

BODIPY类染料荧光发射及应用

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摘要

BODIPY激光染料是现代光化学研究的一个热门主题, 因为它的发色团提供了多种选择, 可用于多种合成路线。通过BODIPY染料的取代模式来调节光谱性质或诱导新的光物理过程的可能性增加了这些荧光团的科技应用数量, 但直到90年代初, 由于Boyer及其同事的先驱工作, BODIPY才成为可调谐染料激光器的活跃媒介。这些染料的最佳激光性能是由于它们的化学稳定性、高耐热性、低光降解性, 以及主要是它们独特的光物理特征, 这些特征深深地依赖于分子结构, 总的来说, 这种发色团很容易溶于大多数有机介质, 其特征是可见光谱的绿-黄部分具有强吸收和荧光光谱带, 荧光效率接近100%, 且与周围环境的性质无关。20世纪90年代后, BODIPY作为可调谐激光染料的用途得到了推广并扩展到固态, 它们还被应用于许多其他科技领域。

关键词

BODIPY, 荧光染料

Fluorescence Emission and Application of BODIPY

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Abstract

BODIPY laser dye is a hot topic in modern photochemical research, because its chromophore provides a variety of options and can be used in a variety of synthetic routes. The possibility of adjusting spectral properties or inducing new photophysical processes through the substitution mode of BODIPY dyes has increased the number of scientific and technological applications of these fluorophores. However, until the early 1990s, due to the pioneering work of Boyer and his colleagues,

BODIPY has become the active medium of tunable dye lasers. The best laser performance of these dyes is due to their chemical stability, high heat resistance, low photodegradability, as well as their unique photophysical characteristics. These characteristics are deeply dependent on the molecular structure. In general, this chromophore is easily soluble in most organic media. Its characteristic is that the green-yellow part of the visible spectrum has strong absorption and fluorescence spectral bands, and the fluorescence efficiency is close to 100%. It has nothing to do with the nature of the surrounding environment. After the 1990s, the use of BODIPY as a tunable laser dye has been promoted and extended to solid state. They have also been used in many other scientific and technological fields.

Keywords

BODIPY, Fluorescent Dye

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1. 引言

上世纪九十年代后[1], 氟化硼络合二吡咯甲川类简称 BODIPY 类染料[2] [3] [4] [5], 因为它优异的光物理性质受到了科学界的广泛关注, 如具有较高的荧光量子产率、良好的光稳定性以及易于进行化学修饰等优异的理化性能, 因此成为一个蓬勃发展和成功的研究领域, 它从液态应用开始朝固态应用发展, 可以发现大量研究测试这些染料作为荧光传感器[6]、开关和探针[7], 用于天线系统的光采集阵列, 用于光伏器件, 用于生物医学, 作为生物成像的荧光标记, 以及作为光动力治疗中的单线态氧发生器等领域。BODIPY 的成功和多功能性的主要原因在于其发色核心, 该核心可用于各种有机合成路线。亲电和亲核取代、Pd 介导的 C-C 偶联、Suzuki 等反应已应用于彻底和选择性地官能化 BODIPY 核, 因此, 大量官能团可以以特定的区域选择性固定在引达省核上。同时, 这样的取代模式调节了生成衍生物的光物理特征, 经过仔细和合理的设计, 定制的 BODIPY 可以根据所需的应用而具有特定的特性。

2. BODIPY 类染料

2.1. BODIPY 类染料光学性质介绍

BODIPY 类荧光染料是近三十几年才发展起来并越来越受到重视的一类较新的荧光化合物。基于 BODIPY 支架的荧光团因其可调的激发和发射谱、温和的合成和生物相容性而备受推崇, 同时因为它易于修饰的母体结构, 许多研究者都在它的结构上根据实际应用添加相应基团以此获得光物理性质更好的 BODIPY 染料[8]-[14]。当然, 这种结构也带来了许多优异的光物理性质。主要体现在以下方面: BODIPY 类荧光染料通常具有较高的摩尔消光系数, 这有利于提高染料的光敏性能, 便于应用在生物分析领域; 稳定的光谱性质。这类荧光染料在没有干扰基团的情况下不易受到溶剂极性和声值的影响, 这一性质对于设计能在不同溶剂中工作的荧光探针意义重大, 还有较窄的荧光光谱峰宽等等。

BODIPY 染料在稀溶液中荧光量子产率较高, 但在固态下几乎不发荧光, 而有机材料的有效固态发射对于诸如有机发光二极管、有机固态激光器和发光电化学电池的光电子器件是必需的[15]-[25]。因此, 分子设计和开发在可见光区域具有高固态发射效率的新型有机荧光材料作为功能材料受到了越来越多的关注, 作为“卟啉的妹妹”, BODIPY 家族最早作为荧光标签和激光染料开发, 已显示出优异的光谱特

性、高激光效率和光稳定性,并在新的应用中发挥着越来越重要的作用。例如,Ziessel 等人使用纯 BODIPY 的膜来产生稳定的电致发光器件,并且使用 BODIPY 掺杂聚合物基质形成的薄膜得到有机发光二极管(OLED)。然而,表现出突出固态发光的 BODIPY 染料是罕见的[26]-[32],这是由于其平坦的 π 共轭体系,通过固相中的 π - π 相互作用的紧密荧光团聚集导致显著的猝灭。抑制分子间聚集的一种简单方法可能是在 π 共轭(引达省)平面的外围引入大体积取代基(图 1)。最近,通过在 BODIPY 核心的中位和 2, 3 位引入大体积取代基成功地实现了这一策略,增加空间位阻并抑制 π - π 相互作用,此外,由于空间位阻和非平面性导致的几何结构变化增加了斯托克斯位移,因此有效地抑制了激发时的自猝灭[33]-[39]。为了研究大体积取代基在增加 BODIPY 固态发射中的作用,合成并表征了一系列在 BODIPY 核的 2 位(单侧)和 2, 6 位(两侧)具有芳基甲硅烷基取代基的 BODIPY 衍生物,研究了在各种溶剂和固态下的光物理性质。从各类表征可以发现,不管是液态还是固态下,它们的光物理性质都发生了改变,尤其呈现出固态发光的性质。

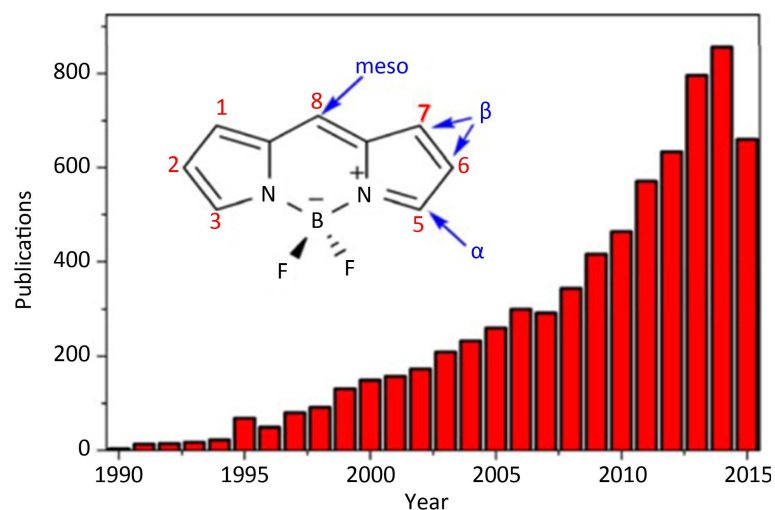


Figure 1. Molecular structure of the BODIPY core and evolution of the number of publications dealing with this chromophore over the last 25 years

图 1. BODIPY 核心的分子结构和过去 25 年中有关该发色团的出版物数量的演变

2.2. BODIPY 类染料应用

在过去几年中,已经开展了大量工作来开发固态荧光发射的 BODIPY(粉末和晶体)。总的来说,这种染料在固态下是不发荧光的,但经过适当的分子设计,如将大体积基团附着到引达省核上以避免 π - π 堆叠后,获得能够在固态下发射荧光的 BODIPY 是可行的,但是仍然不是很强。但它的光谱带可以进行移动,以覆盖广泛的可见光谱,同时保持其最佳的光物理和激光特征。BODIPY 外围有许多活性位点,为进一步功能化所需光物理和治疗性质的所有方面提供了一个多功能平台[40]。

这些合成的新型 BODIPY 可抵抗长时间和强烈的激光照射,也是生物成像中荧光探针的优秀候选者,因为它们不易在荧光显微镜下容易光漂白。目前,基于 BODIPY 的智能大结构被设计和测试为具有吸收和荧光带的荧光团,即使在近红外(700~800 nm),由于这种辐射(深度穿透和选择性激发)在生物光子学中的固有优势,对这种荧光探针的研究构成了 BODIPY 研究的活跃领域。BODIPY 可以作为电子供体或受体,这取决于取代基的电子性质和强度,该分子传感器作为可逆的开/关开关工作,其中环境酸度/碱度可以通过上述还原 PET 来估计;在酸性介质中它是一个明亮的荧光团,但在碱性条件下是一个黑暗的荧光团。BODIPY 的荧光响应仅对目标敏感,没有其他物种的干扰,在某些情况下具有良好的选择性。生物

成像技术的最新进展促进了荧光分子在细胞水平上监测生化事件的使用。在这方面，BODIPY 非常适合这一生物学范围，因为其适应性强的光物理信号性质和衍生化的巨大合成可能性[41] [42] [43]。碳水化合物已用 BODIPY 标记，从而产生明亮且耐光的生物标记，在过去的几年中，有机分子已经应用于生物光子学，不仅用于了解生物分子在细胞中的位置，监测生物化学过程，或更深入地了解周围的生物环境，还用于生物医学中的非侵入性技术对疾病的局部治疗。

在 BODIPY 已被探索的不同领域中，最成功和要求最高的可能是与生物化学相关的领域。荧光显微镜技术的进步促进了对用于生物成像的改进分子探针(在光稳定性和置于红色或 NIR 深处的发射方面)的研究。考虑到 BODIPY 对延长的照射时间具有很高的抵抗力，能够将其光谱带深入到红色边缘(甚至 NIR)，以及为目标生物分子添加特定连接单元的可能性，开发满足上述要求的稳定、明亮的 BODIPY 可能是一个富有成效和前景的研究领域[44]。特别是，应致力于实现红色激光作为激发源，因为这种辐射深入组织，以及红色发射探针，因为避免了来自周围生物分子的荧光引起的背景干扰，所以可以选择性地激发红色激光并提供更好的分辨率。此外，最近在生物医学中，治疗已经成为一个新兴领域，其中需要分子探针能够产生足够高的单线态氧(光敏剂)以破坏肿瘤细胞(治疗)，但同时具有足够有效的荧光发射以能够在荧光显微镜下进行可视化(诊断)。

2019 年，Evan W. Miller [45]课题组报道了 BODIPY 荧光团应用于膜电位成像。目前，BODIPY 染料的水溶性仍然是一个突出的挑战，水溶性 BODIPY 染料的发展通常涉及用可电离基团直接修饰 BODIPY 荧光团核心或在硼中心进行取代。虽然这些策略对于水溶性荧光团的生成是有效的，但在开发基于 BODIPY 的指标时，它们具有挑战性：直接修改 BODIPY 核心可以破坏染料的电子，使功能指标的设计复杂化；而硼中心的取代往往会使合成的 BODIPY 与生成荧光传感器所需的化学转化不兼容。而在该报道中，发现在介孔位置带有磺化芳香基团的 BODIPYs 为水溶性 BODIPYs 提供了解决方法，概述了 5 条合成方法，如图 2，这些化合物可以报告哺乳动物神经元和人类干细胞来源的心肌细胞的动作电位动态。在水溶性 BODIPY 荧光团的背景下，访问一系列取代基提供了调整水溶性 BODIPY 染料的电子特性以用于功能指标的机会。

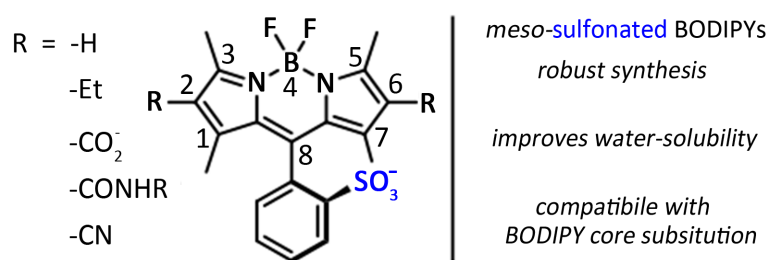


Figure 2. Design of water-soluble BODIPY

图 2. 水溶性 BODIPY 的设计

2021 年，Francisco M. Raymo [46]课题组报道了具有光激活荧光的 BODIPYs。BODIPY 平台的合成可行性及其与进一步结构修饰的不同实验条件的兼容性提供了具有独特光化学和光物理性质的分子结构，硼二吡咯甲基(BODIPY)发色团是构建具有独特性质的光响应染料的通用平台。它与可光解的共价连接可以被利用来设计具有光可切换荧光的化合物，由此产生的光激活荧光团可以增加其发射强度或改变其发射波长以响应开关。这种变化允许光刺激对荧光的时空控制，并实现常规荧光团无法复制的成像策略。事实上，具有光激活荧光的 BODIPYs 能够选择性地突出细胞内目标，亚细胞成分的纳米级可视化，动态事件的实时监测和光条形码的光化学写入。这一研究将会使得 BODIPY 在生物细胞应用上发挥重要作用。

3. 挑战及展望

综上所述, BODIPY 类染料在光物理性能方面的表现十分出色, 它具有许多传统荧光染料无法比拟的优点, 是一类性能优异的生物分析用荧光染料而且染料的可修饰性强, 也能够适应不同荧光分析的要求。如今, 有关 BODIPY 类染料的研究出版物越来越多, 有人认为, 一切都是用这些荧光团完成的, 它们已经被充分利用, 然而, 实际情况却完全相反, BODIPY 仍然有着辉煌而充满希望的未来。这种说法的主要原因是发色团的化学多功能性, 这允许为目标应用设计最方便的分子结构。此外, 在任何需要有机荧光团的应用中, BODIPY 由于其变色行为可能是正确的选择。事实上, 它们的光物理特征可以通过修饰发色核心的功能化图案进行精细调节, 保持其化学、热和光稳定性。因此, 这类染料在未来仍然具有大的发展空间。

参考文献

- [1] Wang, E., Qiao, H., Zhou, Y.M., *et al.* (2015) A Novel “Turn-On” Fluorogenic Probe for Sensing Hypochlorous Acid Based on BODIPY. *RSC Advances*, **5**, 73040-73045. <https://doi.org/10.1039/C5RA14118D>
- [2] Rahn, M.D. and King, T. (1995) Comparison of Laser Performance of Dye Molecules in Sol-Gel, Polycom, Ormosil, and Poly(methyl methacrylate) Host Media. *Applied Optics*, **34**, 8260-8271. <https://doi.org/10.1364/AO.34.008260>
- [3] Yariv, E., Schultheiss, S. and Saraidarov, T. (2001) Efficiency and Photostability of Dye-Doped Solid-State Lasers in Different Hosts. *Optical Materials*, **16**, 29-38. [https://doi.org/10.1016/S0925-3467\(00\)00056-2](https://doi.org/10.1016/S0925-3467(00)00056-2)
- [4] Costela, A., Garcia-Moreno, I. and Sastre, R. (2003) Polymeric Solid-State Dye Lasers: Recent Developments. *Physical Chemistry Chemical Physics*, **5**, 4745-4763. <https://doi.org/10.1039/B307700B>
- [5] Cerdan, L., Enciso, E., Martin, V., *et al.* (2012) FRET-Assisted Laser Emission in Colloidal Suspensions of Dye-Doped Latex Nanoparticles. *Nature Photonics*, **6**, 621-626. <https://doi.org/10.1038/nphoton.2012.201>
- [6] Sunahara, H., Urano, Y., Kojima, H. and Nagano, T. (2007) Design and Synthesis of a Library of BODIPY-Based Environmental Polarity Sensors Utilizing Photoinduced Electron-Transfer-Controlled Fluorescence ON/OFF Switching. *Journal of the American Chemical Society*, **129**, 5597-5604. <https://doi.org/10.1021/ja068551y>
- [7] Qian, X., Xiao, Y., Xu, Y., *et al.* (2010) “Alive” Dyes as Fluorescent Sensors: Fluorophore, Mechanism, Receptor and Images in Living Cells. *Chemical Communications*, **46**, 6418-6436. <https://doi.org/10.1039/c0cc00686f>
- [8] Miao, W., Guo, X., Yan, X., *et al.* (2023) Red-to-Near-Infrared Emitting pyrrolylBODIPY Dyes: Synthesis, Photo-physical Properties and Bioimaging Application. *Chemistry*, **29**, e202203832.
- [9] Loudet, A. and Burgess, K. (2007) BODIPY Dyes and Their Derivatives: Syntheses and Spectroscopic Properties. *Chemical Reviews*, **107**, 4891-4932. <https://doi.org/10.1021/cr078381n>
- [10] Ziessel, R., Ulrich, G. and Harriman, A. (2007) The Chemistry of Bodipy: A New El Dorado for Fluorescence Tools. *New Journal of Chemistry*, **31**, 496-501. <https://doi.org/10.1039/b617972j>
- [11] Shen, Z., Röhr, H., Rurack, K., *et al.* (2004) Boron-Diindomethene (BDI) Dyes and Their Tetrahydrobicyclo Precursors—En Route to a New Class of Highly Emissive Fluorophores for the Red Spectral Range. *Chemistry—A European Journal*, **10**, 4853-4871. <https://doi.org/10.1002/chem.200400173>
- [12] Baruah, M., Qin, W., Vallée, R.A.L., *et al.* (2005) A Highly Potassium-Selective Ratiometric Fluorescent Indicator Based on BODIPY Azacrown Ether Excitable with Visible Light. *Organic Letters*, **7**, 4377-4380. <https://doi.org/10.1021/ol051603o>
- [13] Rohand, T., Baruah, M., Qin, W., Boens, N. and Dehaen, W. (2006) Functionalisation of Fluorescent BODIPY Dyes by Nucleophilic Substitution. *Chemical Communications*, **42**, 266-268. <https://doi.org/10.1039/B512756D>
- [14] McDonnell, S.O. and O’Shea, D.F. (2006) Near-Infrared Sensing Properties of Dimethylamino-Substituted BF₂-Aza-dipyromethenes. *Organic Letters*, **8**, 3493-3496. <https://doi.org/10.1021/ol061171x>
- [15] Jiao, C., Huang, K.-W. and Wu, J. (2011) Perylene-Fused BODIPY Dye with Near-IR Absorption/Emission and High Photostability. *Organic Letters*, **13**, 632-635. <https://doi.org/10.1021/ol102879g>
- [16] Jiao, L., Yu, C., Liu, M., *et al.* (2010) Synthesis and Functionalization of Asymmetrical Benzo-Fused BODIPY Dyes. *The Journal of Organic Chemistry*, **75**, 6035-6038. <https://doi.org/10.1021/jo101164a>
- [17] Kubota, Y., Uehara, J., Funabiki, K., *et al.* (2010) Strategy for the Increasing the Solid-State Fluorescence Intensity of Pyromethene-BF₂ Complexes. *Tetrahedron Letters*, **51**, 6195-6198. <https://doi.org/10.1016/j.tetlet.2010.09.106>
- [18] Ozdemir, T., Atilgan, S., Kutuk, I., *et al.* (2009) Solid-State Emissive BODIPY Dyes with Bulky Substituents as

- Spacers. *Organic Letters*, **11**, 2105-2107. <https://doi.org/10.1021/ol9005568>
- [19] Vu, T.T., Badré, S., Dumas-Verdes, C., *et al.* (2009) New Hindered BODIPY Derivatives: Solution and Amorphous State Fluorescence Properties. *The Journal of Physical Chemistry C*, **113**, 11844-11855. <https://doi.org/10.1021/jp9019602>
- [20] Badré, S., Monnier, V., Méallet-Renault, R., *et al.* (2006) Fluorescence of Molecular Micro- and Nanocrystals Prepared with Bodipy Derivatives. *Journal of Photochemistry and Photobiology A*, **183**, 238-246. <https://doi.org/10.1016/j.jphotochem.2006.07.002>
- [21] Treibs, A., Kreuzer, F.H. and Ann, J.L. (1968) Difluoroboryl-Komplexe von Di- und Tripyrrylmethenen. *Justus Liebigs Annalen der Chemie*, **718**, 208-223. <https://doi.org/10.1002/jlac.19687180119>
- [22] Hepp, A., Ulrich, G., Schmechel, R., *et al.* (2004) Highly Efficient Energy Transfer to a Novel Organic Dye in OLED Devices. *Synthetic Metals*, **146**, 11-15. <https://doi.org/10.1016/j.synthmet.2004.06.016>
- [23] Guggenheimer, S.C., Boyer, J.H., Thangaraj, K., *et al.* (1993) Efficient Laser Action from Two Cw Laser-Pumped Pyromethene-BF₂ Complexes. *Applied Optics*, **32**, 3942-3943. <https://doi.org/10.1364/AO.32.003942>
- [24] Zhao, W. and Carreira, E.M. (2006) Conformationally Restricted Aza-BODIPY: Highly Fluorescent, Stable Near-Infrared Absorbing Dyes. *Chemistry—A European Journal*, **12**, 7254-7263. <https://doi.org/10.1002/chem.200600527>
- [25] Li, F., Yang, S.I., Ciringh, Y., *et al.* (1998) Design, Synthesis, and Photodynamics of Light-Harvesting Arrays Comprised of a Porphyrin and One, Two, or Eight Boron-Dipyrroin Accessory Pigments. *Journal of the American Chemical Society*, **120**, 10001-10017. <https://doi.org/10.1021/ja9812047>
- [26] Bañuelos, J. (2016) BODIPY Dye, the Most Versatile Fluorophore Ever? *The Chemical Record*, **16**, 335-348.
- [27] Zhang, D., Wen, Y., Xiao, Y., *et al.* (2008) Bulky 4-Tritylphenylethynyl Substituted Boradiazaindacene: Pure Red Emission, Relatively Large Stokes Shift and Inhibition of Self-Quenching. *Chemical Communications*, No. 39, 4777-4779. <https://doi.org/10.1039/b808681h>
- [28] Qin, W., Baruah, M., Van der Auweraer, M., *et al.* (2005) Photophysical Properties of Borondipyrromethene Analogues in Solution. *The Journal of Physical Chemistry A*, **109**, 7371-7384. <https://doi.org/10.1021/jp052626n>
- [29] Savoldelli, A., Meng, Q., Paolesse, R., *et al.* (2018) Tetrafluorobenzo-Fused BODIPY: A Platform for Regioselective Synthesis of BODIPY Dye Derivatives. *The Journal of Organic Chemistry*, **83**, 6498-6507. <https://doi.org/10.1021/acs.joc.8b00789>
- [30] Benniston, A.C. and Copley, G. (2009) Lighting the Way Ahead with Boron Dipyrromethene (Bodipy) Dyes. *Physical Chemistry Chemical Physics*, **11**, 4124-4131. <https://doi.org/10.1039/b901383k>
- [31] Gibbs, J.H., Robins, L.T., Zhou, Z., *et al.* (2013) Spectroscopic, Computational Modeling and Cytotoxicity of a Series of Meso-Phenyl and Meso-Thienyl-BODIPYs. *Bioorganic & Medicinal Chemistry*, **21**, 5770-5781. <https://doi.org/10.1016/j.bmc.2013.07.017>
- [32] Chu, G.M., Guerrero-Martinez, A., Fernandez, I. and Sierra, M.A. (2014) Tuning the Photophysical Properties of BODIPY Molecules by π -Conjugation with Fischer Carbene Complexes. *Chemistry—A European Journal*, **20**, 1367-1375. <https://doi.org/10.1002/chem.201303952>
- [33] Waddell, P.G., Liu, X., Zhao, T. and Cole, J.M. (2015) Rationalizing the Photophysical Properties of BODIPY Laser Dyes via Aromaticity and Electron-Donor-Based Structural Perturbations. *Dyes and Pigments*, **116**, 74-81. <https://doi.org/10.1016/j.dyepig.2015.01.010>
- [34] Zatsikha, Y.V., Maligaspe, E., Purchel, A.A., *et al.* (2015) Tuning Electronic Structure, Redox, and Photophysical Properties in Asymmetric NIR-Absorbing Organometallic BODIPYs. *Inorganic Chemistry*, **54**, 7915-7928. <https://doi.org/10.1021/acs.inorgchem.5b00992>
- [35] Thorat, K.G., Kamble, P., Mallah, R., *et al.* (2015) Congeners of Pyromethene-567 Dye: Perspectives from Synthesis, Photophysics, Photostability, Laser, and TD-DFT Theory. *The Journal of Organic Chemistry*, **80**, 6152-6164. <https://doi.org/10.1021/acs.joc.5b00654>
- [36] Ulrich, G., Ziessel, R. and Harriman, A. (2008) The Chemistry of Fluorescent Bodipy Dyes: Versatility Unsurpassed. *Angewandte Chemie International Edition*, **47**, 1184-1201. <https://doi.org/10.1002/anie.200702070>
- [37] Benstead, M., Mehl, G.H. and Boyle, R.W. (2011) 4,4'-Difluoro-4-bora-3a,4a-diaza-s-indacenes (BODIPYs) as Components of Novel Light Active Materials. *Tetrahedron*, **67**, 3573-3601. <https://doi.org/10.1016/j.tet.2011.03.028>
- [38] Boens, N., Leen, V. and Dehaen, W. (2012) Fluorescent Indicators Based on BODIPY. *Chemical Society Reviews*, **41**, 1130-1172. <https://doi.org/10.1039/C1CS15132K>
- [39] Wan, C.W., Burghart, A., Chen, J., *et al.* (2003) Anthracene-BODIPY Cassettes: Syntheses and Energy Transfer. *Chemistry—A European Journal*, **9**, 4430-4441. <https://doi.org/10.1002/chem.200304754>

-
- [40] Souza, F.D., Smith, P.M., Zandler, M.E., *et al.* (2004) Energy Transfer Followed by Electron Transfer in a Supramolecular Triad Composed of Boron Dipyrroin, Zinc Porphyrin, and Fullerene: A Model for the Photosynthetic Antenna-Reaction Center Complex. *Journal of the American Chemical Society*, **126**, 7898-7907. <https://doi.org/10.1021/ja030647u>
- [41] Bozdemir, O.A., Cakmak, Y., Sozmen, F., *et al.* (2010) Synthesis of Symmetrical Multichromophoric Bodipy Dyes and Their Facile Transformation into Energy Transfer Cassettes. *Chemistry—A European Journal*, **16**, 6346-6351. <https://doi.org/10.1002/chem.200903449>
- [42] Iehl, J., Nierengarten, J.F., Harriman, A., *et al.* (2012) Artificial Light-Harvesting Arrays: Electronic Energy Migration and Trapping on a Sphere and between Spheres. *Journal of the American Chemical Society*, **134**, 988-998. <https://doi.org/10.1021/ja206894z>
- [43] Fan, J., Hu, M., Zhan, P. and Peng, X. (2013) Energy Transfer Cassettes Based on Organic Fluorophores: Construction and Applications in Ratiometric Sensing. *Chemical Society Reviews*, **42**, 29-43. <https://doi.org/10.1039/C2CS35273G>
- [44] Fu, Y.L., Chong, Y.Y., Li, H., Feng, W. and Song, Q.H. (2021) Sensitive and Visual Detection of Phosgene by a TICT-Based BODIPY Dye with 8-(*o*-Hydroxy)aniline as the Active Site. *Chemistry—A European Journal*, **27**, 4977. <https://doi.org/10.1002/chem.202005169>
- [45] Franke, J.M., Raliski, B.K., Boggess, S.C., *et al.* (2019) BODIPY Fluorophores for Membrane Potential Imaging. *Journal of the American Chemical Society*, **141**, 12824-12831. <https://doi.org/10.1021/jacs.9b05912>
- [46] Zhang, Y., Zheng, Y.T., Meana, Y. and Raymo, F.M. (2021) BODIPYs with Photoactivatable Fluorescence. *Chemistry—A European Journal*, **27**, 11257-11267. <https://doi.org/10.1002/chem.202101628>