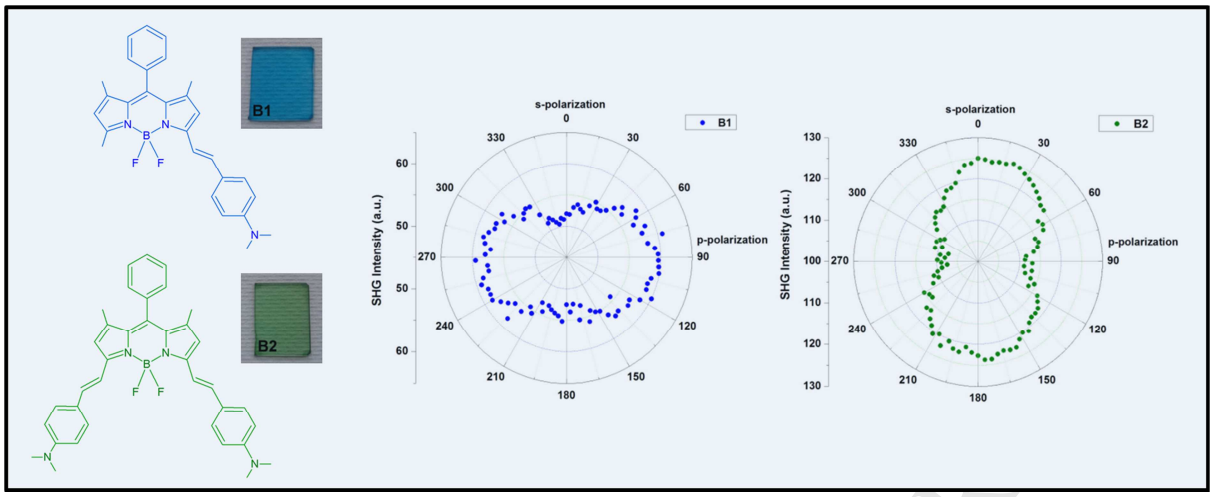

Tuning the Nonlinear Optical Properties of BODIPYs by Functionalization with Dimethylaminostyryl Substituents

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Abstract

Two difluoroboradiazaindacene (BODIPY) scaffolds with attached dimethylaminostyryl substituents were synthesized. Guest-host polymeric films were produced by incorporating these chromophores into polymethylmethacrylate matrices. The second and third nonlinear optical properties of the resulting polymer composites were studied by means of the Maker fringe technique using a laser generating at 1064 nm with a 30 ps pulse duration. The macroscopic and microscopic nonlinearities were found to be comparatively high and dependent on the number of dimethylaminostyryl substituents attached to BODIPY core. The development of integrated optics makes such nonlinear films of particular interest, since they can be used in the creation of efficient nonlinear devices.

Keywords: *BODIPY dye, polymer composites, second/third harmonic generation, nonlinear susceptibility, hyperpolarizability*

1. Introduction

In recent years, difluoroboradiazaindacene (BODIPY) unit has attracted much interest because of valuable spectroscopic and photophysical properties such as its high molar absorptivity coefficient [1], high fluorescence quantum yield [2,3] and good stability towards light and chemicals [4]. Recently many BODIPY derivatives have been synthesized and utilized as fluorescent dyes [5], chemosensors [6-10], polarity sensitive probe [11], light harvesting systems [12,13], and for laser applications [14] and photodynamic therapy [15,16].

This research work is devoted to nonlinear optical (NLO) investigations of BODIPY model compounds by means of SHG and THG (second/third harmonic generation) techniques, which allow the determination of second and third order NLO parameters. Until now a small set of BODIPY derivatives have been investigated for nonlinear optics [17-23]. Recently, much attention has been devoted to functionalized BODIPY dyes that exhibit two-photon absorption (TPA) properties due to their related application in TPA imaging [24-26]. To this end, extending conjugation and forming Intramolecular Charge Transfer (ICT) by means of appropriate electron donor or acceptor groups are effective strategies for the synthesis of highly efficient two-photon active BODIPY compounds. Thus, understanding how incorporating electron donor and/or acceptor groups in the BODIPY architecture affect NLO response remains a challenge.

Our research work is focused on two BODIPY-based models which have one or two dimethylaminostyryl branches, with high ICT strength from the dialkylamino-groups electron donors to the electron acceptor boradipyrrin core. Interestingly, B1 and B2 models not only present intrinsic “push-pull” character, but also differ by their inherent D-A (B1) and D-A-D (B2) structures that potentially govern distinct second and third order optical nonlinearities. Recently, we have shown that dimethylaminostyryl arms affect the nonlinear refraction and absorption activity of the BODIPY structure [27]. Meanwhile, the SHG and THG study of dimethylaminostyryl substituted BODIPY-based derivatives has not been done yet, so the results of this investigation may extend the application range of the dye. The second and third nonlinear optical properties of BODIPY-based materials, as guest-host polymeric films produced by incorporating the chromophores into PMMA matrices, were studied by means of the Maker fringe technique. The NLO susceptibilities and hyperpolarizabilities were extracted, which can give a better understanding on the origin of NLO phenomena and the structure-property relationships in BODIPY chromophores.

2. Experimental section

2.1. Materials

The BODIPY models have been synthesized in good yield by the established Konoevenagel condensation of 3,5 dimethyl-BODIPY dyes with 4-dimethylaminobenzaldehyde, as it is previously described by Rurack [28] and Akkaya [29]. The structures of the resulting difluoroboradiazaindacene chromophores with dimethylaminostyryl substituents (namely B1 and B2) are shown in Fig. 1. The monocondensation was controlled by adjusting the mole ratio and stopping the reaction after few hours, while a larger excess of 4-dimethylaminobenzaldehyde and a longer reaction time increased the yield of by-condensed product B2 (Supporting Information).

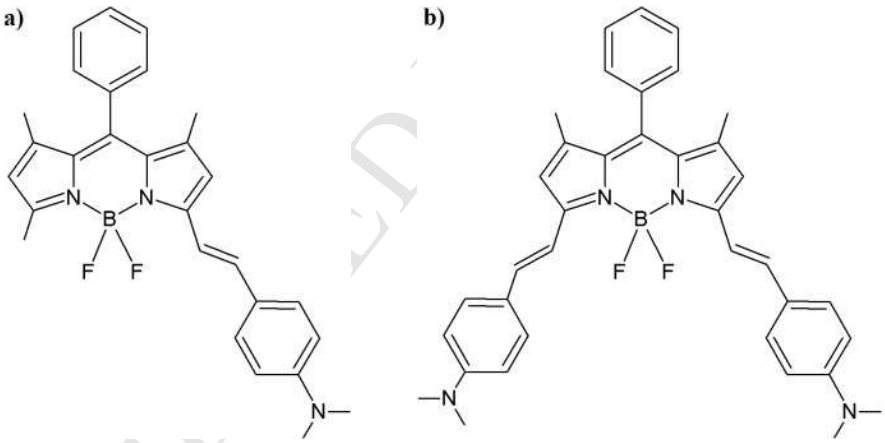

Fig. 1. Structures of the conjugated difluoroboradiazaindacene chromophores with dimethylaminostyryl substituents: a) B1; b) B2.

2.2. Film fabrication

For the polymeric film preparation a solution of PMMA (Sigma-Aldrich, Mw=350,000 g/mol) dissolved in 1,1,2-trichloroethane at concentration of 50 g/L was used as a host system.

The concentration of the compounds was 100 µmol towards 1 g of PMMA. The glass plates were washed in distilled water using ultrasonic bath, acetone, and ethanol and then dried. The solutions were deposited on glass substrates using the spin-coater (SCS G3) at 1000 rpm. Obtained guest-host polymer films were kept at room temperature during few days in order to eliminate any remaining of solvent. The thickness of deposited films was measured with the profilometer (Dektak 6M, Veeco) to be about 700 nm.

2.3. Optical absorption measurements

Absorption spectra of the B1 and B2 films were measured by means of Lambda 950 UV/Vis/NIR spectrophotometer (PerkinElmer) in the range 300-1200 nm. The pure PMMA film on glass plate was used on the way of reference beam in spectrophotometer for the measurements of absorption spectra of chromophores.

2.4. SHG and THG measurements

The phenomena of second and third harmonic generation (SHG and THG) may take place in a material the nonlinear polarization of which, caused by intensive laser irradiation, stimulates the coherent light emission at double and triple laser frequencies. The schematically energy-level diagram of SHG and THG processes is shown in Fig. 2a. SHG and THG measurements were performed by means of the rotational Maker fringe technique [30] in the transmission scheme for the *s*- and *p*-polarized fundamental laser beams (Fig. 2b). A *y*-cut crystalline quartz plate has been used as a reference material for SHG measurements and fused silica plate for THG measurements. The output beam of a mode-locked Nd:YAG/YVO_4 laser (EKSPLA) generating at λ=1064 nm with 30 ps pulse duration and 10 Hz repetition rate was employed as a fundamental beam. The input energy of laser pulses was controlled by laser power/energy meter (LabMax

TOP, COHERENT) to be 90 μJ for SHG and 150 μJ for THG measurements. The detailed setups description can be found elsewhere [31].

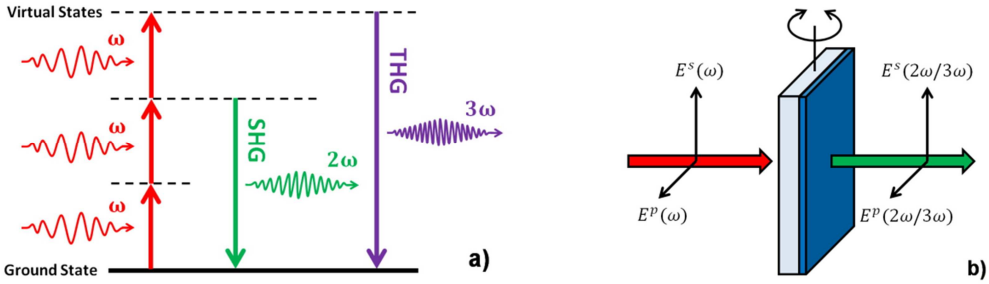

Fig. 2. a) Energy-level diagram of SHG and THG processes and b) the illustration of input-output polarization scheme in Maker fringe experiment.

3. Results and discussion

3.1. Optical absorption properties

The absorption spectra of B1 and B2 compounds embedded in PMMA films at the concentration 100 μmol/g are given in Fig. 3. As expected, attaching the electron donating dimethylamino groups at the 3 and 5 positions, through a conjugated bridge, leads to considerable shift of the absorption band towards the red region, by comparison with the parent BODIPY compound [2, 20]: UV-Vis (CH_2Cl_2) λ_{max}(abs.) = 598 nm (B1), 692 nm (B2). The UV-Vis absorption and fluorescent emission spectra of the THF solutions displayed the maximal absorbance at λ_{max}(abs.) = 601 nm (B1), 694 nm (B2) with a molar extinction coefficient of about 90,000 M^{-1} cm^{-1} and the maximal emission at λ_{max}(em.) = 643 nm (B1), 722 nm (B2) with the fluorescence quantum yield of 0.24 and 0.15 for B1 and B2, respectively [27]. Similarly, the spectra of both films exhibit wide absorption bands with maximum at 605 and 703 nm for B1 and

B2, respectively, which correspond to $S_0 \rightarrow S_1$ (π-π^*) transitions. The short-wavelength vibronic shoulder of these bands can be assigned to a C-H out-of-plane vibration [32]. The absorption peaks at the wavelength less than 500 nm could be attributed to a partially forbidden $S_0 \rightarrow S_2$ (π-π^*) transitions in BODIPY core [33]. As the absorption spectra indicates, introduction of second electron-donor dimethylaminostyryl group exerts almost 100 nm red-shift of absorption band without considerable change of its intensity. At the wavelengths of more than 800 nm the samples show high optical transparency.

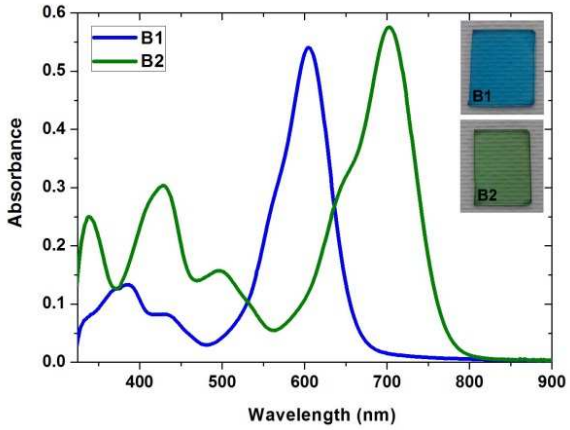

Fig. 3. UV-vis absorption spectra of the B1 and B2 compounds embedded in PMMA films. In inset – the photos of the deposited films.

3.2. SHG response study

The rotational Maker fringe technique was implemented for the measurements of SHG in B1 and B2 guest-host polymeric films for *s*- and *p*-polarized fundamental laser beam. Since the dipole moments of the chromophores are initially randomly oriented within the film, the second order nonlinear optical response of the film is negligible due to its macroscopic centrosymmetry. In order to break the centrosymmetry and induce the uniaxial orientation of NLO chromophores

in the polymeric films, provoking their manifestation of second order NLO behavior, the samples were corona poled just before SHG measurements. The poling temperature was 95°C, a little lower than the glass transition temperature and applied electric field was 5 kV/cm. In Fig. 4 the dependences of the second harmonic intensity generated as the function of incident angle are presented. The obtained angular dependencies are typical for induced $C_{\infty v}$ symmetry view with a maximum signal at 60°-65° and zero intensity at normal incidence of the fundamental beam. The polarization of the second harmonic signal was found to be always *p*-polarized regardless of the incident beam polarization due to the peculiarities of symmetry dependent second order susceptibility tensor components.

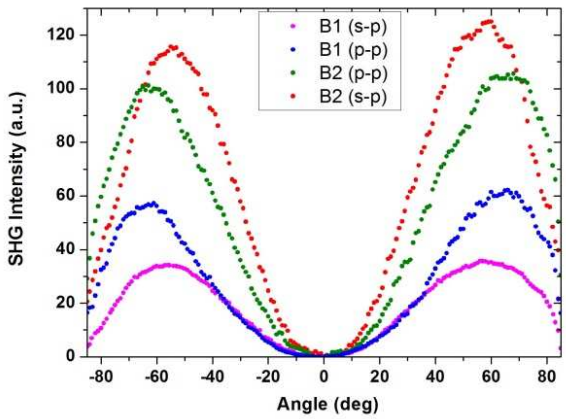

Fig. 4. SHG intensity as a function of incident angle in B1 and B2 guest-host films at the *s*-, and *p*-polarized fundamental beam.

As it can be seen for *s-p* or *p-p* polarizations, the intensity of SHG from B2 compound which has two dimethylaminostyryl units is almost two-to-three times higher than the intensity of B1 with one dimethylaminostyryl unit. In contrast to B1 film, the SHG response from B2 film for *s-p* (input-output) polarization is higher than for *p-p* polarization. For B1 the higher SHG signal can

be obtained when the polarization of incident beam is close to parallel to its dipole moment or direction between donor (D) amine group and acceptor (A) BODIPY core, meanwhile the higher SHG signal in B2 can be obtained when the polarization of incident beam is rather perpendicular to D-A direction. In the Fig. 5 the dependences of SHG intensity on polarization of incident beam measured at 60° are presented, which confirm the contrary directions in the molecules where highest response occurs. The second order nonlinearity of BODIPY with attached dimethylaminostyryl substituents is more efficient in D-A-D architecture (B2), in which two ICT processes contribute to the NLO response, than in D-A (B1).

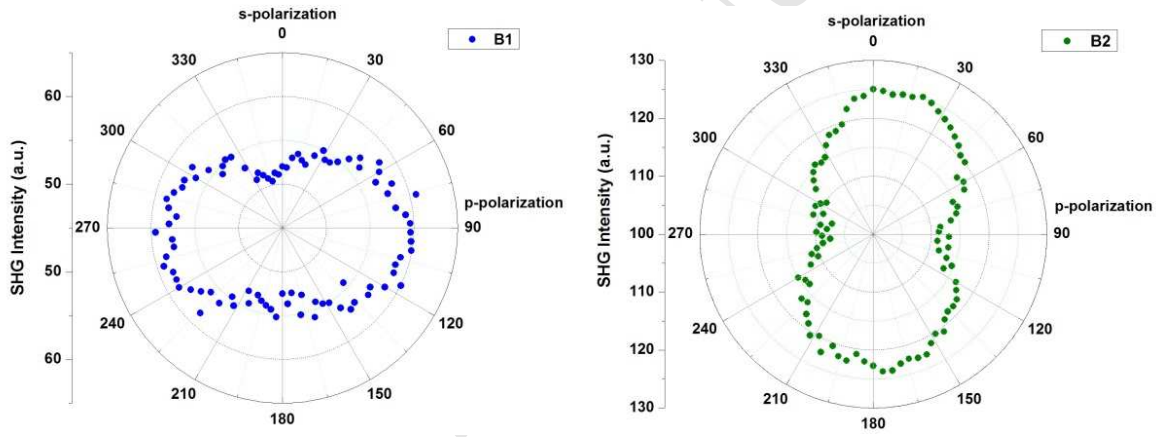

Fig. 5. The dependences of SHG intensity on incident beam polarization in B1 and B2 films.

Since the films have the thickness much less than their coherence length, the intensities of SHG from films were compared to that from a quartz plate and the quadratic NLO susceptibilities were calculated using following equation taking into account linear optical absorption [34]:

$$\chi^{(2)} = \chi^{(2)}_{Quartz}\left(\frac{2}{\pi}\right)\left(\frac{l^{coh}_{Quartz}}{d}\right)\left(\frac{\frac{\alpha d}{2}}{1-e^{-\frac{\alpha d}{2}}}\right)\left(\frac{I^{2\omega}}{I^{2\omega}_{Quartz}}\right)^{1/2}, \quad (1)$$

where $\chi^{(2)}_{Quartz}$ is the quadratic susceptibility of quartz, l^{coh}_{Quartz} is the coherent length of quartz, α is the absorption coefficient at doubled laser wavelength, d is the film thickness, $I^{2\omega}$ and $I^{2\omega}_{Quartz}$ are the SHG intensities from the sample and quartz under the same conditions of measurement, respectively. The obtained effective quadratic NLO susceptibilities are presented in Table 1. Here again, the effective values of $\chi^{(2)}$ for B2 compound were found to be higher than that for B1 due to the doubled amount of ICT which plays a crucial role in nonlinear behavior of a molecule. The obtained values of quadratic susceptibility are quite high and comparable with those which we have recently obtained for spin-deposited thin films of azobenzene-based push-pull compounds [35]. Meanwhile, in the microscopic approach, the first hyperpolarisabilities of B1 and B2 extracted form $\chi^{(2)}$ assuming parallel orientations of dipole moment of molecules towards polar axis induced by the poling field are found to be one order of magnitude lower than for other BODIPY-based derivatives [19].

Table 1. The values of $\chi^{(2)}_{eff}$, $\chi^{(3)}_{elec}$, β_{eff} and γ_{elec} obtained for B1 and B2.

Compound	$\chi^{(2)}_{eff}$, *s-p* (pm V^{-1})	$\chi^{(2)}_{eff}$, *p-p* (pm V^{-1})	β_{eff}, (10^{-38} m^{4}V^{-1})	$\chi^{(3)}_{elec}$, *s-s* (10^{-20} m^{2}V^{-2})	γ_{elec}, (10^{-47} m^{5}V^{-2})
B1	2.75	3.61	1.86	0.32	1.16
B2	5.86	5.42	2.79	1.79	6.37

3.3. THG response study

The measurements of THG response in B1 and B2 films were performed for *s-s* incident-generated polarization scheme (Fig. 6). It can be seen that B2 film represents much higher THG

response compared to B1 film. As the THG originates from the film together with the glass substrate, the impact of substrate was taken into account during data processing and the cubic NLO susceptibility calculation.

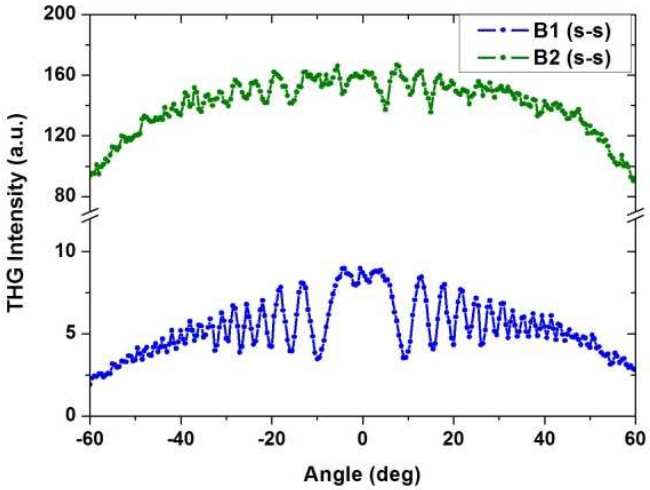

Fig. 6. THG intensities from B1 and B2 films as a function of incident angle for the *s*-*s* polarization of the fundamental beam – generated signal.

Third order NLO susceptibility was calculated using the comparative model which takes into account linear optical absorption [36]:

$$\chi^{(3)} = \chi^{(3)}_{Silica}\left(\frac{2}{\pi}\right)\left(\frac{l^{coh}_{Silica}}{d}\right)\left(\frac{\frac{\alpha d}{2}}{1-e^{-\frac{\alpha d}{2}}}\right)\left(\frac{I^{3\omega}}{I^{3\omega}_{Silica}}\right)^{1/2}, \quad (2)$$

where $\chi^{(3)}_{Silica}$ is the cubic susceptibility of silica, l^{coh}_{Silica} is the coherent length of silica, α is the absorption coefficient at triple laser wavelength, d is the film thickness, $I^{3\omega}$ and $I^{3\omega}_{Silica}$ are the THG intensities of the samples and silica at the same conditions, respectively. The calculated

values of $\chi^{(3)}$ for the B1 and B2 films are given in Table 1 and they are one-to-two orders of magnitude higher than for silica ($2 \cdot 10^{-20}$ m^2V^{-2}). The compound B2 is characterized with a much higher third order NLO susceptibility than B1 due to more effective electron delocalization caused by charge transfers from the dimethylamino groups to the BODIPY center together with its D-A-D structure, contributing to the microscopic nonlinearity.

The electronic contribution of second hyperpolarizability γ_{elec} for B1 and B2 molecules was deducted from third order susceptibility (Table 1), as THG measurements are only dealing with electronic constituent, taking into account the concentration of the molecule and the local field factor [37, 38]. The comparatively higher γ_{elec} for B2 is attributed to the presence of two dimethylaminostyryl substituents which imparts a greater intramolecular charge-transfer character compared to B1 compound. It is worth noting that except for the intra-molecular electronic contribution some role may also play vibrational contribution to hyperpolarizability of the systems.

4. Conclusions

In summary, B1 and B2 BODIPY-based derivatives with one and two conjugated dimethylaminostyryl substituents exhibit considerable second and third order NLO responses at 1064 nm, which can be tuned by the number of these peripheral substituents. In particular, the expansion of the π-conjugated system by two electron donor groups, leading to a D-A-D structure, results in significant increase of both SHG and THG responses comparing to the D-A structure. Attaching strong electron-donating groups on the BODIPY core can thus promote charge transfer character in these compounds and enhance their second and third order NLO properties. Varying the electron donating efficiency and the respective position of donor and

acceptor groups in BODIPY conjugated systems will be the object of further studies with the aim to establish applicable structure-property relationships.

Acknowledgements

B. K. acknowledges the Pays de la Loire region for the financial support of research work in the framework of the "Molecular Systems for Nonlinear Optical Application" (MOSNOA) LUMOMAT project. S. T. acknowledges the MESRSFC, IFM, and CNRST of Morocco.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/

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BODIPY models with attached dimethylaminostyryl substituents were synthesized.

The nonlinear optical properties of functionalized BODIPY models were studied.

The nonlinearities are dependent on the number of dimethylaminostyryl substituents.

Electron-donating groups enhance second and third order NLO response of BODIPY.