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Benzothiadiazole substituted aza-BODIPY dyes: two-photon absorption enhancement for improved optical limiting performances in the SWIR range.

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Supporting information for this article is given via a link at the end of the document.

Abstract: Aza-boron dipyrromethenes (aza-BODIPYs) presenting a benzothiadiazole substitution on upper positions are described. The strong electron-withdrawing effect of the benzothiadiazole moiety permits to enhance the accepting strength and improve the delocalisation of the aza-BODIPY core to attain a significant degree of electronic communication between the lower donating groups and the upper accepting groups. The nature of the intramolecular charge transfer is studied both experimentally and theoretically. Linear spectroscopy highlighted the strongly red-shifted absorption and emission of the synthesized molecules with recorded fluorescence spectra over 1000 nm. Nonlinear optical properties were also investigated. Strong enhancement of the two-photon absorption of the substituted dyes compared to the unsubstituted one (up to 4520 GM at 1300 nm) results in a ca. 15 - 20% improvement of the optical power limiting performances. These dyes are therefore a good starting point for further improvement of optical power limiting in the SWIR range.

Introduction

Aza-BODIPY is a versatile synthetic platform for designing dyes featuring photophysical properties shifted to the red/near infra-red (NIR) spectral range. This has made them popular since the seminal works of O'Shea in the early 2000's when the benchmark dyes **1** and **2** featuring methoxy or amino substituents at the bottom position, respectively (Figure 1), were reported.[1] The simplicity and synthetic accessibility of these emissive chromophores make them suitable for a wide range of applications, especially in biology.[2] The structural diversity around the aza-BODIPY platform was used to open new opportunities in several fields, e.g., organic photovoltaic cells,[3] fluoro-electrochromism,[4] NIR sensors,[5] fluorescence imaging,[6] and photodynamic therapy.[1c, 7]

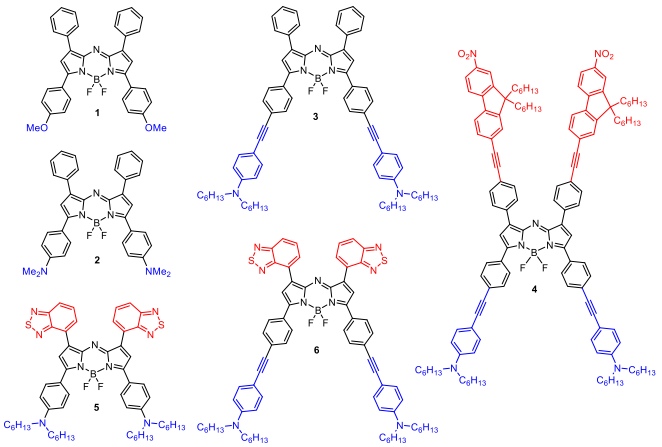


Figure 1. Structures of the different aza-BODIPY dyes designed for advanced photonic applications.

As a common feature, these dyes are very robust and present excellent photo-, redox and chemical stabilities.[8] This makes

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them suitable for applications in harsh conditions such as in nonlinear optics where very intense and focalized laser beams are used. In an earlier work by our group, the two-photon absorption (2PA) properties in the short-wave infrared (SWIR) region, has been described for the functionalized aza-BODIPY dyes **3** (Figure 1), featuring an extended conjugated skeleton.[9]

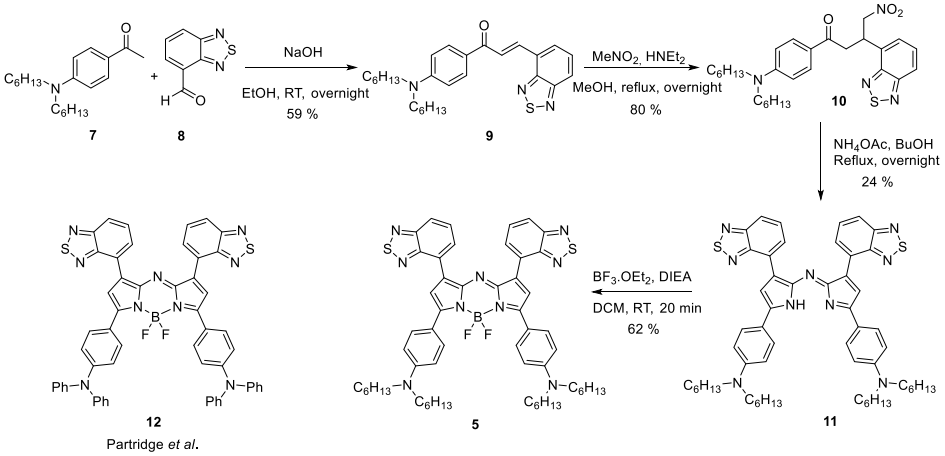
Whilst many chromophores including polymethine dyes, squaraines, extended or fused porphyrins, porphyrin arrays, dithiolene transition metal complexes, and diradical polyaromatic dyes[10] have been reported to exhibit significant 2PA cross-section in the SWIR, the excellent solubility, photostability, and chemical robustness of **3** enabled the report of a rare example of optical power limiting (OPL) material working at telecommunication wavelengths (1550 nm).[11] OPL results on **3** were reported in solution[9] and for the first time in a doped or grafted sol-gel glass matrix.[12]

Optical power limiters are photonic devices transparent at low fluence and absorbent when the fluence exceeds a certain threshold. They can therefore be used to protect highly sensitive optical detectors against optical radiation.[13] Indeed, there is a growing interest in OPL devices working at 1550 nm, an eye-safe wavelength. This interest is due to the spreading of LIDAR (LIght Detection And Ranging) systems for aeronautics (telemetry), military applications (active imaging), and civilian transportation (autonomous vehicles guiding systems). Optimization of molecular structures for OPL applications at telecommunication wavelengths requires fulfilling a precise list of requirements. Firstly, the target chromophore must present the highest 2PA cross-section possible in the range-of-interest (ROI) wavelengths, alongside with the possibility to induce simultaneously excited state absorption (ESA) at the same wavelengths within the same incident laser pulse. This overall three-photon absorption (2+1) process becomes even more favorable when the laser pulse duration is long, typically in the ns-regime for OPL experiment.[14] Secondly, the target chromophore must present enhanced solubility in organic solvents, generally chlorinated solvents like dichloromethane or carbon tetrachloride (around 1-10^{-1} mol.L^{-1}) as well as enhanced chemical and photochemical stability. In this context, we have previously developed a family of aza-BODIPYs, taking advantage of the synthetic versatility of this platform, in order to optimize the spectral overlap between 2PA and ESA processes in the ROI, although, the 2PA cross-section above 1300 nm of the dyes remained modest.[9b,c]

It is well known that obtaining large molecular 2PA cross-sections requires a strong electronic polarizability generally achieved in extended π-conjugated systems substituted by electron donating or withdrawing substituents resulting in the formation of charge transfer (CT) transitions.[15] Using these general molecular engineering rules, we previously designed chromophore **4** bearing auxiliary nitrofluorene accepting groups of top 1,7 positions (Figure 1), expecting that this substitution would increase both the conjugation length and the CT character of the transition.[9b] However, this study showed that the strong electron-withdrawing aza-BODIPY core was acting as an “accepting trap”, forbidding direct electronic communication between the dialkylamino phenylethynyl donor and the nitrofluorene accepting groups. The nitrofluorene groups had indeed very little effect on the effective conjugation length and 2PA cross-section, likely because they are weaker acceptors than the aza-BODIPY core itself. To circumvent this issue, electron-withdrawing groups as strong as the aza-BODIPY core should be used. One example is the benzothiadiazole (BTZ) unit, commonly used for advanced photonic applications: dye sensitized solar cells (DSSC),[16] NIR-bioimaging,[17] and optoelectronics.[18] BTZ has been rarely used in combination with the aza-BODIPY structure.[19] In the present paper, original aza-BODIPY dyes featuring benzothiadiazole moiety at the top position (**5, 6** in Figure 1) have been synthesized. The molecules revealed interesting linear and nonlinear photophysical properties in the NIR and SWIR regions, respectively. The improved CT character induced by the BTZ groups was unambiguously evidenced by a comprehensive photophysical study and confirmed by TD-DFT calculations. Finally, the OPL behavior at telecommunication wavelengths revealed a significant improvement compared to the reference chromophore **3**.

Results and Discussion

Synthesis. In order to assess the impact of the BTZ moieties on the spectroscopic properties of the aza-BODIPY dyes, the two molecules **5** and **6** have been synthesized (Figure 1). **5**, inspired by the recent work of Partridge *et al.*[19] where the diphenylamine donors have been replaced by dihexylamine for a stronger donating effect and improved solubility in organic solvents, is the BTZ-analogue of the historical reference dye **2**.[1] In addition, **6**, featuring extended conjugated skeleton, is the BTZ-analogue of our chromophore **3**, previously used in nonlinear optical applications.[9b]

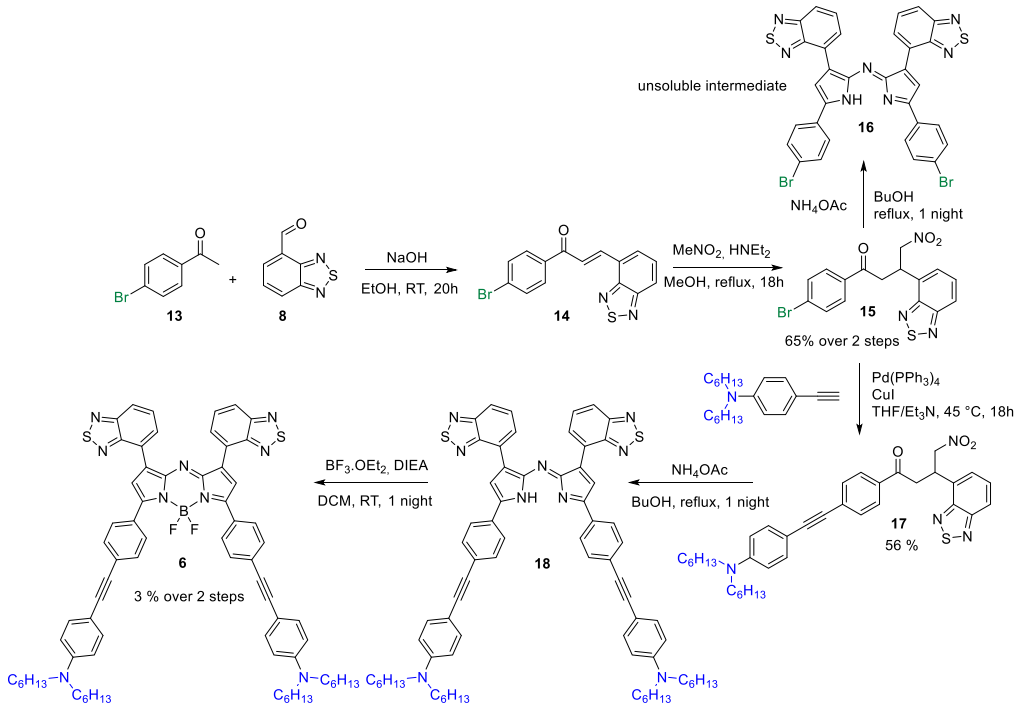


Scheme 1. Synthetic procedure for the preparation of **5**. In the left corner is represented the previously published dye (**12**).[19]

The synthesis of compound **5**, depicted in Scheme 1, follows the classical procedure for the preparation of symmetrical aza-BODIPY compounds,[1c] starting from the coupling between 4’-dihexylaminoacetophenone and commercial 2,1,3-benzo-

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Scheme 2. Synthetic procedure for the preparation of **6**.

thiadiazole-4-carbaldehyde. The chalcone **9**, then undergoes a Michael addition with nitromethane and the dipyrromethene **11** is obtained after cyclization with an ammonium salt at high temperature. The yield of this step is rather modest, 24% after purification by column chromatography, but the large availability of the precursor enables us to realize gram scale synthesis. Finally, the aza-BODIPY **5** was readily obtained after borylation and purification in 62% yield. The synthesis of molecule **6** is directly inspired by a previous methodology.[9b] In contrast to its phenyl-analogue, the brominated BTZ-dipyrromethene **16** is insoluble in organic solvents and could not be fully characterized or used as a reactive intermediate. Consequently, the Pd-catalyzed Sonogashira coupling of dihexylaminophenyl-ethynyl was performed using the Michael adduct **17**. As already observed,[18] the cyclization of the substituted Michael adduct is complicated and difficult to purify. It is therefore obtained in a poor yield. This is why the final borylation step was immediately conducted on the crude mixture, and purification led to the target compound **6** with a very low yield (3% over the two steps). All compounds have been fully characterized by ^{1}H, ^{13}C and ^{18}F NMR techniques and high-resolution mass spectrometry (see the Supporting Information for details).

Linear spectroscopy. The photophysical properties of aza-BODIPYs **5** and **6** featuring BTZ substituents were studied in organic solvents and compared to their structural analogs **2** and **3**, respectively (Figure 2, Table 1). As expected, BTZ substitution red-shifts the maximum absorption for both molecules **5** (+ 95 nm) and **6** (+ 42 nm) compared to **2** and **3**, respectively. Compound **6** also presents a significant broadening of the lowest energy transition band compared to compound **3** (full width at half maximum; $\omega_{1/2}$ = 2149 cm^{-1} and 2051 cm^{-1}, respectively). In addition, the cut-off wavelength, $\lambda_{cut\text{-}off}$, being defined as the intersection of the red tail of the absorption band with the x-axis, is significantly red-shifted in compound **6** compared to **3** (900 nm and 837 nm, respectively, see Figure S1). It has been previously shown that this lowest energy absorption band has a mixed CT-cyanine character.[9b] The broadening of the absorption band accompanied by the related red-shift of the cut-off wavelength from **3** to **6**, could be explained by the increased contribution of the CT character, which would *in fine* lead to higher two-photon absorption. In order to obtain a deeper insight into this hypothesis, solvatochromism experiments in absorption and emission have been conducted on both compounds **5** and **6** in solvents ranging from cyclohexane to dimethylformamide (Figures 3 and S2, Tables S1 and S2). The plots of the absorption maxima, shoulder, and cut-off energies versus Reichardt's polarity scale[20] are shown in Figure S3. Concerning compound **6**, the maximum absorption is barely affected by the solvent polarity with all maximum included in a 20 nm interval (slope = +728 cm^{-1}). However, the cut-off wavelength shows a more pronounced positive solvatochromism (slope = -1889 cm^{-1}). Due to limited emission in polar solvents, only two emission spectra have been measured for compound **6** with a maximum emission at λ_{em} = 890 nm in toluene.

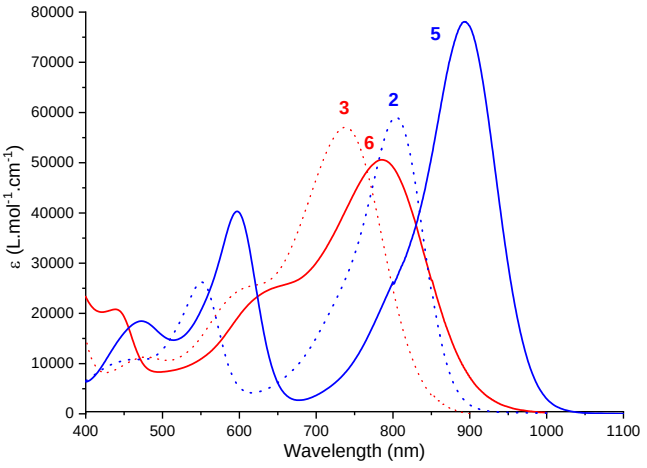


Figure 2. Molar absorptivity comparison of aza-BODIPYs **5** and **6** featuring BTZ substituents (straight line) with related dyes **2** and **3** featuring phenyl substituents (dotted lines) at the 1,7 positions. Spectra were recorded at room temperature in diluted DCM solution.

Compound **5** shows a slightly different behaviour with a positive solvatochromic shift for the maximum absorption, emission, and cut-off wavelengths (slope = - 1111 cm^{-1}; - 2905 cm^{-1} and – 2488 cm^{-1}, respectively) indicating a strong dependence of the

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spectroscopic properties with the solvent polarity. Interestingly, the maximum emission of compound **5** goes above 1000 nm in a polar solvent, with a maximum at 1034 nm in DMF. It is worth noting that the quantum yield of the NIR-dyes **5** was determined to 0.9% in dichloromethane with the absolute integrating sphere method[21] and 1,7% with the relative one using PD2631 as standard.[22] As expected, decreasing the solvent polarity results in a significant enhancement of the relative quantum yield up to 2.9 % in carbon tetrachloride (Table S2, measurement in integrating sphere).

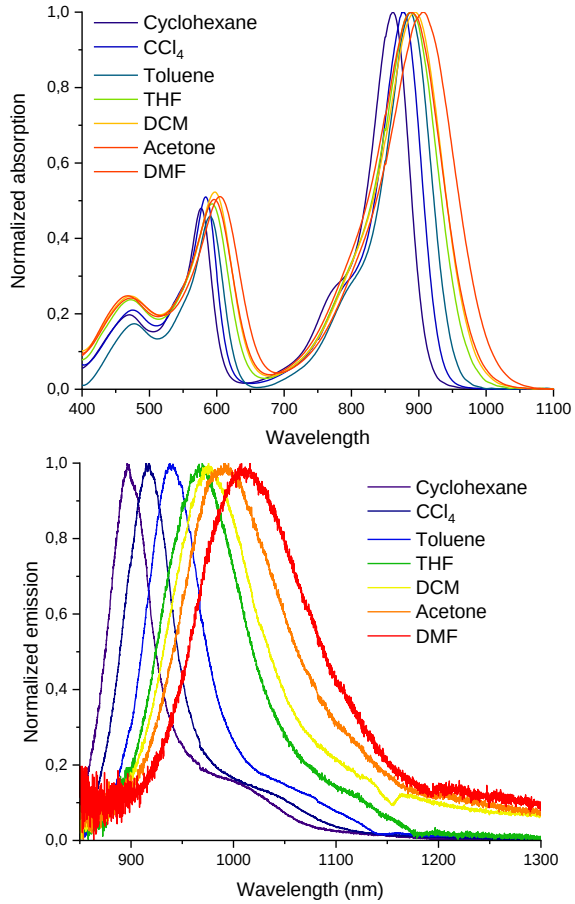


Figure 3. Normalized absorption (top) and emission (bottom) of **5** in different solvents indicated in inset.

Theoretical simulations. In order to have a better understanding of the nature of the optical transition for compounds **5** and **6**, theoretical simulations have been conducted on simplified compounds featuring smaller dimethylamino donor group at the bottom position. Computational details are given in supporting information and the main results are summarized below.

Table 1. Photophysical properties of aza-BODIPY dyes **2**, **3**, **5** and **6** in DCM or in toluene when precised.

	λ_{max}	ε	λ_{em}	ϕ
2	804	59000	872	0.015
3	740	57000	826[a]	0.04[a]
5	895	78000	975	1.7
6	782	50500	890[a]	0.016[a]

[a] measurements in toluene.

The computed vertical transition energies are larger than the energy corresponding to the experimental λ_{max}, (error in the 0.17-0.27 eV range). Both the sign and the magnitude of these differences are expected, as, on the one hand, the calculations neglect vibrational couplings (that would red-shift the theoretical energies), and, on the other hand, we consider aza-BODIPY derivatives for which it is known that TD-DFT tends to provide too large transition energies as well. Both aspects are discussed in details in the literature.[23] However, the trends are reproduced. Note that in going from dyes **2** to **3** (**5** to **6**), theory predicts a small (significant) blue-shift of the lowest band, which fits the measurements (Figure 2). The EDD (Electronic Density Difference) plots in Figure 4, can explain this trend: in the more compact compounds **2** and **5** the bottom amino groups play a stronger electron-donating role, whereas in dyes **3** and **6**, the distance between the amino groups and the aza-BODIPY cores becomes too large and it is the less potent ethynyl segments that act as secondary donor groups. Still focussing on the lowest energy transition (S_0-S_1), and now comparing **2** to **5** and **3** to **6**, we notice that the CT character of the transition significantly increases when replacing the top phenyl rings by BTZ groups, the latter playing a minor yet not trifling role in the lowest transition according to the EDDs. This induces a significant increase of the d^{CT} value. These facts indicate that the BTZ moieties increase the electron-withdrawing strength of the aza-BODIPY core and simultaneously expand the π-delocalization, in turn, induce red-shifts of the 1PA transition. Considering the second transition, it is clear from Figure 4 that it presents much stronger CT character in all cases (see the increase of d^{CT}). Importantly, in both compounds **2** and **5**, we compute a large separation (ca. 1.0 eV) between the two lowest excited states, indicating that the S_0-S_2 excitation is responsible for the second absorption band at ca. 550 nm (**2**) and 600 nm (**5**) in the experimental spectra (see Figure 2). In contrast, in both extended chromophores **3** and **6**, the separation between the two first excited states is notably smaller (ca. 0.7 eV), hinting that the strong shoulder at ca. 600 nm in the experimental spectra (Figure 2) are likely a combination of vibronic effects and this second electronic transition. This interpretation is also consistent with the significantly broader bands in the extended compounds, and it has a strong consequence on the 2PA spectra (see below).

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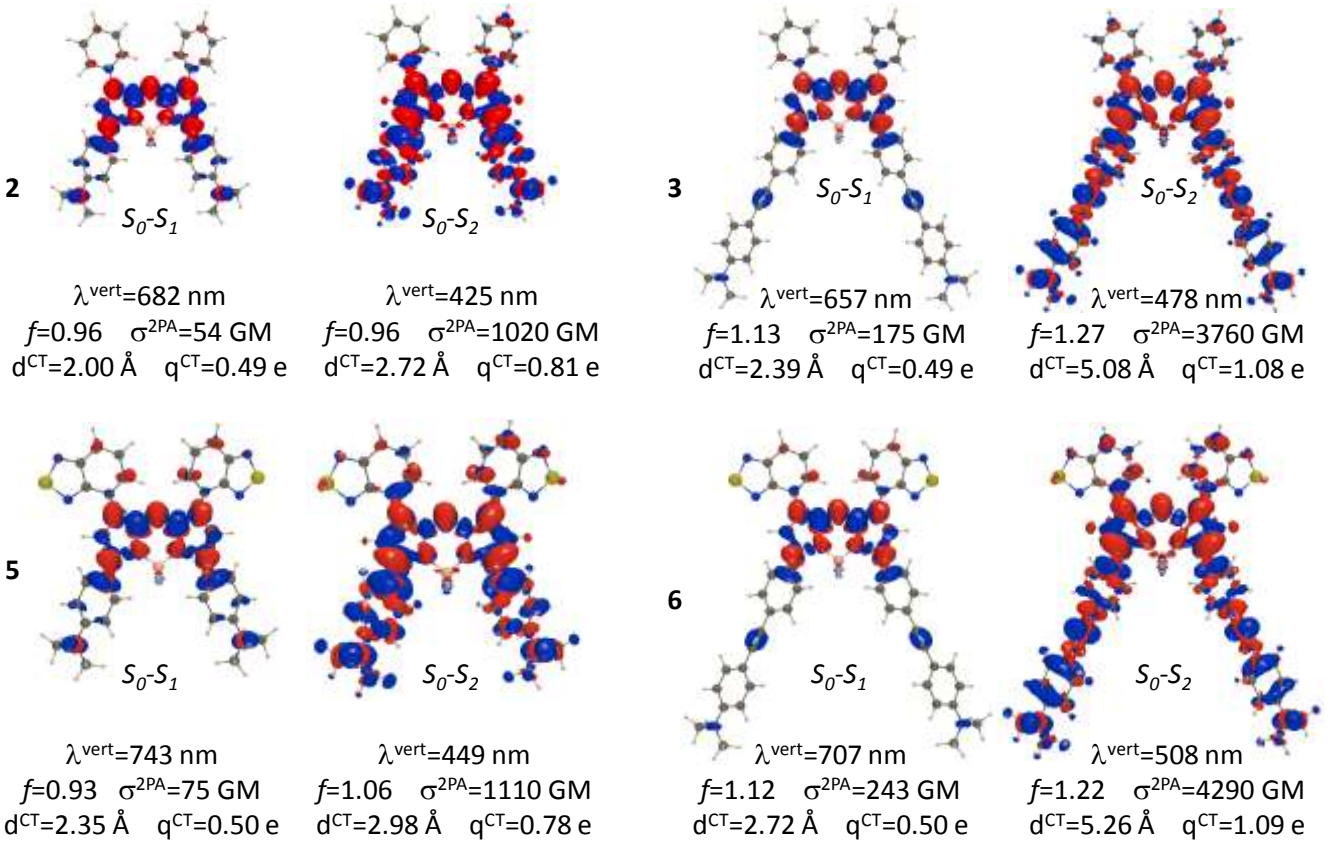


Figure 4. Summary of the main theoretical results. We represent for the key transitions, the density difference plots (red: increase of density, blue: decrease of density upon excitation, 0.0008 isovalue), and provide the vertical 1PA transition energies and oscillator strengths, as well as the 2PA cross sections. We also give the CT distance and charge computed using Le Bahers' model.[24]

Nonlinear optical properties. The SWIR nonlinear two-photon absorption properties of compounds **5** and **6** were determined by open aperture Z-scan in DCM solution using a fs-optical parametric amplifier pumped by a Ti:Sapphire source (typical pulse duration of 150 fs) between 1100 and 1700 nm.[25] For each wavelength, the experimental nonlinear transmittance curves (Figure 5) were measured and fitted using the complete propagation equation (eq. 1) taking into account both 2PA and ESA, where I represents the light irradiance, z the propagation axis, α_2 the 2PA coefficient, σ_{ESA} the ESA cross-section, and N_e describes the first excited-state population after 2PA absorption:

$$\frac{dI}{dz} = -\alpha_2 I^2 - \sigma_{ESA} N_e I. \qquad (1)$$

Using this model, both 2PA coefficient and ESA cross-sections could be determined simultaneously for a given wavelength (Table 2). Then, the 2PA cross-section was determined using equation (2) where *N* represents the molecular density and $\hbar\omega$ the photon energy at the operating wavelength. σ_{2PA} is given in Göppert-Mayer (1 GM = 10^{-50} cm^4.s.molecule^{-1}.photon^{-1}).

$$\sigma_{2PA} = \frac{\hbar\omega\alpha_2}{N} \qquad (2)$$

The 2PA cross-section is then reported in wavelength doubled-scale and superimposed with the 1PA (Figure 6). Both **5** and **6** exhibit the typical features of V-shaped, pseudo-C_{2v} symmetric aza-BODIPY derivatives.[9b] The weak, red-shifted 2PA transition overlaps with the first intense 1PA band featuring a main "cyanine" character with a moderate CT. The experimental data (σ_{2PA}(1700) = 80 GM and σ_{2PA}(1550) = 970 GM for **5** and **6**, respectively) are in reasonable agreement with the theoretical

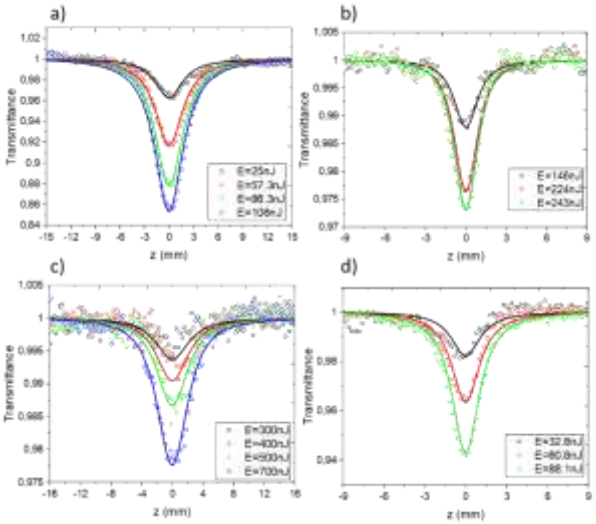


Figure 5. Nonlinear transmittance of **5** (a,b) and **6** (c,d) at 1300 (a,c) and 1550 nm (b, d). The open circles indicate the experimental points at a given incident pulse energy. The line represents the fit using eq.1 enabling to extract the 2PA and ESA cross-sections.

values (σ_{2PA} = 75 and 243 GM for **5** and **6**, respectively, see Figure 4). In marked contrast, the most intense 2PA band is blue shifted and overlaps with the 1PA transition presenting the most pronounced CT character corresponding to the 600 nm band for **5** and the shoulder at 650 nm for **6**. For **5**, the measured value for this second transition (280 GM) is significantly smaller than the theoretical one, but the above-mentioned attributions of the S_0-S_1

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and S_0-S_2 excitations to the peaks at ca. 900 and 600 nm is clearly confirmed.

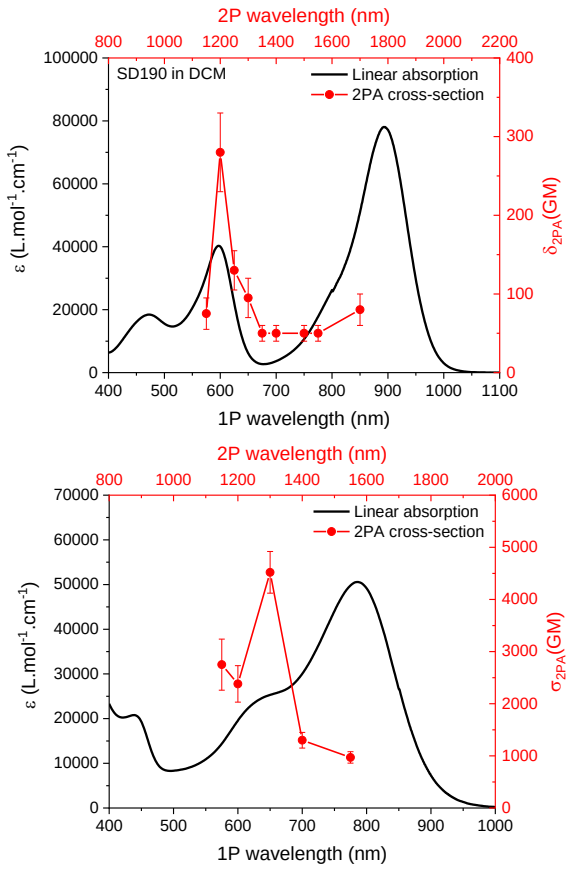


Figure 6. Comparison between linear absorption (black line and corresponding black scale) and two-photon absorption (red dot and corresponding red scale) for compounds **5** (top) and **6** (bottom).

Table 2. Nonlinear absorption coefficients for compounds **5** and **6** in DCM: 2PA cross-section, σ_{2PA}, in GM; one-photon ESA cross-section, σ_{ESA}, in 10^{-20} m^2.

Wavelength [nm]	5		6	
	σ_{2PA}	σ_{ESA}	σ_{2PA}	σ_{ESA}
1150	75 ± 20	7.1 ± 1.9	2750 ± 490	0.13 ±0.05
1200	280 ± 50	7.1 ± 1.9	2380 ± 350	3.1 ± 0.8
1250	130 ± 25	4.2 ± 1.0		
1300	95 ± 25	3.6 ± 1.3	4520 ± 500	0.22 ± 0.12
1350	80 ± 15	0.5 ± 0.1		
1400	50 ± 10	0.5 ± 0.15	1300 ± 150	0.08 ± 0.05
1550	50 ± 10	0.85 ± 0.2	970 ± 110	0.55 ± 0.15
1700	80 ± 20	-	-	-

As expected, the more extended phenyl-ethynyl conjugated skeleton in **6**, results in a very significant increase of the 2PA cross-section for which a very large maximal value of 4520 GM has been reached at 1300 nm. For comparison, the theoretical value of the S_0-S_2 excitation is 4290 GM. Although such perfect agreement cannot be obtained without some error compensation, this confirms the overlapping character of the two lowest transitions in **6**, which contrast to **5**. Interestingly, this maximal 2PA cross-section is twice larger than those measured for the benchmark compound **3** (σ_{2PA} = 1970 GM at 1150 nm) and of the extended compound **4** (σ_{2PA} = 2250 GM at 1220 nm)[9b] and is also significantly red-shifted. This result unambiguously illustrates the strong impact of the benzothiadiazole substituent that reinforces the CT character with the chromophore allowing strongly enhancing the aza-BODIPY nonlinear properties. To the best of our knowledge, this compound presents the highest 2PA cross-section among all aza-BODIPY dyes.

Optical Power Limiting. OPL performances in SWIR were performed for the new compounds **5, 6** and **3** for comparison, in a set-up based on the f/5 system[26] (see Supporting Information for description) and ~4 ns pulses (source an EKSPLA NT342C OPO).

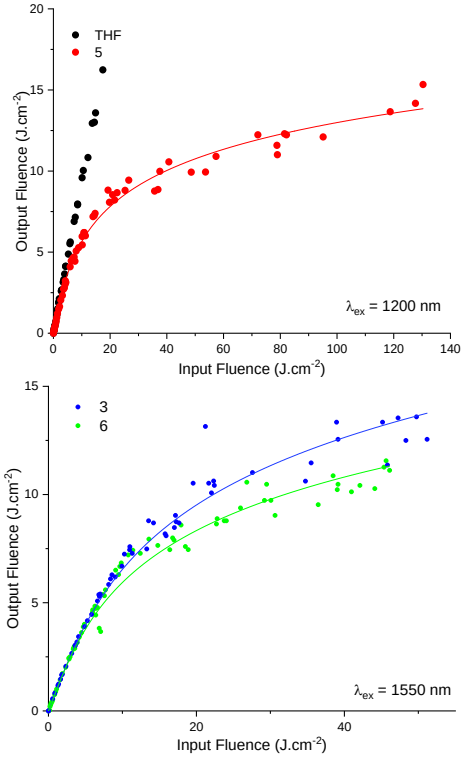


Figure 7. Top: OPL experiment for compound **5** in THF, (red circles) and pure THF (black circles) at 1200 nm. Bottom: OPL experiments for compounds **3** (blue) and **6** (green) at 1550 nm in CCl_4. All measurements were done in 50 mM solutions, performed in a f/5 set-up and 4 ns pulses.

Compound **6** was evaluated at 1400 and 1550 nm (eye-safe wavelength) using 50 mM solutions in carbon tetrachloride. Due to the relatively low 2PA cross-section at these wavelengths, compound **5** was only evaluated at 1200 nm using 50 mM solution in THF (Figures 7 and S6). For compound **5** a blank measurement using THF only was performed to make sure that no nonlinear effects due to THF were affecting the OPL measurements. OPL results show a good transmission above 80% for lower input fluences (< 3 $J.cm^{-2}$). Above this threshold, the OPL effect is pronounced and a reduction to 50% transmission is reached for an input fluence of 14 $J.cm^{-2}$. The output fluence is limited to below 15 $J.cm^{-2}$ (for input fluences up to 140 $J.cm^{-2}$). These results are interesting considering the straightforward synthesis and small conjugation length of compound **5**. Also, this compound seems to compensate its moderate 2PA cross section values by

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a very high ESA (σ_{ESA} = 7.1 ± 0.9 cm^{-2} at 1200 nm) which has been shown to be of first importance for the efficiency of optical power limiters exposed to nanosecond laser pulses.[9b]
Compound **6** OPL performance was compared to benchmark chromophore **3**. At 1550 nm, the linear transmission, for **3** and **6**, were above 90%. At a fluence of 2 $J.cm^{-2}$ the OPL effect is pronounced and a reduction to 50% transmission was obtained, at an input fluence of 15 $J.cm^{-2}$ and 19 $J.cm^{-2}$ for compounds **6** and **3**, respectively. For an input fluence of F_{in} = 45 $J.cm^{-2}$, the output fluence was F_{out} = 11 $J.cm^{-2}$ and 13 $J.cm^{-2}$ for compounds **6** and **3**, respectively. For compound **6** an approximate 15% enhancement in OPL performance is achieved due to the benzothiadiazole substitution, as compared to **3**. At 1400 nm, similar results were obtained with a maximum output fluence of 12 vs 10 $J.cm^{-2}$ for compound **3** and **6** respectively, at an input fluence of 86 $J.cm^{-2}$ (Figure S6). This result was attributed to the increase of the 2PA cross section of compound **6** compared to benchmark chromophore **3**.

Conclusions

Two new aza-BODIPY dyes presenting a benzothiadiazole substitution have been synthesized and characterized. This particular moiety induced a strong bathochromic shift in maximum absorption and emission. Through spectroscopic measurements and theoretical calculations, the role of the strong electron withdrawing substituent was rationalized. Indeed, we have shown that benzothiadiazole allows overcoming the ‘’accepting trap’’ effect of the aza-BODIPY core, thus reinforcing the accepting character of the aza-BODIPY core. This allows a partial yet significant electronic communication between the upper and lower parts of the molecule which hasn’t been observed earlier. The benzothiadiazole substitution allowed for a significant increase in the CT character of the main transition of molecule **6**. This resulted in a strong increase in 2PA in the 1.1 – 1.6 µm region, which is reflected in the OPL performance: an approximate 20% enhancement in OPL performance (at 1400 and 1550 nm) is achieved due to the benzothiadiazole substitution, compared to **3**. In compound **5**, on the other hand, a weaker 2PA cross section is compensated by a strong ESA to give OPL behavior at 1200 nm.

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Reference

[1] a) J. Killoran, L. Allen, J. F. Gallagher, W. M. Gallagher, D. F. O′ Shea, *Chem. Commun.* **2002**, 1862-1863; b) M. Tasior, J. Murtagh, D. O. Frimannsson, S. O. McDonnell, D. F. O'Shea, *Org. Biomol. Chem.* **2010**, *8*, 522-525; c) A. Gorman, J. Killoran, C. O'Shea, T. Kenna, W. M. Gallagher, D. F. O'Shea, *J. Am. Chem. Soc.* **2004**, *126*, 10619-10631.
[2] a) Y. Ge, D. F. O'Shea, *Chem. Soc. Rev.* **2016**, *45*, 3846-3864; b) Z. Shi, X. Han, W. Hu, H. Bai, B. Peng, L. Ji, Q. Fan, L. Li, W. Huang, *Chem. Soc. Rev.***2020**, *49*, 7533-7567.
[3] R. Feng, N. Sato, T. Yasuda, H. Furuta, S. Shimizu, *Chem. Comm.* **2020**, *56*, 2975-2978.
[4] H. Lim, S. Seo, S. Pascal, Q. Bellier, S. Rigaut, C. Park, H. Shin, O. Maury, C. Andraud, E. Kim, *Sci. Rep.* **2016**, *6*, 18867.
[5] H. J. Xiang, H. P. Tham, M. D. Nguyen, S. Z. Fiona Phua, W. Q. Lim, J. G. Liu, Y. Zhao, *Chem Commun.* **2017**, *53*, 5220-5223.
[6] a) M. Grossi, M. Morgunova, S. Cheung, D. Scholz, E. Conroy, M. Terrile, A. Panarella, J. C. Simpson, W. M. Gallagher, D. F. O'Shea, *Nat. Commun.* **2016**, *7*, 10855; b) J. Pliquett, A. Dubois, C. Racoeur, N. Mabrouk, S. Amor, R. Lescure, A. Bettaieb, B. Collin, C. Bernhard, F. Denat, P.-S. Bellaye, C. Paul, E. Bodio, C. Goze, *Bioconjug. Chem.* **2019**, *30*, 1061-1066 ; c) M. H. Y. Cheng, K. M. Harmatys, D. M. Charron, J. Chen, G. Zheng, *Angew. Chem. Int. Ed.* **2019**, *58*, 13394-13399; d) A. Godard, G. Kalot, J. Pliquett, B. Busser, X. Le Guevel, K. D. Wegner, U. Resch-Genger, Y. Rousselin, J. L. Coll, F. Denat, E. Bodio, C. Goze, L. Sancey, *Bioconjug. Chem.* **2020**, *31*, 1088-1092.
[7] a) Y. Zhang, S. Bo, T. Feng, X. Qin, Y. Wan, S. Jiang, C. Li, J. Lin, T. Wang, X. Zhou, Z. X. Jiang, P. Huang, *Adv Mater* **2019**, e1806444; b) N. Adarsh, P. S. S. Babu, R. .R Avirah, M. Viji, S. A. Nair, D. Ramaiah, *J. Mat. Chem. B* **2019**; *7*, 2372-2377 c) Q. Wang, D. K. P. Ng and P.-C. Lo, *J. Mater. Chem. B*, **2018**, *6*, 3285-3296; d) Ł. Łapok, I. Cieślar, T. Pędziński, K. M. Stadnicka, M. Nowakowska, *ChemPhysChem* **2020**, *21*, 725-740.
[8] M. Obloza, L. Lapok, T. Pedzinski, K. M. Stadnicka, M. Nowakowska, *Chemphyschem* **2019**, *20*, 2482-2497.
[9] a) P.-A. Bouit, K. Kamada, P. Feneyrou, G. Berginc, L. Toupet, O. Maury, C. Andraud, *Adv. Mater.* **2009**, *21*, 1151-1154; b) S. Pascal, Q. Bellier, S. David, P.-A. Bouit, S.-H. Chi, N. S. Makarov, B. Le Guennic, S. Chibani, G. Berginc, P. Feneyrou, D. Jacquemin, J. W. Perry, O. Maury, C. Andraud, *J. Phys. Chem. C* **2019**, *123*, 23661-23673; c) S. David, G. Pilet, G. Berginc, C. Andraud, O. Maury *New. J. Chem.* **2020**, *44*, 13125-13130.
[10] a) J. M. Hales, S. Barlow, H. Kim, S. Mukhopadhyay, J.-L. Brédas, J. W. Perry, S. R. Marder, *Chem. Mater.* **2013**, *26*, 549-560; b) K. S. Kim, J. M. Lim, A. Osuka, D. Kim, *J. Photochem. Photobiol. C: Photochem. Rev.* **2008**, *9*, 13-28; c) H. Hu, O. V. Przhonska, F. Terenziani, A. Painelli, D. Fishman, T. R. Ensley, M. Reichert, S. Webster, J. L. Bricks, A. D. Kachkovski, D. J. Hagan, E. W. Van Stryland, *Phys. Chem. Chem. Phys.* **2013**, *15*, 7666-7678; d) L. A. Padilha, S. Webster, O. V. Przhonska, H. Hu, D. Peceli, T. R. Ensley, M. V. Bondar, A. O. Gerasov, Y. P. Kovtun, M. P. Shandura, A. D. Kachkovski, D. J. Hagan, E. W. V. Stryland, *J. Phys. Chem. A* **2010**, *114*, 6493-6501; e) K. Kurotobi, K. S. Kim, S. B. Noh, D. Kim, A. Osuka, *Angew. Chem. Int. Ed.* **2006**, *45*, 3944-3947; f) T. K. Ahn, K. S. Kim, D. Y. Kim, S. B. Noh, N. Aratani, C. Ikeda, A. Osuka, D. Kim, *J. Am. Chem. Soc.* **2006**, *128*, 1700-1704; g) K. Kamada, S.-i. Fukuen, S. Minamide, K. Ohta, R. Kishi, M. Nakano, H. Matsuzaki, H. Okamoto, H. Higashikawa, K. Inoue, S. Kojima, Y. Yamamoto, *J. Am. Chem. Soc.* **2013**, *135*, 232-241; h) Y. Ni, S. Lee, M. Son, N. Aratani, M. Ishida, A. Samanta, H. Yamada, Y. T. Chang, H. Furuta, D. Kim, J. Wu, *Angew. Chem. Int. Ed.* **2016**, *55*, 2815-2819; i) J. M. Hales, J. Matichak, S. Barlow, S. Ohira, K. Yesudas, J. L. Bredas, J. W. Perry, S. R. Marder, *Science* **2010**, *327*, 1485-1488; j) S. Barlow, J.-L. Brédas, Y. A. Getmanenko, R. L. Gieseking, J. M. Hales, H. Kim, S.

Accepted Manuscript

R. Marder, J. W. Perry, C. Risko, Y. Zhang, *Mater. Horiz.* **2014**, *1*, 577-581; k) T. G. Allen, S. Benis, N. Munera, J. Zhang, S. Dai, T. Li, B. Jia, W. Wang, S. Barlow, D. J. Hagan, E. W. Van Stryland, X. Zhan, J. W. Perry, S. R. Marder, *J. Phys. Chem A* **2020**, *124*, 4367-4378.
[11] a) J. M. Hales, M. Cozzuol, T. E. O. Screen, H. L. Anderson, J. W. Perry, *Optics Express* **2009**, *17*, 18478-18488; b) P.-A. Bouit, G. Wetzel, G. Berginc, B. Loiseaux, L. Toupet, P. Feneyrou, Y. Bretonnière, K. Kamada, O. Maury, C. Andraud, *Chem. Mater.* **2007**, *19*, 5325-5335; c) P.-A. Bouit, R. Westlund, P. Feneyrou, O. Maury, M. Malkoch, E. Malmström, C. Andraud, *New J. Chem.* **2009**, *33*, 964-968.
[12] a) D. Château, Q. Bellier, F. Chaput, P. Feneyrou, G. Berginc, O. Maury, C. Andraud and S. Parola, *J. Mater. Chem. C* **2014**, *2*; b) S. David, D. Chateau, H.-J. Chang, L. H. Karlsson, M. V. Bondar, C. Lopes, B. Le Guennic, D. Jacquemin, G. Berginc, O. Maury, S. Parola, C. Andraud, *J. Phys. Chem C* **2020** *124*, 24344-24350.
[13] D. Dini, M. J. Calvete, M. Hanack, *Chem. Rev.* **2016**, *116*, 13043-13233.
[14] Q. Bellier, N. S. Makarov, P. A. Bouit, S. Rigaut, K. Kamada, P. Feneyrou, G. Berginc, O. Maury, J. W. Perry, C. Andraud, *Phys. Chem. Chem. Phys.* **2012**, *14*, 15299-15307.
[15] a) G. S. He, L.-S. Tan, Q. Zheng, P. N. Prasad, *Chem. Rev.* **2008**, *108*, 1245-1330; b) M. Pawlicki, H. A. Collins, R. G. Denning and H. L. Anderson, *Angew. Chem. Int. Ed.* **2009**, *48*, 3244-3266.
[16] a) S. H. Park, A. Roy, S. Beaupré, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. Lee, A. J. Heeger, *Nat. Photonics* **2009**, *3*, 297-302; b) J. Du, A. Fortney, K. E. Washington, C. Bulumulla, P. Huang, D. Dissanayake, M. C. Biewer, T. Kowalewski, M. C. Stefan, *ACS Appl. Mater. & Interf.* **2016**, *8*, 33025-33033.
[17] a) S. Zhu, S. Herraiz, J. Yue, M. Zhang, H. Wan, Q. Yang, Z. Ma, Y. Wang, J. He, A. L. Antaris, Y. Zhong, S. Diao, Y. Feng, Y. Zhou, K. Yu, G. Hong, Y. Liang, A. J. Hsueh and H. Dai, *Adv. Mater.* **2018**, *30*, e1705799; b) G. Hong, A. L. Antaris, H. Dai, *Nat. Biomed.Eng.* **2017**, *1*; c) A. L. Antaris, H. Chen, K. Cheng, Y. Sun, G. Hong, C. Qu, S. Diao, Z. Deng, X. Hu, B. Zhang, X. Zhang, O. K. Yaghi, Z. R. Alamparambil, X. Hong, Z. Cheng, H. Dai, *Nat. Mater.* **2016**, *15*, 235-242.
[18] H. N. Tsao, D. M. Cho, I. Park, M. R. Hansen, A. Mavrinskiy, D. Y. Yoon, R. Graf, W. Pisula, H. W. Spiess, K. Müllen, *J. Am. Chem. Soc.* **2011**, *133*, 2605-2612.
[19] E. M. A. Al-Imarah, P. J. Derrick, A. Partridge, *J. Photochem. Photobiol. A: Chem.* **2017**, *337*, 82-90.
[20] C. Reichardt, *Chem.Rev.* **1994**, *94*, 2319-2358.
[21] K.-L. Wong, J.-C. G. Bünzli, P. A. Tanner, *J. Lumin.* **2020**, *224*.
[22] S. Webster, L. A. Padilha, H. Hu, O. V. Przhonska, D. J. Hagan, E. W. Van Stryland, M. V. Bondar, I. G. Davydenko, Y. L. Slominsky, A. D. Kachkovski, *J. Lumin.* **2008**, *128*, 1927-1936.
[23] a) B. Le Guennic, D. Jacquemin, *Acc. Chem. Res.* **2015**, *48*, 530-537; b) S. Chibani, B. Le Guennic, A. Charaf-Eddin, O. Maury, C. Andraud, D. Jacquemin, *J. Chem. Theory Comput.* **2012**, *8*, 3303-3313; c) B. Le Guennic, O. Maury, D. Jacquemin, *Phys. Chem. Chem. Phys.* **2012**, *14*, 157-164; d) S. Chibani, B. Le Guennic, A. Charaf-Eddin, A. D. Laurent, D. Jacquemin, *Chem. Sci.* **2013**, *4*; e) M. R. Momeni, A. Brown, *J. Chem. Theory Comput.* **2015**, *11*, 2619-2632; f) R. Berraud-Pache, F. Neese, G. Bistoni, R. Izsák, *J. Phys. Chem. Lett.* **2019**, *10*, 4822-4828.
[24] T. Le Bahers, C. Adamo, I. Ciofini, *J. Chem. Theory Comput.* **2011**, *7*, 2498-2506.
[25] M. Sheik-Bahae, A. A. Said, T. H. Wei, D. J. Hagan, E. W. Van Stryland, *IEEE J. Quantum Elect.* **1990**, *26*, 760-769.
[26] Thesis H. Lundén, PhD Thesis, Linköping University (Linköping, Sweden), May, 2019).

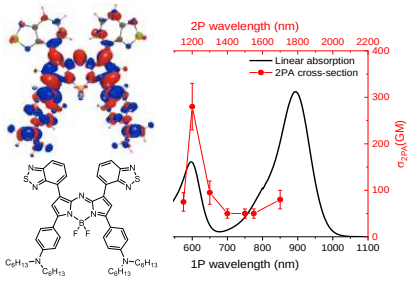
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Benzothiadazole moieties act as powerful electron-withdrawing auxiliaries enforcing the accepting character of aza-BODIPY dyes and resulting in a significant red-shift of both absorption and emission and a remarkable enhancement of the nonlinear optical properties (two-photon absorption and optical limiting) as compared to traditional aryl substituents.

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