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<https://pubs.acs.org/doi/10.1021/acs.jpcc.6b00096>

DOI: 10.1021/acs.jpcc.6b00096

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Linear and Nonlinear Optical Spectroscopy of Fluoroalkylated BODIPY Dyes

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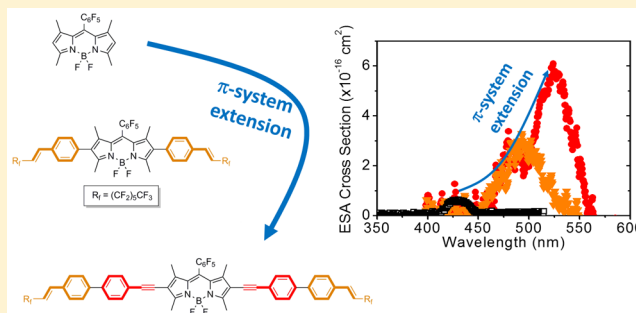
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Supporting Information

ABSTRACT: A series of fluoroalkyl-labeled BODIPY dyes have been synthesized with different substituents on the 2- and 6-positions and investigated in terms of their spectroscopic properties. The dyes were decorated with aryl, alkenyl, and alkynyl substituents, respectively. Those substituents are able to extend the dyes' delocalized π -electron system to different extents. Detailed linear and nonlinear optical spectroscopy methods as well as quantum-chemical calculations have been employed to verify the influence of those different substituents on the electronic distribution and, ultimately, on the molecules' optical properties. From the nonlinear optical measurements, we find that the substituents highly influence the excited-state absorption properties, which could be tuned in wavelength by ~ 100 nm and in magnitude by over 1 order of magnitude, reaching peak values close to 10^{-15} cm² for one of the alkynyl-containing dyes.



INTRODUCTION

The first boron dipyrromethene (BODIPY) dyes were prepared in 1968 by Treibs and Kreuzer,¹ and since the end of the 1980s they have been broadly used as fluorophores.² BODIPY dyes generally possess several desirable photophysical properties. They are strongly absorbing and have relatively sharp fluorescence emission with high quantum yields.³ Their absorption and emission properties can be tuned conveniently by changing the substitution pattern of the BODIPY framework. Thereby, the fluorescence can even be pushed into the near-infrared (NIR) region.^{3–6} Furthermore, BODIPY dyes are known to be little influenced by pH or the polarity of the solvent (no halo- or solvatochromism). In general, the dyes have excellent thermal and photochemical stability and negligible triplet-state formation.^{2,3} Because of their remarkable photophysical properties, BODIPY dyes are nowadays widely used, for example, as fluorescent labels,^{7–9} chemosensors,^{10–12} or agents for photodynamic therapy.^{13–15}

Despite extensive studies of the molecular structure and linear optical properties relationships of BODIPY dyes, very little is known about their nonlinear optical behavior, including multiphoton and excited-state absorption (ESA). Nonlinear absorption spectroscopy gives valuable information regarding the molecular electronic structure¹⁶ and also creates perspec-

tives for novel applications.^{17–19} Nonlinear optical materials are of interest for several applications including all-optical signal processing, optical limiters,²⁰ and microscopic imaging.¹⁹ Through nonlinear spectroscopy and guided molecular engineering, it is possible to optimize nonlinear optical response to attend the application requirements.²¹ In particular, materials with large ratios between excited- and ground-state absorption cross-section are desired for application in optical limiting devices.

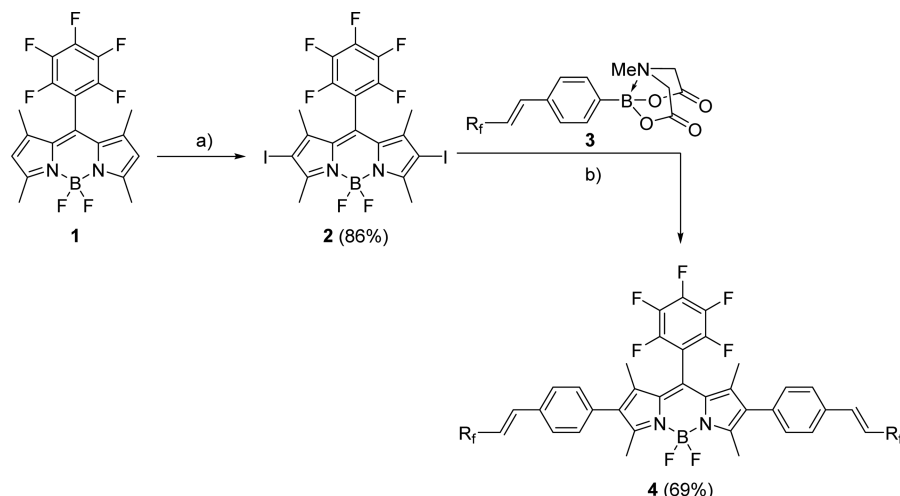
We recently reported on the preparation of a set of fluorous-labeled rhodamine dyes that combine the advantage of facile compound purification via fluorous solid-phase extraction (F-SPE)^{22,23} with the excellent photophysical properties of rhodamines.²⁴ Thereby, we could show that the photophysics was not negatively affected by the incorporation of perfluorinated moieties, for example, perfluorohexyl residues.

Lately, polyfluorinated fluorophores received even more attention because they can be used for the preparation of fluorescent perfluorocarbon nanoemulsions.²⁵ This novel class of imaging agents is very promising because it could be used for

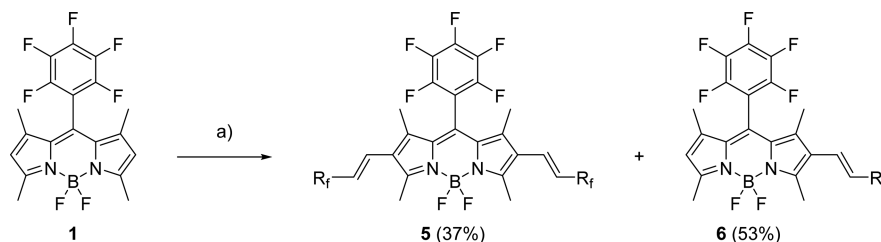
Received: January 5, 2016

Revised: February 4, 2016

Published: February 4, 2016

Scheme 1. BODIPY Functionalization via Suzuki–Miyaura Coupling^a

^aConditions: (a) I_2 , HIO_3 , H_2O , $EtOH$, $60\text{ }^\circ C$, overnight; (b) $Pd(PPh_3)_4$, $NaOH$, H_2O , toluene, $80\text{ }^\circ C$, overnight. $R_f = (CF_2)_5CF_3$.

Scheme 2. BODIPY Functionalization via Pd(II)-Catalyzed C–H Activation^a

^aConditions: (a) $1H,1H,2H$ -perfluoro-1-octene, $Pd(OAc)_2$, *tert*-butyl peroxybenzoate, $AcOH$, dioxane, $DMSO$, $35\text{ }^\circ C$, 5 d. $R_f = (CF_2)_5CF_3$.

a combination of fluorescence imaging and ^{19}F magnetic resonance imaging (^{19}F MRI),^{26–29} but as Swager et al. pointed out,²⁵ there is just a small number of polyfluorinated fluorophores that have been published to date. To the best of our knowledge, hitherto only two BODIPY dyes with incorporated perfluoroalkyl residues of considerable length³⁰ have been reported: one dye with a perfluoropropyl³¹ and another fluorophore with a perfluoroheptyl³² residue in the meso position. Here we report on the synthesis of a series of fluorous-labeled BODIPY dyes and thereby extend the scope of polyfluorinated dyes.

To investigate the effect of different substituents on the photophysical properties systematically, we set out to synthesize a series of BODIPY dyes with various substituents in the 2- and 6-positions. In essence, we prepared aryl-, alkenyl-, and alkynyl-substituted dyes. Because those substituents are able to expend the dyes' delocalized π -electron system to different extents, this should lead to a set of BODIPY dyes with broad spectral dispersion and strongly influence the nonlinear optical properties. The mentioned substituents should also provide the perfluoroalkyl moiety to render the dyes fluorous. Our previous studies with fluorous rhodamine dyes have shown that perfluorohexyl residues are sufficient to facilitate strong interactions with a fluorous phase.²⁴ To aid readability, the abbreviation R_f will be used throughout this article to represent the perfluorohexyl moiety ($R_f = (CF_2)_5CF_3$).

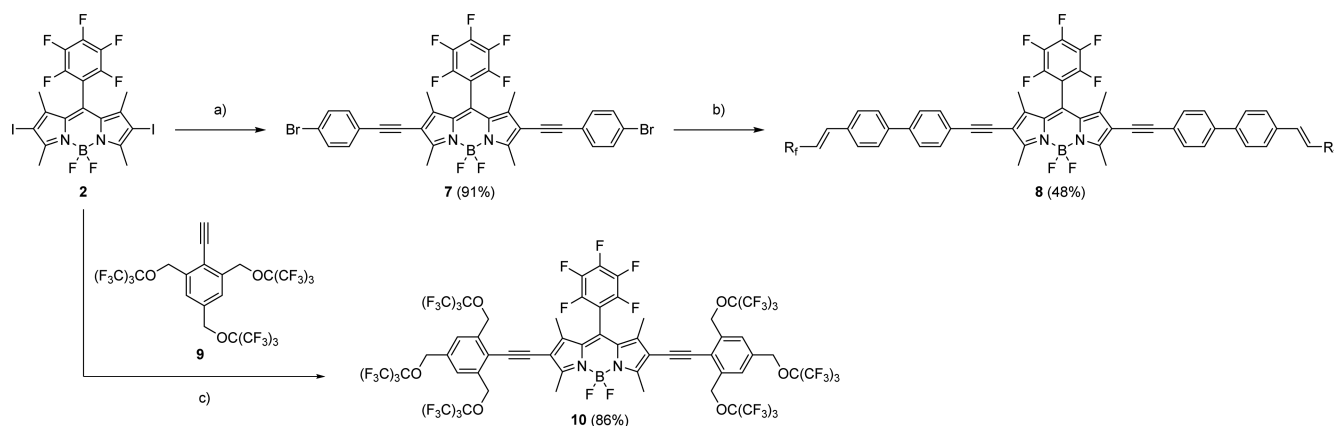
Linear and nonlinear spectroscopy as well as quantum-chemical calculations are performed for this series of dyes to help understanding the influence of the molecular structure on the optical properties. The nonlinear optical studies are focused

on the ESA and performed over a broad spectral range across the visible. It is shown that increasing the size of the delocalized π -electron system drastically changes the ESA cross-section while maintaining a nearly constant ground-state cross-section. This results in high excited- to ground-state cross-section ratios, nearly 30, while maintaining long excited-state lifetimes, above 1 ns.

RESULTS AND DISCUSSION

Synthesis of the BODIPY Dyes. The perfluorophenyl-substituted fluorophore **1** (Scheme 1) was chosen as the starting material for the synthesis of our fluorous-labeled BODIPY dyes. The synthesis of this dye was previously reported by McClenaghan et al.³³ They also showed that the perfluorophenyl residue in the meso position is susceptible to para-selective nucleophilic aromatic substitution, which can be used to functionalize the BODIPY dye with various amines or thiols.³³ BODIPY dye **1** was iodinated in excellent yield using reported procedures (Scheme 1).^{34,35} The molecular structure of iodinated dye **2** was also determined via X-ray crystallography (see Supporting Information). The iodinated dye **2** was subsequently used for Suzuki–Miyaura coupling with fluorous *N*-methyliminodiacetic acid (MIDA) boronate **3**.³⁶ The 2,6-diaryl-substituted dye **4** could be obtained in good yield.

Next, diiodide **2** should be used for Heck coupling with a fluorous alkene; however, the BODIPY dye was not stable and decomposed completely under typical Heck conditions. Thus, the fluorous alkene should be coupled via a Heck-analogous reaction that was previously presented by Burgess et al.³⁷ They discovered that unfunctionalized 1,3,5,7-tetramethyl BODIPY

Scheme 3. BODIPY Functionalization via Sonogashira Coupling^a

^aConditions: (a) 1-bromo-4-ethynylbenzene, Pd(PPh₃)₂Cl₂, CuI, DIPEA, THF, rt, 1.5 d; (b) MIDA boronate 3, Pd(PPh₃)₄, NaOH, H₂O, toluene, 110 °C, 2.5 h; (c) Pd(PPh₃)₂Cl₂, CuI, DIPEA, THF, rt, 2.5 d. R_f = (CF₂)₅CF₃.

Table 1. Spectral Properties of the BODIPY Dyes 1, 2, 4–8, and 10^a

dye	$\lambda_{\text{max,abs}}$ (nm) ^b	ϵ_{max} (M ⁻¹ cm ⁻¹)	$\lambda_{\text{max,em}}$ (nm) ^c	Stokes shift (nm/cm ⁻¹)	Φ_{F}	τ (ns)
1	518	83000 ± 11000	528	10/365	1.00 ± 0.09	3.9 ± 0.1
2	556	84000 ± 8000	576	20/625	0.033 ± 0.005	0.09 ± 0.01
4	551	79000 ± 12000	588	37/1142	0.97 ± 0.07	3.7 ± 0.1
5	562	90000 ± 8000	587	25/758	0.94 ± 0.06	3.6 ± 0.1
6	535	91000 ± 6000	561	26/866	1.00 ± 0.16	n.d.
7	602	73000 ± 18000	636	34/888	0.28 ± 0.04	1.89 ± 0.01
8	611	46000 ± 5000	652	41/1030	0.14 ± 0.02	1.21 ± 0.01
10 ^d	594	80000 ± 8000	626	32/861	0.40 ± 0.06	2.17 ± 0.01

^aAll spectra were measured in CH₂Cl₂, if not indicated otherwise. ^bAbsorption maxima have a ±1 nm imprecision. ^cFluorescence maxima are reproducible within a ±2 nm range. ^dMeasured in THF.

dyes can be conjugated with electron-deficient alkenes by Pd(II)-mediated C–H activation in the 2- and 6-positions (Scheme 2).

The outcome of this reaction is the same as for the attempted Heck reaction with the halogenated dye. After the reaction, a mixture of mono- and disubstituted product was obtained. The mono- and disubstituted dyes 5 and 6 could be easily separated from each other and were isolated with a combined yield of 90%.

To prepare alkynyl-substituted BODIPY dyes, we used the diiodide 2 for Sonogashira coupling with different acetylene derivatives (Scheme 3). After coupling with 1-bromo-4-ethynylbenzene, the disubstituted dye 7 was isolated in excellent yield. It is noteworthy that this reaction proceeds at room temperature and without substitution of the bromine atom, even in the presence of an excess of the alkyne. The dibromide 7 could be used for a second cross coupling with MIDA boronate 3, which results in the fluorous biphenyl-containing BODIPY dye 8. Recently, Horváth et al. reported about the beneficial properties of perfluoro-*tert*-butoxy moieties for fluorous partition and solubility.³⁸ Following this example, we synthesized the perfluoro-*tert*-butyl containing alkyne 9 (see Supporting Information), which was used for the preparation of the second dialkynyl BODIPY dye. In contrast with the perfluorohexyl-containing BODIPY dyes, fluorophore 10 was only sparsely soluble in many organic solvents; however, dye 10 could be easily dissolved in fluorophilic solvents, like THF. This underlines the fact that BODIPY dye 10 has indeed a higher fluorophilicity than the other dyes.

Linear Absorption and Fluorescence. With these compounds in hand, we investigated their photophysical properties (Table 1). Linear absorption spectra for all dyes are shown in Figure 1. The maximum absorption peaks vary from 518 to 611 nm, and emission maxima are in a range between 528 and 652 nm, depending on the substituents.

Referring to this, the absorption maxima and the emission maxima are related to the size of the delocalized π -system. Therefore, the maximum wavelengths for the alkynyl substituents are shifted to longer wavelengths than for the alkenyl and phenyl moieties. The absorption maximum of the phenyl-substituted dye 4 might not be as expected. It shows a lower absorption maximum than dye 5, which contains two ethenyl moieties. Phenyl rings have a more extended conjugated π -system than alkenes, which should lead to a stronger bathochromic shift of the absorption maximum, but this is not the case.

The maxima of the emission spectra are related to the delocalization of the π -system in the excited state. Here the emission peaks show longer wavelengths for alkynyl than for phenyl and ethenyl groups as well as for the unsubstituted dye (alkynyl > phenyl/ethenyl > iodide > unsubstituted). The Stokes shifts are in the same order but with a higher Stokes shift for the phenyl-substituted dye 4 (37 nm/1142 cm⁻¹) than for the ethenyl-substituted dyes 5 and 6 (25 nm/758 cm⁻¹ and 26 nm/866 cm⁻¹, respectively). All compounds present high extinction coefficients, ranging between (4.6 and 9.1) × 10⁴ M⁻¹ cm⁻¹. Also, the quantum yields are >10%, except for the iodinated compound 2, which is sufficiently high for photoluminescence applications.

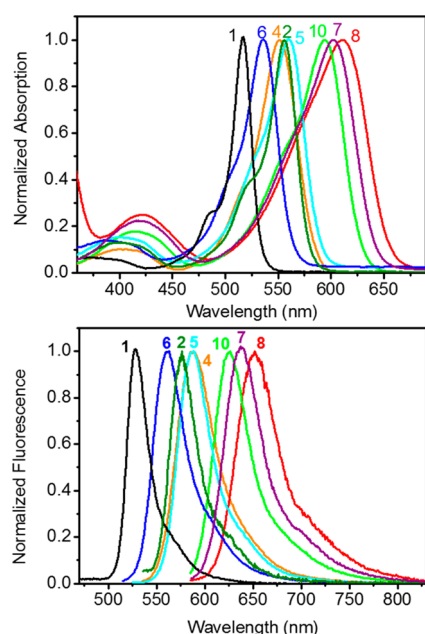


Figure 1. Linear absorption and emission spectra of BODIPY dyes 1, 2, 4–8, and 10.

Computational Studies. To gain further insight into the geometric and electronic structure of the newly synthesized dyes, we carried out quantum-chemical calculations. We used density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods as implemented in the program package TURBOMOLE.³⁹ For further details and references, see the [Supporting Information](#).

The structure of the fluoroalkyl part was simplified ($R_f = \text{CF}_3$ instead of $(\text{CF}_2)_5\text{CF}_3$) to facilitate the calculations. To avoid ambiguity, this structural modification is denoted by adding an asterisk to the respective molecule number. [Figure 2](#) shows the optimized structures of dyes 1, 4*, 5*, 6*, and 8* together with the shape of the respective frontier orbitals, that is, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Identical results were obtained for $R_f = (\text{CF}_2)_5\text{CF}_3$, and we therefore conclude that the length of the perfluoroalkyl chain has no significant effect

on structural and electronic properties. This is also supported by computational studies showing that the electron-withdrawing effect does not significantly increase when trifluoromethyl groups are exchanged for longer perfluoroalkyl moieties.⁴⁰ We find that for dyes 4*, 5*, and 6*, the substituents are rotated with respect to the plane of the BODIPY core for steric reasons (torsion angles of about 55° for 4* and 20° for 5* and 6*), while the substituents of the alkynyl-containing dye 8* stay in the BODIPY core plane up to the first phenyl ring. Dye 8* thus extends the π -electron system to a much larger extent, which can also be seen from the delocalization of the respective HOMO.

The energy differences between the HOMO and LUMO are summarized in [Table 2](#) and are a first approximation of the lowest excitation energy. As expected, dye 6* shows the smallest and dye 8* shows the largest bathochromic shift.

Table 2. Computed Energies and Energy Differences of Highest Occupied and Lowest Unoccupied Molecular Orbitals

dye	$E_{\text{HOMO}} (E_h)$	$E_{\text{LUMO}} (E_h)$	$\Delta E \text{ (eV)}$
1	−0.2148	−0.1078	2.91
4*	−0.2204	−0.1184	2.77
5*	−0.2303	−0.1284	2.77
6*	−0.2232	−0.1186	2.85
8*	−0.2088	−0.1211	2.39

Vertical excitation energies for the simplified dyes ($R_f = \text{CF}_3$) were also computed within TDDFT response theory. It is well known that TDDFT methods overestimate the excitation energies of BODIPY-based molecules;⁴¹ however, because the BODIPY core structure remains the same, we expect to be able to reproduce the trends with respect to the bathochromic shift. The results for different density functionals are given in [Table 3](#). In all cases, the lowest transition is of HOMO \rightarrow LUMO character. Inclusion of solvent effects with the conductor-like screening model (COSMO⁴²) decreases the gas-phase values by ~ 0.1 eV. Overall, the B3LYP⁴³ and M06-2X⁴⁴ functionals show similar performance; however, M06-2X gives a better description of transitions with charge-transfer character, as observed in dye 8* (see also the [Supporting Information](#)).

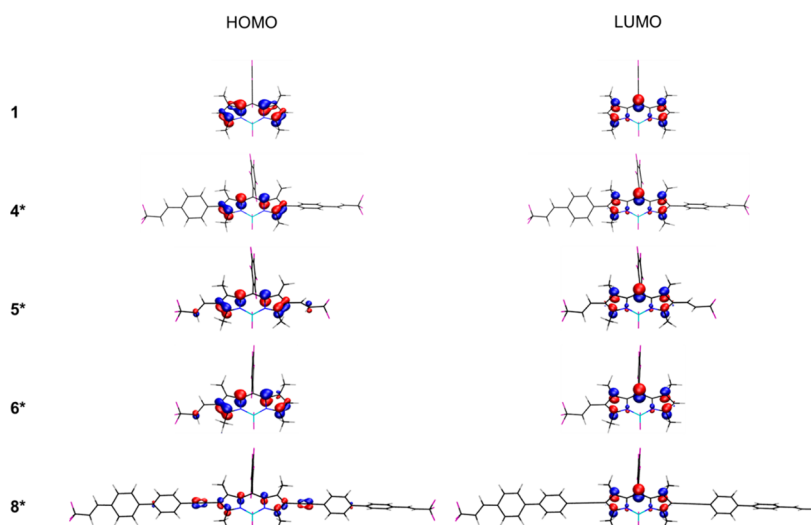


Figure 2. Highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of dyes 1, 4*, 5*, 6*, and 8*.

Table 3. Computed Lowest Vertical Excitation Energies (VEE) Including Solvent Effects (CH₂Cl₂ with Gas-Phase Values in Brackets) and Dominant Orbital Contributions to the Excitation

dye	method	VEE (nm)	dominant contribution
1	B3LYP	441 (422)	96% HOMO → LUMO
	M06-2X	443 (422)	97% HOMO → LUMO
4*	B3LYP	489 (474)	91% HOMO → LUMO
	M06-2X	470 (452)	97% HOMO → LUMO
5*	B3LYP	480 (467)	93% HOMO → LUMO
	M06-2X	464 (446)	98% HOMO → LUMO
6*	B3LYP	460 (446)	93% HOMO → LUMO
	M06-2X	452 (433)	98% HOMO → LUMO
8*	B3LYP	597 (587)	97% HOMO → LUMO
	M06-2X	515 (501)	92% HOMO → LUMO

Comparison of the computed excitation energies with the measured ones shows good agreement concerning the trends; the absolute M06-2X+COSMO values are constantly shifted by ~0.4 eV. The largest deviation is found for dye 5* (2,6-diethenyl), which according to the calculations has a slightly smaller bathochromic shift than dye 4* (2,6-diphenyl). This is contrary to the experimentally observed shift. Apart from the fact that the discrepancy lies within the error bars of the calculation, the difference in the bathochromic shift of 4* and 5* is believed to be a subtle interplay between the substituent's ability to extend the π -electron system (phenyl > ethenyl) and the torsion angle (phenyl > ethenyl).

On the basis of the M06-2X+COSMO values, we tentatively assigned further transitions in the absorption spectra (see the [Supporting Information](#)). The experimentally observed weak band at around 400–425 nm would then correspond to HOMO–1 → LUMO and HOMO–2 → LUMO transitions for all computed dyes.

Singlet Excited-State Lifetimes. Singlet excited-state lifetimes were measured using a TCSPC (time-correlated single-photon counting) system with 200 ps resolution and excitation at 405 nm with a picosecond diode laser. For nearly all dyes, except dye 2, the fluorescence decay follows a single exponential dynamics with lifetimes above 1 ns, which corresponds to fluorescence quantum yields of at least 14%. These dynamics indicate direct depopulation of the singlet excited state and absence of significant triplet states. The fluorescence lifetimes are shown in [Figure 3](#) and [Table 1](#) for all dyes. (Fittings for the lifetimes are shown in the [Supporting Information](#).)

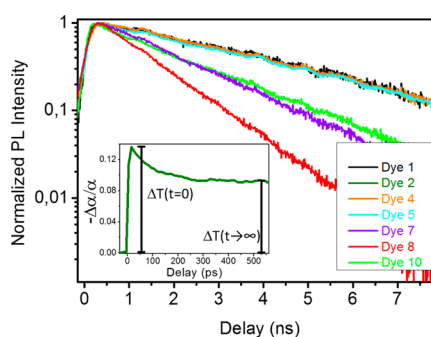


Figure 3. Fluorescence lifetimes of dyes 1, 2, 4, 5, 7, 8, and 10. Inset: Singlet to triplet decay for dye 2.

For the case of the iodinated dye 2, the value for the lifetime measured by TCSPC is limited by the response time of the system. In fact, iodinated dye 2 presents a very short lifetime and a low singlet emission quantum yield, suggesting that the measured lifetime is related mostly to the singlet–triplet intersystem crossing rate due to the presence of heavy atoms.^{45–48} To obtain the correct value for that lifetime, we measured the dynamics via transient absorption with tens of femtoseconds resolution, with the probe set at the S₀ → S₁ transition energy, measuring the evolution of the population of the S₀ and S₁ states. The result, shown in the inset of [Figure 3](#), reveals a fast initial decay (~90 ps) and a slow decay channel (longer than 1 ns), which appears in the inset as a plateau. The fast decay represents the S₁ depopulation, which is dominated by the intersystem crossing to the triplet level, while the long decay is due to the repopulation of the S₀ level. For the transient absorption studies, the excitation was performed with sub-100 fs pulses, which is at least three orders of magnitude faster than the other characteristic times involved on the dynamics. In this case, the excitation can be assumed to be an impulse excitation and, following the model of ref 46, the triplet yield may be calculated from $\Phi_3 = \left(\frac{\Delta T(t \rightarrow \infty)}{\Delta T(t=0) - \Delta T(t \rightarrow \infty)} \right)$ (see inset in [Figure 3](#)), resulting in $\Phi_3 = 0.64$ for dye 2.

As predicted by our quantum-chemical calculations, the BODIPY functionalization methods described in [Schemes 1](#) and [2](#) result in molecules with effectively short π -conjugated systems due to the twist off from the core plane. Consequently, they show rather small bathochromic shifts and emission quantum yields of nearly unity (except for the iodinated dye 2). For the dyes synthesized by the method in [Scheme 3](#), the functional groups are mostly in the plane of the core, resulting in molecules with a longer conjugated π -electron system. Strong correlation between the bathochromic shift and the shortening of the excited-state lifetime is observed, suggesting that the shorter lifetime is the result of the elongation of the π -electron system.

Excited-State Absorption. ESA spectra were measured by pump-and-probe spectroscopy using a femtosecond white-light continuum as a probe. The magnitude of the ESA cross-section was measured via Z-Scan⁴⁹ and calculated using the method described in ref 50. More details of the experimental and fitting methods for ESA are given in the [Supporting Information](#). No ESA signal was measurable for the alkenyl-containing dyes 5 and 6. The data for all other dyes are shown in [Figures 4](#) and [5](#). [Figure 4](#) shows the ESA spectra for the precursor dye 1 and dyes 2 and 4. When compared with the 2,6-diaryl-substitution,

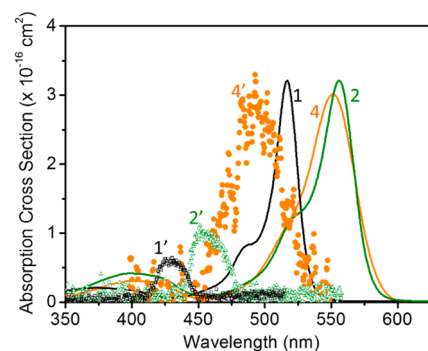


Figure 4. Excited-state absorption (numbers with apostrophe) in comparison with the linear absorption spectra.

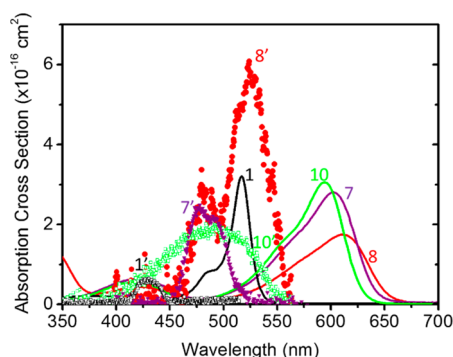


Figure 5. Excited-state absorption (numbers with apostrophe) in comparison with the linear absorption spectra.

the iodine substitution does not influence strongly the ESA spectrum, causing a red shift of ~ 170 meV and a 2-fold increase of the peak magnitude, while for dye 4 the bathochromic shift is ~ 370 meV and the peak magnitude is enhanced by a factor of nearly 6. These results suggest that the 2,6-diaryl-substitution delocalizes the π -electron wave function more in the higher lying excited state than in the ground state. We do not observe the same effect for the iodinated dye 2, suggesting a weaker influence of the halide on the excited state.

The ESA spectra for the dyes synthesized via Sonogashira coupling are shown in Figure 5 together with the ESA for the precursor dye 1. In this case, there is a clear correlation between the magnitude and red shift of the ESA spectra and the length of the π -conjugated system. According to our calculations, dye 8 possesses the longest effective π -conjugated chain because the first phenyl ring is in the same plane as the BODIPY core. Evidence of the electron wave function delocalization could be seen from the linear optical properties, that is, from the absorption red shift and the shortening of the excited state lifetime. This strongly influences the ESA for dye 8, which presents a maximum cross-section of almost 10^{-15} cm². This is about three times larger than the ground-state cross-section peak. Such a remarkable ESA cross-section enhancement, combined with a decreasing of the ground-state cross-section, leads to large excited- to ground-state absorption cross-section ratios, $\sigma_{\text{ESA}}/\sigma_{\text{g}}$. At 483 nm this ratio is ~ 30 , while at the ESA peak, at 525 nm, it is ~ 20 . It is also important to point out that in addition to a high ESA cross-section dye 8 has a relatively long excited-state lifetime (1.21 ns). The combination of high ESA cross-section, high excited- to ground-state absorption cross-section ratio, and long excited-state lifetime turns dye 8 into a promising candidate for nonlinear optical applications, in particular, for optical limiting in the visible range. For many years, much effort has been put toward developing photostable molecules with large ESA cross-section. For long-chain polymethine dyes, an excited- to ground-state absorption cross-section ratio of ~ 100 has been demonstrated;⁵⁰ however, those dyes present very short fluorescence lifetimes, ~ 10 ps, which is not desirable for applications in, for example, optical limiters for light pulses longer than 100 ps due to repopulation during the same pulse. For practical applications, it is desirable that the molecule stays in the excited state for a longer time, as is the case for dye 8.

CONCLUSIONS

The synthesis of a series of five novel BODIPY dyes with various fluororous substituents in the 2- and 6-position is

presented. These dyes are among the first fluororous BODIPY dyes that have been reported to date. We used extensive linear and nonlinear optical spectroscopy methods to investigate the influence of different substituents, namely, aryl, alkenyl, and alkynyl moieties, on the fluorophores' photophysical properties. In addition, quantum-chemical calculations were carried out to better understand the linear absorption spectra. The lowest excitation is of HOMO \rightarrow LUMO character for all investigated dyes, and the size of the bathochromic shift is shown to be related to the substituent's ability to extend the π -electron system of the BODIPY core.

The nonlinear optical studies show that the biphenyl-containing BODIPY dye 8, which is predicted to have the most extended delocalized π -electron system, presents the largest enhancement of the ESA magnitude. It is important to point out that the substituents of dye 8 do not strongly affect the ground-state absorption cross-section, which makes $\sigma_{\text{ESA}}/\sigma_{\text{g}}$ be up to 30 while maintaining a long-lived excited state population. Comparing the ratio $\sigma_{\text{ESA}}/\sigma_{\text{g}}$ for all investigated dyes, we notice that for the unsubstituted dye 1 the ratio is not more than 9 and increases with the length of the π -electron system, reaching values near 20 for dyes 7 and 10. These findings shed some light on the optimization of BODIPY dyes for nonlinear optical applications, which includes optical limiters and biolabeling.

Fluororous dyes are generally of broad interest because they can be used for unique applications such as fluororous separation techniques or the preparation of brightly fluorescent fluorocarbon nanoemulsions, which could be used for simultaneous fluorescence and ¹⁹F MRI imaging. The presented fluororous BODIPY dyes will be applied to this dual-imaging approach in the near future.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b00096. CCDC 1442275 (BODIPY dye 2) and 1442277 (precursor S1) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Details of the synthesis and characterization of the prepared compounds (including MIDA boronate 3 and alkyne 9), crystallographic data for BODIPY dye 2 and tetrabromide S1 (precursor of alkyne 9), as well as details of the computational studies and the nonlinear optical spectroscopy techniques. (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The Chemical Industry Fund (fellowship to D.K.K.), the Karlsruhe School of Optics & Photonics (fellowship to D.K.K. and A.H.), the Carl Zeiss Foundation (fellowship to A.H.), and the Karlsruhe House of Young Scientists (KHYS, fellowship abroad A.H.) are acknowledged. We acknowledge support from

the Deutsche Forschungsgemeinschaft through GRK 2165 and SFB 1176 (project A4 of S.B. and project Q4 of A.B.). J.A.C. and J.A.P.F. acknowledge CAPES and CNPQ—Brazilian Funding Agencies for their scholarship, and L.A.P. acknowledges funding from the Sao Paulo State Funding Agency (FAPESP) under the grant 2013/16911-2

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