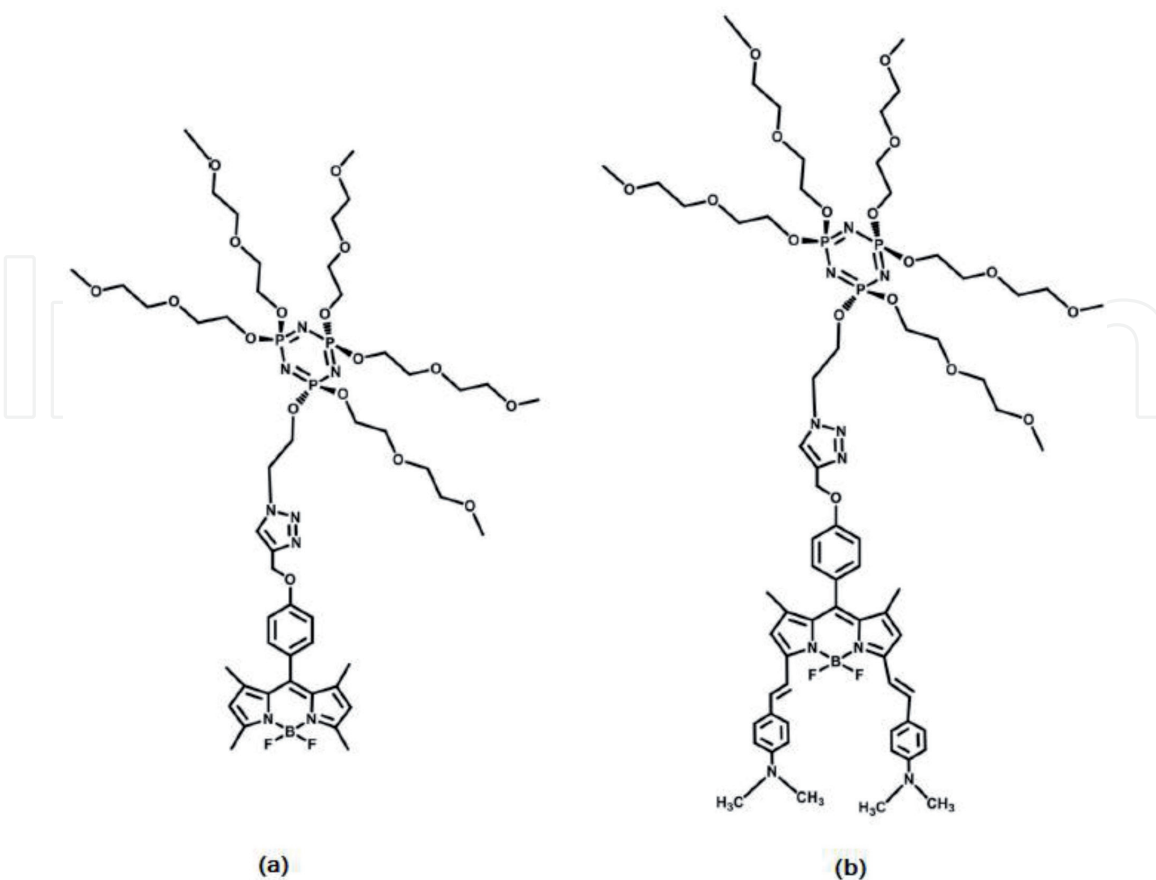

(a) (b)

Figure 6.
Chemical structures of (a) BODIPY and (b) distyryl-BODIPY substituted cyclophosphazenes.

Synthesis, photophysics, and photobiological activities of a series of neutral heteroleptic cyclometalated iridium (III) complexes including BODIPY substituted N-heterocyclic carbene (NHC) ligands reported by Liu et al. [62]. The effect of the substitution position of BODIPY on the NHC ligands, either on C4 of the phenyl ring or C5 of the benzimidazole unit, and its linker type on the photophysical properties was investigated. All complexes showed BODIPY-localized intense [1]IL (intraligand)/[1]MLCT (metal-to-ligand charge transfer) absorption at 530–543 nm and [1,3]IL/[1,3]CT (charge transfer) emission at 582–610 nm. However, the lowest triplet excited state of these complexes is the BODIPY-localized $^3\pi,\pi^*$ states. It was demonstrated that the position of the BODIPY pendant on the NHC ligand impacted both the [1]IL/[1]MLCT absorption and [1,3]IL/[1,3]CT emission bands. This study indicated that the substitution position of BODIPY on the NHC ligand plays an important role in the cytotoxicity and photocytotoxicity of this new type of complexes. BODIPY-substitution at C5 of benzimidazole compared to C4-phenyl substitution leads to lower $^1O_2$ quantum efficiencies but more efficient phototoxic effects. The effect of BODIPY substitution position at the NHC ligand is more cleared on the photobiological activities than on the photophysical properties. Two water-soluble cyclotriphosphazene derivatives by "click" reactions between cyclotriphosphazene derivative with hydrophilic glycol side groups and BODIPY's (**Figure 6**) were reported in 2019 [63]. The photophysical properties of these compounds were examined inside the water and many organic solvents such as acetone, THF, dichloromethane, dimethyl sulfoxide, etc., and the results were compared with each other. These compounds have good solubility in many different organic solvents and especially acetone: water systems that are suitable to use in environmental and biological applications.

3. Photophysical properties of aza-BODIPY dyes

Replacement of the meso-carbon with nitrogen creates a similar class of compounds mentioned as aza-BODIPYs (**Figure 7**). In contrast to the well-known BODIPYs, aza-BODIPYs have not been extensively studied. Aza-BODIPY skeletons are generally prepared from nitromethane adducts to the corresponding chalcone, but butanol, rather than methanol or solvent-free conditions, are the preferred medium. The syntheses are completed by adding $BF_3.OEt_2$ at room temperature [1]. Like BODIPY derivatives, aza-BODIPY derivatives also have high molar extinction coefficients and moderate fluorescence quantum yields (ca. 0.20–0.40). The addition of the lone pair on the nitrogen properly affects the HOMO-LUMO energy gap owing to stabilization [1]. This improved stability causes a red-shift in the absorption and emission profiles into the 650–850 nm range [64]. Aza-BODIPY core offers several advantages including ease of synthesis and an inherent bathochromic shift in the absorption maxima in comparison to the carbon analog. Aza-BODIPY dyes have a marked red shift of the absorption and emission bands relative to traditional BODIPY dyes can be accomplished without modifying the key properties of BODIPY dyes, such as their high molar absorption coefficients, narrow and structured absorption and emission bands, small Stokes shifts, high fluorescence quantum yields, and photostability. The UV absorption maxima of the aza-BODIPY dyes are comparatively insensible to solvent polarity; only small blue shifts tend to be observed (6–9 nm) when switching solvents from toluene to ethanol. Their absorptions are strong, with a full width at a half-maximum height changing from 51 to 67 nm in aqueous solution and 47–57 nm in chloroform indicating that the dyes do not aggregate under those conditions. The extinction coefficients range from 7.5 x 10^4 to 8.5 x 10^4 M^{-1} cm^{-1}. Fluorescence emission spectra of the aza-BODIPY
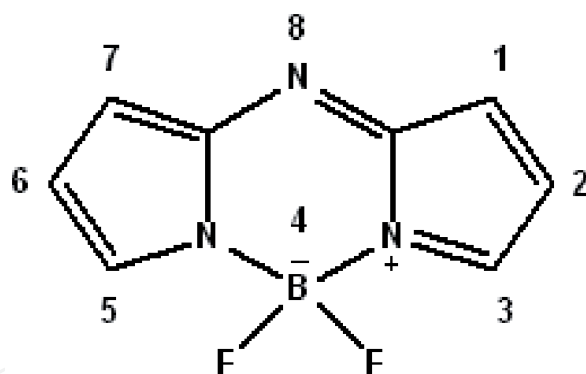
Figure 7.
Chemical structure and numbering of aza-BODIPY core.

dyes are also relatively insensitive to the solvent polarity [1]. Aza-BODIPYs are of great interest due to their appealing optical properties of strong absorbance and emission in the NIR region and easy structural modification. For this reason, this class of BODIPY has found use as photosensitizers [65, 66], near-IR emitting chemosensors and imaging probes [67–70], and as fluorescent labels [71, 72].

The synthesis and photophysical properties of a NIR absorbing acenaphtho-fused aza-BODIPY dye with using 1,2-dicyanoacetonaphthylene as a precursor [73] were reported by Majumdar et al. [74]. In contrast with its naphtho-fused analog [75], a stable complex was obtained due to the differing effects of the fused ring moieties on the energies of the frontier π molecular orbitals (MOs). The Φ_F values obtained for this aza-BODIPY are comparatively low in a set of solvents with different polarities, limiting the benefit of this compound for sensor and bioimaging applications, but the comparatively broad absorption band at the red end of the visible region may make the compound appropriate for use in solar cells. The synthesis and photophysical properties of two NIR absorbing conjugates based on orthogonally arranged rhodium (III) tetrakis-4-tolylporphyrin [Rh^{III}(ttp)] and BF$_2$-chelated aza-BODIPY linked by a covalent Rh—C(aryl) bond were reported by Zhou et al. in 2016 [76]. These conjugates display intense absorption and moderate fluorescence bands around 700 nm, which do not correspond with those of their aza-BODIPY precursors, due to the strong ground-state interaction between the aza-BODIPY and metal porphyrin moieties. Minor changes in the linkage position on the aza-BODIPY moiety can alter the relative energies of MOs and hence have a significant impact on the optical and photophysical properties. This study sheds light on the actual role of the heavy atom in excited-state processes that cannot be separated from its ligands. Besides, this approach gives promise as a strategy for overcoming the two main problems that have been encountered throughout dye research in the NIR region: the first one is the relatively weak absorption of transition-metal porphyrins in this spectral region, and the second one is the relatively weak $^1O_2$ yields of organic fluorophores. The influence of halogen atom substitution (Br and I), in different amounts and positions on an aza-BODIPY skeleton, was investigated by De Simone et al. The heavy atom effect on excitation energies, singlet-triplet energy gaps and spin–orbit matrix elements has been investigated. The maximum absorption within the therapeutic window has been approved for all the aza-BODIPY derivatives. Possible intersystem spin crossing pathways for the population of the lowest triplet state, which will depend on the values of the spin–orbit matrix elements, the energy gaps as well as the orbital combination of the concerned states have been found to most likely concern the S_1 and T_1 or T_2 states. The potential therapeutic use of these compounds as photosensitizers in PDT was reported [77]. The comparison of optical and electrochemical properties

of aza-BODIPY dyes that differ under the substituents at 1,7- and 3,5-positions of the aza-BODIPY backbone was reported by Gut et al. [78]. Especially, the influence of highly electron-withdrawing nitro substituents on these properties was investigated. The aza-BODIPYs studied display a broad absorption band extending from ca. 600 nm to ca. 700 nm, a spectral region that is highly searched after for biomedical applications, and have high molar absorption coefficients (ε) ranging from 6.4×10^4 (M^{-1} cm^{-1}) to 8.5×10^4 (M^{-1} cm^{-1}) in THF. These compounds were weakly emissive as non-radiative decay is the overpowering route of the excited state energy spreading. The fluorescence quantum efficiencies (Φ_{fl}) measured in THF was between 0.03 and 0.06 for the aza-BODIPYs. Transient absorption experiments divulged $T_1 \rightarrow T_n$ absorption extend from ca. 400 nm to ca. 600 nm and allowed determination of the triplet state lifetimes. The estimated triplet lifetimes (τ_T) in deaerated THF ranged from 77 to 130 µs. As predicted by the CV/DPV measurements, all aza-BODIPYs displayed one irreversible oxidation and two quasi-reversible reductions. Prediction of the E_{HOMO} gave a value of ca. 5.8 eV while the E_{LUMO} was found to be located at ca. 4.5 eV. Exceptionally high photostability and thermal durability up to near 300°C were found for the nitro-substituted aza-BODIPYs.

In 2019, Obloza et al. [79] reported a series of aza-BODIPY dyes substituted with meta-(dimethylamino) phenyl groups. Highly attractive photophysical and photochemical properties were induced in meta-(Me_2N) Ph-substituted aza-BODIPY by bromination of the aromatic rings at the 3 and 5 positions. High values of $^1O_2$ quantum yields were measured, ranging from 0.36 to 0.58. The photosensitized oxygenation process of a sample compound, diphenylisobenzofuran (DPBF), continuous over a Type II mechanism for the di-bromo derivative, while for the tetra-bromo derivative a mixed mechanism including both $^1O_2$ and other forms of oxygen formation (Type I and/or Type III) was assigned. Nanosecond laser photolysis (NLP) experiments of the brominated aza-BODIPYs divulged $T_1 \rightarrow T_n$ absorption extending between ca. 350 nm and ca. 510 nm with τ_T ranged between 15.6 and 26.0 µs. The brominated aza-BODIPYs studied displayed an absorption band therein so-called "therapeutic window", with λ_{abs} placed among 620 and 636 nm. As predicted by cyclic voltammetry (CV)/ differential pulse voltammetry (DPV) measurements, the meta-(Me_2N) Ph-substituted aza-BODIPYs studied displayed a multi-electron oxidation process at a relatively low oxidation potential (E_{ox}), pointing to the very good electron-donating features of these molecules. These compounds showed high photo- and thermal stability. The synthesis of a series of aza-BODIPY dyes substituted with p-(dimethylamino) phenyl groups was also reported by Obloza et al. [80]. Especially, the effect of p-(Me_2N) Ph-moieties on these characteristics was of importance. For two aza-BODIPYs studied, a near-IR absorption band was monitored at ca. λ_{abs} = 796 nm. Owing to the prominent ICT applied by the existence of strongly electron-donating p-(Me_2N) Ph-substituents, the compounds studied were weakly emissive with the singlet lifetimes (τ_S) in the picosecond range. NLP experiments of the brominated aza-BODIPYs divulged $T_1 \rightarrow T_n$ absorption extending between ca. 350 nm and ca. 550 nm with τ_T ranged between 6.0 and 8.5 µs. The optical features of the aza-BODIPYs studied were pH-sensitive. Upon protonation of the dimethylamino groups with TFA in toluene, a stepwise extinction of the NIR absorption band at λ_{abs} = 790 nm was monitored with the accompanying view of a blue-shifted absorption band at λ_{abs} = 652 nm, which was accompanied by an important emission band at λ_{emi} = 680 nm. The conversion from a non-emissive to an emissive compound is concerned with the prevention of the ICT. CV/DPV measurements were showed that these aza-BODIPYs displayed two irreversible oxidation and two quasi-reversible reduction processes. All these studied compounds displayed extremely high photo and thermal stability.

4. Conclusion

In this chapter, the basic photophysical properties of BODIPY and aza-BODIPY derivatives are introduced briefly. Unsubstituted BODIPY absorbs near 500 nm and emits around 510 nm. Substitution of amino- or alkoxy-moieties at the meso-position of BODIPY core is expected to provide a shorter excitation and emission wavelength at the blue region with high quantum yields. Substitution of styryl- or distyryl moieties from 3,5-positions is expected to produce more red-shifted emissions. Aza-BODIPY derivatives also show red-shift in the absorption and emission profiles, because of the lone pair on the nitrogen. According to the recent advances on BODIPY dyes, it has seen that they have many application areas especially on bioimaging, laser-dyes, OPV devices, chemosensors, and PDT, because of their superior photophysics. It seems that BODIPY derivatives still will remain popular in the future.

Author details

Seda Çetindere
Department of Chemistry, Faculty of Science, Gebze Technical University,
Gebze, Kocaeli, Turkey

*Address all correspondence to: sdemirer@gtu.edu.tr

IntechOpen

References

[1] Loudet A, Burgess K. BODIPY dyes and their derivatives: Syntheses and spectroscopic properties. Chemical Reviews. 2007;**107**:4891-4932. DOI: 10.1021/cr078381n

[2] Ulrich G, Ziessel R, Harriman A. The chemistry of fluorescent bodipy dyes: Versatility unsurpassed. Angewandte Chemie, International Edition. 2008;**47**:1184-1201. DOI: 10.1002/anie.200702070

[3] Ziessel R, Ulrich G, Harriman A. The chemistry of Bodipy: A new El Dorado for fluorescence tools. New Journal of Chemistry. 2007;**31**:496-501. DOI: 10.1039/B617972J

[4] Descalzo AB, Xu HJ, Shen Z, Rurack K. Red/near-infrared boron-dipyrromethene dyes as strongly emitting fluorophores. Annals of the New York Academy of Sciences. 2008;**1130**:164-171. DOI: 10.1196/annals.1430.016

[5] Treibs A, Kreuzer FH. Difluorboryl-Komplexe von Di- und Tripyrrylmethenen. Justus Liebigs Annalen der Chemie. 1968;**718**:208-223. DOI: 10.1002/jlac.19687180119

[6] Li L, Nguyen B, Burgess K. Functionalization of the 4,4-difluoro-4-bora-3a, 4a-diazas-indacene (BODIPY) core. Bioorganic & Medicinal Chemistry Letters. 2008;**18**:3112-3116. DOI: 10.1016/j.bmcl.2007.10.103

[7] Thivierge C, Bandichhor R, Burgess K. Spectral dispersion and water solubilization of BODIPY dyes via palladium-catalyzed C-H functionalization. Organic Letters. 2007;**9**:2135-2138. DOI: 10.1021/ol0706197

[8] Wael EV, Pardoen JA, Koevering JA, Lugtenburg J. Pyrromethene-BF2 complexes (4,4′-difluoro-4-bora-3a,4a-diaza-s-indacenes). Synthesis and luminescence properties. Physical-Organic Chemistry. 1977;**96**:306-309. DOI: 10.1002/recl.19770961205

[9] Bandichhor R, Thivierge C, Bhuvanesh NSP, Burgess K. 4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene. Acta Crystallographica Section E. 2006;**62**:o4310-o4311. DOI: 10.1107/S1600536806032235

[10] Hu R, Lager E, Aguilar-Aguilar A, Liu J, Lam JWY, Sung HHY, et al. Twisted intramolecular charge transfer and aggregation-induced emission of BODIPY derivatives. Journal of Physical Chemistry C. 2009;**113**:15845-15853. DOI: 10.1021/jp902962h

[11] Kalai T, Hideg K. Synthesis of new, BODIPY-based sensors and labels. Tetrahedron. 2006;**62**:10352-10360. DOI: 10.1016/j.tet.2006.08.079

[12] Karolin J, Johansson LBA, Strandberg L, Ny T. Fluorescence and absorption spectroscopic properties of dipyrromethaneboron difluoride (BODIPY) derivatives in liquids, lipid-membranes, and proteins. Journal of the American Chemical Society. 1994;**116**:7801-7806. DOI: 10.1021/ja00096a042

[13] Ehrenschwender T, Wagenknechet HA. 4,4-Difluoro-4-bora-3a,4a-diaza-s-indacene as a bright fluorescent label for DNA. The Journal of Organic Chemistry. 2011;**76**:2301-2304. DOI: 10.1021/jo102519k

[14] Giessler K, Griesser H, Goehringer D, Sabirov T, Richert C. Synthesis of 3'-BODIPY-labeled active esters of nucleotides and a chemical primer extension assay on beads. European Journal of Organic Chemistry. 2010;**19**:3611-3620. DOI: 10.1002/ejoc.201000210

[15] Kim D, Ma D, Kim M, Jung Y, Kim NH, Lee C, et al. Fluorescent labeling of protein using blue-emitting 8-amino-BODIPY derivatives. Journal of Fluorescence. 2017;**27**:2231-2238. DOI: 10.1007/s10895-017-2164-5

[16] Baysec S, Minotto A, Klein P, Poddi S, Zampetti A, Allard S, et al. Tetraphenylethylene-BODIPY aggregation-induced emission luminogens for near-infrared polymer light-emitting diodes. Science China: Chemistry. 2018;**61**:932-939. DOI: 10.1007/s11426-018-9306-2

[17] Zampetti A, Minott A, Squeo BM, Gregorious VG, Allard S, Scherf U, et al. Highly efficient solid-state nearinfrared Organic light-emitting diodes incorporating A-D-A dyes based on α,β-unsubstituted "BODIPY" moieties. Scientific Reports. 2011;**7**:1611-1617. DOI: 10.1038/s41598-017-01785-2

[18] Gao H, Gao Y, Wang C, Hu D, Xie Z, Liu L, et al. Anomalous effect of intramolecular charge transfer on the light emitting properties of BODIPY. ACS Applied Materials & Interfaces. 2018;**10**:14956-14965. DOI: 10.1021/acsami.7b13444

[19] Liu X, Chen B, Li X, Zhang L, Xu Y, Liu Z, et al. Self-assembly of BODIPY based pH-sensitive near infrared polymeric micelles for drug controlled delivery and fluorescence imaging applications. Nanoscale. 2015;**7**:16399-16416. DOI: 10.1039/C5NR04655F

[20] Quan L, Liu S, Sun T, Guan X, Lin W, Xie Z, et al. Near-infrared emitting fluorescent BODIPY nanovesicles for in vivo molecular imaging and drug delivery. ACS Applied Materials & Interfaces. 2014;**6**:16166-16173. DOI: 10.1021/am5042115

[21] De la Torre B, Hornillos V, Luque-Ortega JR, Abengozar MA, Amat-Guerri F, Acun AU, et al. A BODIPY-embedding miltefosine analog linked to cellpenetrating Tat(48-60) peptide favors intracellular delivery and visualization of the antiparasitic drug. Amino Acids. 2014;**46**:1047-1058. DOI: 10.1007/s00726-013-1661-3

[22] Filatov MA. Heavy-atom-free BODIPY photosensitizers with intersystem crossing mediated by intramolecular photoinduced electron transfer. Organic & Biomolecular Chemistry. 2020;**18**:10-27. DOI: 10.1039/C9OB02170A

[23] Wang L, Bai J, Qian Y. Synthesis of a triphenylamine BODIPY photosensitizer with D–A configuration and its application in intracellular simulated photodynamic therapy. New Journal of Chemistry. 2019;**43**:16829-16834. DOI: 10.1039/C9NJ04166D

[24] Wang C, Qian Y. A novel BODIPY-based photosensitizer with pH-active singlet oxygen generation for photodynamic therapy in lysosomes. Organic & Biomolecular Chemistry. 2019;**17**:8001-8007. DOI: 10.1039/C9OB01242G

[25] Bill NL, Lim JM, Davis CM, Bahring S, Jeppesen JO, Kim D, et al. π-Extended tetrathiafulvalene BODIPY (ex-TTF-BODIPY): a redox switched "on–off–on" electrochromic system with two near-infrared fluorescent outputs. Chemical Communications. 2014;**50**:6758-6761. DOI: 10.1039/C4CC02567A

[26] Haldar U, Sharma R, Ruidas B, Lee H. Toward rapid and selective detection of hypochlorous acid in pure aqueous media and its application to cell imaging: BODIPY-derived water-soluble macromolecular chemosensor with high sensitivity. Dyes and Pigments. 2020;**172**:107858. DOI: 10.1016/j.dyepig.2019.107858

[27] Gao J, Chen X, Chen S, Meng H, Wang Y, Li C, et al. The BODIPY-based

chemosensor for fluorometric/colorimetric dual channel detection of RDX and PA. Analytical Chemistry. 2019;**91**:13675-13680. DOI: 10.1021/acs.analchem.9b02888

[28] Li S, Cao D, Hu Z, Li Z, Meng X, Hana X, et al. A chemosensor with a paddle structure based on a BODIPY chromophore for sequential recognition of Cu^{2+} and HSO_3. RSC Advances. 2019;**9**:34652-34657. DOI: 10.1039/C9RA08345F

[29] Xue Z, Liu T, Liu H. Naked-eye chromogenic and fluorogenic chemosensor for mercury (II) ion based on substituted distyryl BODIPY complex. Dyes and Pigments. 2019;**165**:65-70. DOI: 10.1016/j.dyepig.2019.01.061

[30] Spiege JD, Lyskov I, Kleinschmidt M, Marian CM. Charge-transfer contributions to the excitonic coupling matrix element in BODIPY-based energy transfer cassettes. Chemical Physics. 2017;**482**:265-276. DOI: 10.1016/j.chemphys.2016.10.004

[31] Bag S, Tseng JC, Rochford J. A BODIPY-luminol chemiluminescent resonance energy-transfer (CRET) cassette for imaging of cellular superoxide. Organic & Biomolecular Chemistry. 2015;**13**:1763-1767. DOI: 10.1039/C4OB02413C

[32] Zhao Y, Zhang Y, Lv X, Liu Y, Chen M, Wang P, et al. Through-bond energy transfer cassettes based on coumarin–Bodipy/distyryl Bodipy dyads with efficient energy efficiences and large pseudo-Stokes' shifts. Journal of Materials Chemistry. 2011;**21**:13168-13171. DOI: 10.1039/C1JM12503F

[33] Wan CW, Burghart A, Chen J, Bergström F, Johansson LBA, Wolford MF, et al. Anthracene-BODIPY cassettes: Syntheses and energy transfer. Chemical Europian Journal.

2003;**9**:4430-4441. DOI: 10.1002/chem.200304754

[34] Ortiz A. Triarylamine-BODIPY derivatives: A promising building block as hole transporting materials for efficient perovskite solar cells. Dyes and Pigments. 2019;**171**:107690. DOI: 10.1016/j.dyepig.2019.107690

[35] Shah MF, Mirloup A, Chowdhury TH, Alexandra S, Hanbazazah AS, Ahmed A, et al. A near-infrared thienyl-BODIPY co-sensitizer for high-efficiency dye-sensitized solar cells. Sustainable Energy & Fuels. 2019;**3**:2983-2989. DOI: 10.1039/C9SE00300B

[36] Huaulme Q, Aumaitre C, Kontkanen OV, Beljonne D, Sutter A, Ulrich G, et al. Functional panchromatic BODIPY dyes with near-infrared absorption: Design, synthesis, characterization and use in dye-sensitized solar cells. Beilstein Journal of Organic Chemistry. 2019;**15**:1758-1768. DOI: 10.3762/bjoc.15.169

[37] Dos Santos JM, Jagadamma LK, Latif NM, Ruseckas A, Samuel IVD, Cooke G. BODIPY derivatives with near infra-red absorption as small molecule donors for bulk heterojunction solar cells. RSC Advances. 2019;**9**:15410-15423. DOI: 10.1039/C9RA01750J

[38] Meng G, Velayudham S, Smith A, Luck R, Liu HY. Color tuning of polyfluorene emission with BODIPY monomers. Macromolecules. 2009;**42**:1995-2001

[39] Bonardi L, Ulrich G, Ziessel R. Tailoring the properties of boron-dipyrromethene dyes with acetylenic functions at the 2,6,8 and 4-B substitution positions. Organic Letters. 2008;**10**:2183-2186

[40] Benniston AC, Copley G. Lighting the way ahead with boron dipyrromethene (Bodipy) dyes.

Physical Chemistry Chemical Physics. 2009;**11**:4124-4131

[41] Galangau O, Dumas-Verdes C, Méallet-Renault R, Clavier G. Rational design of visible and NIR distyryl-BODIPY dyes from a novel fluorinated platform. Organic & Biomolecular Chemistry. 2010;**8**:4546-4553. DOI: 10.1039/C004812G

[42] Niu SL, Massif C, Ulrich G, Ziessel R, Renard PY, Romieu A. Water solubilisation and bio-conjugation of a red-emitting BODIPY marker. Organic & Biomolecular Chemistry. 2011;**9**:66-69. DOI: 10.1039/C0OB00693A

[43] Bura T, Retailleau P, Ulrich G, Ziessel R. Highly substituted Bodipy dyes with spectroscopic features sensitive to the environment. The Journal of Organic Chemistry. 2011;**76**:1109-1117. DOI: 10.1021/jo102203f

[44] Majumdar P, Yuan X, Li S, Le Guennic B, Ma J, Zhang C, et al. Cyclometalated Ir(III) complexes with styryl-BODIPY ligands showing near IR absorption/emission: Preparation, study of photophysical properties and application as photodynamic/luminescence imaging materials. Journal of Materials Chemistry B. 2014;**2**:2838-2854. DOI: 10.1039/C4TB00284A

[45] Gai L, Mack J, Lu H, Yamada H, Kuzuhara D, Lai G, et al. New 2,6-distyryl-substituted BODIPY isomers: Synthesis, photophysical properties, and theoretical calculations. Chemical European Journal. 2014;**20**:1091-1102. DOI: 10.1002/chem.201303291

[46] Pan ZH, Zhou JW, Luo GG. Experimental and theoretical study of enol–keto prototropic tautomerism and photophysics of azomethine–BODIPY dyads. Physical Chemistry Chemical Physics. 2014;**16**:16290-16301. DOI: 10.1039/C4CP02151G

[47] Yang Y, Zhang L, Gao C, Xua L, Baia S, Liu X. Pyrene-based BODIPY: Synthesis, photophysics and lasing properties under UV-pumping radiation. RSC Advances. 2014;**4**:38119-38123. DOI: 10.1039/C4RA04759A

[48] Cetindere S, Cosut B, Yesilot S, Durmus M, Kilic A. Synthesis and properties of axially BODIPY conjugated subphthalocyanine dyads. Dyes and Pigments. 2014;**101**:234-239. DOI: 10.1016/j.dyepig.2013.10.015

[49] Orte A, Debroye E, Ruedas-Ram J, Garcia-Fernandeza E, Robinson D, Crovetto L, Talavera EM, et al. Effect of the substitution position (2, 3 or 8) on the spectroscopic and photophysical properties of BODIPY dyes with a phenyl, styryl or phenylethynyl group. RSC Advances 2016;6:102899-102913. DOI:10.1039/C6RA22340K

[50] Schmitt A, Hinkeldey B, Wild M, Jung G. Synthesis of the core compound of the BODIPY dye class: 4,4′-difluoro-4-bora-(3a,4a)-diaza-s-indacene. Journal of Fluorescence. 2009;**19**:755-758. DOI: 10.1007/s10895-008-0446-7

[51] Groves BR, Crawford SM, Lundrigan T, Matta CF, Sowlati-Hashjin S, Thompson A. Synthesis and characterisation of the unsubstituted dipyrrin and 4,4-dichloro-4-bora-3a,4a-diaza-s-indacene: Improved synthesis and functionalisation of the simplest BODIPY framework. Chemical Communications. 2013;**49**:816-818. DOI: 10.1039/C2CC37480C

[52] Qin W, Baruah M, Van der Auweraer M, De Schryver FC, Boens N. Photophysical properties of borondipyrromethene analogues in solution. The Journal of Physical Chemistry. A. 2005;**109**:7371-7384. DOI: 10.1021/jp052626n

[53] Qin W, Baruah M, Stefan A, Van der Auweraer M, Boens N. Photophysical

properties of BODIPY-derived hydroxyaryl fluorescent pH probes in solution. ChemPhysChem. 2005;**6**:2343-2351. DOI: 10.1002/cphc.200500341

[54] Boens N, Wang L, Leen V, Yuan P, Verbelen B, Dehaen W, et al. 8-HaloBODIPYs and their 8-(C, N, O, S) substituted analogues: Solvent dependent UV–Vis spectroscopy, variable temperature NMR, crystal structure determination, and quantum chemical calculations. Journal of Physical Chemistry A. 2014;**118**:1576-1594. DOI: 10.1021/jp412132y

[55] Hendel SJ, Poe AM, Khomein P, Bae Y, Thayumanavan S, Young ER. Photophysical and electrochemical characterization of BODIPY containing dyads comparing the influence of an A−D−A versus D−A motif on excited-state photophysics. Journal of Physical Chemistry A. 2016;**120**:8794-8803. DOI: 10.1021/acs.jpca.6b06590

[56] Cetindere S, Tümay SO, Kilic A, Durmus M, Yesilot S. Hexa-BODIPY linked-triazole based on a cyclotriphosphazene core as a highly selective and sensitive fluorescent sensor for Fe^{2+} ions. Journal of Fluorescence. 2016;**26**:1173-1181. DOI: 10.1007/s10895-016-1797-0

[57] Chong H, Fron E, Liu Z, Boodts S, Thomas J, Harvey JN, et al. Acid-sensitive BODIPY dyes: Synthesis through Pd-catalyzed direct C(sp3)−H arylation and photophysics. Chemical European Journal. 2017;**23**:4687-4699

[58] Cetindere S, Tümay SO, Kilic A, Durmus M, Yesilot S. Synthesis and physico-chemical properties of cyclotriphosphazene-BODIPY conjugates. Dyes and Pigments. 2017;**139**:517-523. DOI: 10.1016/j. dyepig.2016.12.035

[59] Kang H, Si Y, Liu Y, Zhang X, Zhang W, Zhao Y, et al. Photophysical/ chemistry properties of distyryl-BODIPY derivatives: An experimental and density functional theoretical study. The Journal of Physical Chemistry. A. 2018;**122**:5574-5579. DOI: 10.1021/acs. jpca.8b02656

[60] Mallah R, Sreenath MC, Subramaniyan C, Joe IH, Sekar N. Excitation energy transfer processes in BODIPY based donor-acceptor system—Synthesis, photophysics, NLO and DFT study. Optical Materials. 2018;**84**:795-806. DOI: 10.1016/j. optmat.2018.08.007

[61] Cetindere S, Tümay SO, Senocak A, Kilic A, Durmus M, Demirbas E, et al. Novel pyrene-BODIPY dyes based on cyclotriphosphazene scaffolds: Synthesis, photophysical and spectroelectrochemical properties. Inorganica Chimica Acta. 2019;**494**:132-140. DOI: 10.1016/j.ica.2019.05.022

[62] Liu B, Monro S, Jabed MA, Cameron CG, Colón KL, Xu W, et al. Neutral iridium(III) complexes bearing BODIPY-substituted N-heterocyclic carbene (NHC) ligands: Synthesis, photophysics, in vitro theranostic photodynamic therapy, and antimicrobial activity. Photochemical & Photobiological Sciences. 2019;**18**:2381-2396. DOI: 10.1039/C9PP00142E

[63] Cetindere S, Okutan E, Tümay SO, Yesilot S, Kilic A. Novel water-soluble cyclotriphosphazene-Bodipy conjugates: Synthesis, characterization and photophysical properties. Journal of Fluorescence. 2019;**29**:1143-1152. DOI: 10.1007/s10895-019-02424-x

[64] McDonnell SO, O'Shea DF. Near-infrared sensing properties of imethlyaminosubstituted BF2-azadipyrromethenes. Organic Letters. 2006;**8**:3493-3496. DOI: 10.1021/ol061171x

[65] Gresser R, Hartmann H, Wrackmeyer M, Leo K, Riede M. Synthesis of thiophenesubstituted aza-BODIPYs and their optical

and electrochemical properties. Tetrahedron. 2011;**67**:7148-7155. DOI: 10.1016/j.tet.2011.06.100

[66] Adarsh N, Avirah RR, Ramaiah D. Tuning photosensitized singlet oxygen generation efficiency of novel Aza-BODIPY dyes. Organic Letters. 2010;**12**:5720-5723. DOI: 10.1021/ol102562k

[67] Zhao WL, Carreira EM. Conformationally restricted aza-bodipy: A highly fluorescent, stable, near-infrared-absorbing dye. Angewandte Chemie, International Edition. 2005;**44**:1677-1679. DOI: 10.1002/anie.200461868

[68] Li Y, Dolphin D, Patrick BO. Synthesis of a BF2 complex of indol-2-yl-isoindol-1-ylidene-amine: A fully conjugated azadipyrromethene. Tetrahedron Letters. 2010;**51**:811-814. DOI: 10.1016/j.tetlet.2009.12.003

[69] Loudet A, Bandichhor R, Burgess K, Palma A, McDonnell SO, Hall MJ, et al. B, O-chelated azadipyrromethenes as near-IR probes. Organic Letters. 2008;**10**:4771-4774. DOI: 10.1021/ol8018506

[70] Loudet A, Bandichhor R, Wu L, Burgess K. Functionalized BF2 chelated azadipyrromethene dyes. Tetrahedron. 2008;**64**:3642-3654. DOI: 10.1016/j.tet.2008.01.117

[71] Palma A, Tasior M, Frimannsson DO, Vu TT, Meallet-Renault R, O'Shea DF. New on-bead near-infrared fluorophores and fluorescent sensor constructs. Organic Letters. 2009;**11**:3638-3641. DOI: 10.1021/ol901413u

[72] Yoshii R, Nagai A, Chujo Y. Highly near-infrared photoluminescence from Aza-borondipyrromethene-based conjugated polymers. Journal of Polymer Science Part a-Polymer Chemistry. 2010;**48**:5348-5356. DOI: 10.1002/pola.24335

[73] Herold DA, Rieke RD. Synthesis of 1,2-disubstituted acenaphthylenes. Journal of Organic Chemistry. 1979;**44**:1359

[74] Majumdar P, Mack J, Nyokong T. Synthesis, characterization and photophysical properties of an acenaphthalene fused-ring-expanded NIR absorbing aza-BODIPY dye. RSC Advances. 2015;**5**:78253-78258. DOI: 10.1039/C5RA14916A

[75] Lu H, Mack J, Yang Y, Shen Z. Structural modification strategies for the rational design of red/NIR region BODIPYs. Chemical Society Reviews. 2014;**43**:4778-4823. DOI: 10.1039/C4CS00030G

[76] Zhou J, Gai L, Mack J, Zhou Z, Qiu H, Chan KS, et al. Synthesis and photophysical properties of orthogonal rhodium(III)–carbon bonded porphyrin-aza-BODIPY conjugates. Journal of Materials Chemistry C. 2016;**4**:8422-8428. DOI: 10.1039/C6TC03130G

[77] De Simone BC, Mazzone G, Pirillo J, Russo N, Sicilia E. Halogen atom effect on the photophysical properties of substituted aza-BODIPY derivatives. Physical Chemistry Chemical Physics. 2017;**19**:2530-2536. DOI: 10.1039/C6CP07874E

[78] Gut A, Łapok L, Jamróz D, Gorski A, Solarski J, Nowakowska M. Photophysics and redox properties of aza-BODIPY dyes with electron-withdrawing groups. New Journal of Chemistry. 2017;**41**:12110-12122. DOI: 10.1039/C7NJ02757E

[79] Obłoza M, Łapok L, Pędziński T, Nowakowska M. A beneficial effect of bromination on the photophysical and photochemical properties of

Aza-BODIPY dyes with electron-donating groups. Asian Journal of Organic Chemistry. 2019;**8**:1879-1892. DOI: 10.1002/ajoc.201900385

[80] Obłoza M, Łapok L, Pędziński T, Stadnicka KM, Nowakowska M. Synthesis, photophysics and redox properties of Aza-BODIPY dyes with electron-donating groups. ChemPhysChem. 2019;**20**:2482-2497. DOI: 10.1002/cphc.201900689