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Dyes and Pigments



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New triazine bridged triads based on BODIPY-porphyrin systems: Extended absorption, efficient energy transfer and upconverted emission

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ARTICLE INFO

Keywords: Porphyrins BODIPY Triazine triads Energy transfer

ABSTRACT

Two novel triads connecting a BODIPY to ethylenediamine substituted porphyrins via triazine linker have been synthesized and characterized. One of the triads is a linear D-A structure with one BODIPY (D) and one porphyrin (A) bridged by the triazine linker and the other one is a branched A-D₄ structure with the porphyrin core linked to four BODIPY units. The triads show extended absorption in the visible region with contributions from both porphyrin (Soret band centred at 410–430 nm) and BODIPY units (strong absorption at \approx 502 nm) in good agreement with the expected molar ratio. Both triads exhibit linear and nonlinear optical properties featuring an efficient energy transfer from the BODIPY donor to the porphyrin acceptor. The nonlinear upconverted emission properties of the triads were studied by two-photon excitation in the Near-infrared (NIR, 710–930 nm). The maximum two-photon absorption cross-section values for the triads (40–70 GM) are larger than those typically reported in this wavelength range for porphyrins and BODIPY. Both the green emission of BODIPY (\approx 514 nm) and the red emission for porphyrins (650–750 nm) were observed under NIR excitation at 930 nm. The distinct features of triads, namely i) an extended absorption; ii) an efficient energy transfer and iii) the nonlinear upconverted emission featuring a large separation between the excitation and emission wavelengths could be beneficial for application in sensing and imaging procedures.

1. Introduction

In recent years, a wide range of compounds have been combined to construct multichromophoric and π -conjugated macromolecules with excellent photophysical profiles [1,2]. The presence of conjugated systems improves the efficiency of electron and energy transfer processes [3,4]. Porphyrins, which are tetrapyrrolic ligands with high chemical stability, unique optical properties and strong redox activity are an example of these compounds [5–7]. During the last two decades, such compounds have been extensively studied for use in numerous applications such as solar cells [8,9], chemosensors [10–13], artificial photosynthesis [14], catalysis [15–19], and biomedical applications

https://doi.org/10.1016/j.dyepig.2021.109137

Received 27 October 2020; Received in revised form 15 December 2020; Accepted 2 January 2021 Available online 9 January 2021 0143-7208/© 2021 Elsevier Ltd. All rights reserved.

[20–22]. The absorption spectrum of porphyrins has a typical profile consisting of an intense Soret band at $\lambda = 400-450$ nm followed by a weaker quartet of bands at $\lambda = 550-650$ nm known as the Q bands. The absorption gap between 450 and 550 nm is a significant limitation for the use of these macrocycles in photocurrent generation phenomena. One of the approaches to expand the absorption profile of porphyrin derivatives is their association to chromophores with strong absorption in the above region. Green chromophores such as 4,4-difluor-o-4-bora-3a,4a-diaza-s-indacene, commonly known as BODIPY, with absorption features complementary to porphyrins, are excellent candidates for a synergistic improvement of the intrinsic optical properties of the individual units [4,23–29]. BODIPY derivatives have been widely

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used as light harvesting antenna groups due to their excellent photochemical stability, high molar extinction coefficient ($\varepsilon > 6 \times 10^4$ cm⁻¹M⁻¹ at the maximum absorption wavelength) and easily tunable optical and electrochemical properties [30]. However, the light harvesting ability of BODIPY fluorophores is also limited by their typically narrow absorption spectra. Panchromaticity can be achieved by coupling the BODIPY fluorophores with porphyrins. In addition, the preparation of compounds carrying multiple BODIPY units [31–33] can increase the amount of light that is collected by molecular chromophores avoiding undesired effects associated with aggregation in highly concentrated films.

BODIPY fluorophores are also particularly popular in bioimaging and sensing applications due to their near unitary fluorescence quantum yield [34–36]. However, like most organic dyes, their small Stokes shift (10–20 nm) limits the signal-to-noise ratio due to reabsorptions of emitted photons and cross-talk between the excitation source and the fluorescent emission. In this sense, molecules containing both porphyrin and BODIPY units are promising [37–40], and have been the focus of our recent effort to achieve conjugates able to combine the properties of photosensitizers (PS) for photodynamic therapy (PDT) with those of fluorescent markers for biologic studies by exploring efficient intramolecular energy transfer processes and enhanced optoelectronic properties in the blue-green region of the spectrum.

For the construction of the conjugates, we selected 1,3,5-triazine as the linker between the BODIPY and the porphyrin units due to its suitability to join up to three substituents of interest, according to the wellknown temperature-dependent stepwise substitutions of the three Cl atoms from the starting cyanuric chloride [41]. In fact, triazine bridged triads having covalently bonded porphyrin and/or BODIPY constituents have been considered in the literature as promising agents in fast transfer systems [42] and in dye sensitized solar cells (DSSC) [43–45]. In the present study we constructed a fluorescent framework that can accommodate a combination of three different functional groups, where the BODIPY block acts as the fluorophore energy donor (D), the porphyrin core serves as the energy acceptor/photosensitizer (A) and the third substituent functions as an auxiliary group (Fig. 1).

Two triads were synthesized, a linear D-A structure with one BODIPY and one porphyrin unit bridged by the triazine linker and one branched A-D₄ structure with the porphyrin core linked to four BODIPY units. The structure and optical properties of the triads were fully characterized. The nonlinear upconverted emission properties of the triads where studied by two-photon excitation in the Near-infrared (NIR, 730–930 nm). NIR excitation is of outmost convenience for the use of fluorophores in high resolution imaging of 3D samples (e.g. *in vitro* imaging



Fig. 1. General framework highlighting triazine bridged triads.

of organoids and *in vivo* imaging of small animals) or photosensitizers in scattering media [46–48]. Two-photon induced processes hold also great interest for applications in micromachining and optical power limiting [49]. NIR excitation grants the possibility of penetrating deeper into most materials and thick biological tissue due to reduced absorption and scattering of NIR radiation. The synthesized triads exhibit linear and nonlinear optical properties shaped by the efficient energy transfer from the BODIPY to the porphyrin. We observed both green and red emission upon excitation at 930 nm featuring a large separation between excitation and emission wavelengths that can be of potential value for sensing and imaging purposes.

2. Material and METHODS

2.1. Chemicals

The reagents used for the preparation of porphyrins and BODIPY-Porphyrin conjugates were purchased from Sigma-Aldrich. All solvents were used as received from different commercial sources, with the exception of tetrahydrofuran that was dried using standard procedures.

2.2. Instrumentation

Melting points are uncorrected and were determined on a Büchi B-540 device. The mass spectra were recorded using a ESI-MS MALDI-Micromass Q-TOF2 equipment (potential 40-260 eV). UV-Vis spectra were recorded on a Shimadzu UV-2501PC spectrophotometer. NMR spectra were obtained on a Varian Unity Plus/Bruker Advance DPX spectrometer (300 or 500 MHz): ¹H: 300.13 MHz or 500.13 MHz; ¹³C: 75.47 MHz or 125.76 MHz and ¹⁹F: 282.38 MHz or 470.27 MHz ¹³C assignments were made based on 2D HSQC and HMBC experiments (delay for long-range J C/H couplings were optimized for 7 Hz). Samples were dissolved in the specified solvent, $CDCl_3$ or $DMSO-d_6$. Chemical shifts were expressed in δ (ppm) for the following references: tetramethylsilane (internal) for ¹H and ¹³C and hexafluorobenzene (external) for ¹⁹F. Coupling constants (*J*) were expressed in Hertz (Hz) and the areas of the signals were obtained by electronic integration. Multiplicity of signals was noted as: s-singlet, d-doublet, t-triplet, q-quartet, quint-quintet, m-multiplet.

2.3. Spectroscopic measurements

The linear absorption spectra were recorded on a JASCO V-540 spectrophotometer. The fluorescence spectra were recorded using a Horiba Jobin Yvon Fluorlog 3–22 Spectrofluorimeter with a xenon lamp of 450 W. The spectra were recorded in spectroscopic grade dimethylsulfoxide (DMSO) using 5 × 5 mm quartz cells. The fluorescence quantum yields where determined upon excitation of the Soret band at 422 nm and the BODIPY at 470 nm using 5,10,15,20-tetraphenylporphyrin (TPP) in toluene ($\Phi = 0.11$) and fluorescein at pH 11 as standards ($\Phi = 0.92$) [50].

Two-photon absorption (TPA) spectra were measured in 5–10 μ M DMSO solutions by two-photon fluorescence (TPF) using fluorescein at pH 11 and TPP in CCl₄ as standards, to account for collection efficiency and pulse characteristics [51]. A modified setup that follows closely the one described by Xu and Webb was used to estimate the TPA cross section in the 710–930 nm region. The two-photon emission (TPE) was measured within a narrow wavelength bandwidth selected by the H20Vis Jobin Yvon monochromator placed at the entrance of a PMC-100-4 photomultiplier tube (Becker and Hickl GmbH). The excitation source was a Ti:sapphire laser (Tsunami BB, Spectra-Physics, 710–990 nm, 1.7 W, 100 fs, 82 MHz).

The integrated TPE over the entire emission band was extrapolated using the overall emission spectra measured in the fluorimeter upon excitation at half the two-photon excitation wavelength ($\lambda_{TPA}/2$). The two photon absorption cross section was calculated from Equation (1):

$$\sigma = (F_2/\Phi Cn)_s (\Phi Cn\sigma_2/F_2) ref$$
⁽¹⁾

where F_2 stands for integrated fluorescence intensity, Φ is the fluorescence quantum yield, n refers to the refractive index in solution, C is the concentration, and s and ref are relative to the sample and the TPA reference, respectively. The emission intensity dependence of the excitation power was checked. The relative error of the cross sections values is at most $\pm 20\%$. The fluorescence decays were measured in 5 mm quartz cuvettes by the Single-Photon Timing technique under excitation at 330 nm by collecting the emission at 514 and 700 nm. The excitation source was the 2nd harmonic of a Coherent Radiation Dve laser 700 series (laser dve DCM, 610-680 nm, 130 mW, 5 ps, 4 MHz). The emission was collected at the magic angle by a Jobin Yvon HR320 monochromator (Horiba Jovin Ivon Inc.). The instrument response functions (35-80 ps FWHM) was estimated using a scattering dispersion of colloidal silica in water. Decay curves were stored in 1024 channels with 24.4–48.8 ps per channel and an accumulation of 20k counts in the peak channel. The fluorescence decays were analyzed by a nonlinear leastsquares reconvolution method using the TRFA DP software by SSTC (Scientific Software Technologies Centre, Belarusian State University, Minsk, Belarus).

2.4. Single-crystal X-ray diffraction studies

Single crystals of compound **7** were manually harvested from the crystallization vials and immersed in highly viscous FOMBLIN Y perfluoropolyether vacuum oil (LVAC 140/13, Sigma-Aldrich) to avoid degradation caused by the evaporation of the solvent [52]. Crystals were mounted on either Hampton Research CryoLoops or MiTeGen Micro-Loops, typically with the help of a Stemi 2000 stereomicroscope equipped with Carl Zeiss lenses.

Crystal data were collected at 150(2) K on a Bruker X8 Kappa APEX II CCD area-detector diffractometer (Mo K α graphite-monochromated radiation, $\lambda=0.71073$ Å) controlled by the APEX3 software package [53] and equipped with an Oxford Cryosystems Series 700 cryostream monitored remotely using the software interface Cryopad [54]. Diffraction images were processed using the software package SAINT+[55], and data were corrected for absorption by the multiscan semi-empirical method implemented in SADABS 2016/2 [56].

All structures were solved using the algorithm implemented in SHELXT-2014/5 [57], which allowed the immediate location of almost all of the heaviest atoms composing the molecular unit of compound 7. The remaining missing and misplaced non-hydrogen atoms were located from difference Fourier maps calculated from successive full-matrix least-squares refinement cycles on F^2 using SHELXL from the 2018/3 release [58]. All structural refinements were performed using the graphical interface ShelXle [59].

Hydrogen atoms bound to carbon were placed at their idealized positions using appropriate *HFIX* instructions in SHELXL: 43 (aromatic carbon atoms) and 137 (for the methyl groups). These hydrogen atoms were included in subsequent refinement cycles with isotropic thermal displacements parameters ($U_{\rm iso}$) fixed at 1.2 (for the former family of hydrogen atoms) or $1.5 \times U_{\rm eq}$ (solely for those associated with the methyl group) of the parent carbon atoms.

The last difference Fourier map synthesis showed for 7, the highest peak (0.813 $e^{A^{-3}}$) and the deepest hole ($-0.392 e^{A^{-3}}$) located at 1.54 and 0.58 Å from Cl1, respectively. Structural drawings have been created using the software package Crystal Impact Diamond [60].

Crystallographic data (including structure factors) for the crystal structure of **7** has been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 2EZ, U.K. FAX: (+44) 1223 336033. E-mail: deposit@ccdc.cam.ac.uk.

Crystal data for 7: C₃₄H₂₈BClF₂N₆O, M = 620.88, monoclinic, space group P2₁/n, Z = 4, a = 10.8010(12) Å, b = 18.800(2) Å, c = 15.1359 (17) Å, β = 105.547(2)°, V = 2961.0(6) Å³, μ(Mo-Kα) = 0.182 mm⁻¹, D_c = 1.393 g cm⁻³, red plate with crystal size of $0.19 \times 0.19 \times 0.08$ mm³. Of a total of 43,098 reflections collected, 5406 were independent ($R_{int} = 0.0437$). Final R1 = 0.0600 [$I > 2\sigma(I$)] and wR2 = 0.1646 (all data). Data completeness to theta = 25.24°, 99.7%. CCDC 1951549.

2.5. Synthesis

All reactions sensitive to air or moisture were carried out under N₂. Chemicals of analytical grade were purchased from commercial sources (Sigma-Aldrich or Merck) and were used as received. Solvents were distilled and dried, according to known methodologies. Analytical TLC was carried out on precoated sheets with silica gel (0.2 mm thick, Merck), the eluents were prepared volume-by-volume (v/v) and visualization was performed by revelation under ultraviolet radiation (254/ 366 nm) and/or iodine. Column chromatography was carried out with silica gel 70–230 mesh (Aldrich). 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (**TPPF**₂₀), *tert*-butyl-(2-aminoethyl)carbamate **1**, and 4,4-difluoro-1,3,5,7-tetramethyl-8-(4-hydroxyphenyl)-4-bora-3a,4a-diaza-s-indacene (**BODIPY-OH**) were synthesized as described in the literature [61–63].

Synthesis of TPPF19NHCH2CH2NHBoc (2). A 50 mL round-bottom flask containing a magnetic stirring bar was charged with 75 mg of TPPF₂₀ (0.0767 mmol), 12 mg of mono-protected ethylenediamine 1 (0.0767 mmol), 5.5 mg of potassium carbonate (0.0384 mmol) and 20 mL of toluene. The mixture was heated at 120 °C for 24 h under nitrogen atmosphere. The flask was allowed to cool to room temperature and the solvent was removed under reduced pressure. Then, the residue was diluted with chloroform and the organic phase was washed with water $(3 \times 20 \text{ mL})$. After separation of the organic phase, the solvent was removed under vacuum and the residue was purified by silica gel preparative TLC using chloroform as the eluent. From the first fraction was recovered the starting porphyrin (6%) and compound 2 was obtained from the second fraction in 68% yield, after recrystallization in a mixture of chloroform and methanol. Compound 2 was characterized by ¹H and ¹⁹F NMR, UV–Vis and MS (Figs. S1–S4, Supplementary Information).

Synthesis of TPPF₁₆(NHCH₂CH₂NH-Boc)₄ (3). Under inert atmosphere (N₂), a round-bottom flask, equipped with a magnetic stirring bar was charged with 75 mg of TPPF₂₀ (0.0767 mmol), 49 mg of *tert*-butyl (2-aminoethyl) carbamate 1 (0.11 mmol), 21 mg of potassium carbonate (0.015 mmol) and 20 mL of toluene. The mixture was refluxed for 72 h until consumption of the starting porphyrin TPPF₂₀. After cooling to room temperature, the mixture was diluted with chloroform and washed with water (3 × 20 mL). The organic phase was concentrated under vacuum and the residue was purified by silica gel preparative TLC using as eluent a mixture of chloroform-methanol (9:1) Compound **3** was isolated in 63% and characterized by ¹H and ¹⁹F NMR and UV–Vis (Figs. S5–S8, Supplementary Information).

Synthesis of TPPF₁₉NHCH₂CH₂NH₂ (4) and TPPF₁₆(NHCH₂CH₂NH₂)₄ (5). In a two necked round-bottom flask containing porphyrin 2 or 3 (15 mg) and dichloromethane (1 mL) it was added TFA (1 mL, 1.5 equiv.). The resulting mixture was maintained under stirring for 2 h at room temperature. At this time, TLC showed the complete consumption of the starting material. Then, the reaction was neutralized with an aqueous solution of NaOH 1 M until pH to \sim 12. Finally, the organic product was extracted with chloroform, the organic phase separated, dried over anhydrous Na₂SO₄ and the solvent removed under reduced pressure. The products (4 and 5) were fully characterized by NMR, mass and UV-Vis techniques (Figs. S9-S16, Supplementary Information).

Synthesis of 4,6-dichloro-*N*,*N*-diphenyl-1,3,5-triazin-2-amine (6) [64]. Under a nitrogen atmosphere 1.84 g (0.01 mol) of cyanuric chloride and 2.12 g (0.02 mol) of sodium carbonate were dissolved in 20 mL of dry acetone at 0 °C. To this mixture a solution of 1.42 g (0.0084 mol) of diphenylamine in 10 mL of dry acetone was added dropwise. The reaction was kept at 0 °C and stirred for about 4 h, monitored by TLC.

Upon reaction completion the white precipitate was filtered off and the solvent evaporated under reduced pressure. The remained solid was washed with acetone three times, then purified by column chromatography using CH₂Cl₂:hexane (2:1) as the eluent. A pale yellow solid (m.p. 178–179 °C) was obtained in 64% yield (see characterization in Figs. S17–S18, Supplementary Information).

Synthesis of compound 7. Under nitrogen atmosphere 41.0 mg (0.12 mmol) of **BODIPY-OH** and 38.06 mg (0.12 mmol) of 1,3,5-triazin 6 were dissolved in 9 mL of dry acetone, then 19 mg (0.18 mmol) of sodium carbonate was added. The mixture was stirred at 35 °C for 27 h, and the evolution of the reaction was monitored by TLC. Upon reaction completion the white precipitate was filtered off and the solvent evaporated under reduced pressure. The crude product was purified by column chromatography using CH₂Cl₂:hexane as the eluent (gradient 2:1 to 4:1). A bright orange-red solid (dec. > 230 °C) was obtained in 56% yield and fully characterized by NMR, mass and UV–Vis (see characterization in Figs. S19–S25, Supplementary Information).

Synthesis of compound 8. Under nitrogen atmosphere 5.5 mg (0.0054 mmol) of **4** and 3.06 mg (0.0049 mmol) of **7** were dissolved in 7 mL of THF. Two drops of DIPEA were added and the resulting mixture was refluxed for 5 h. Upon reaction completion (monitored by TLC) the white precipitate was filtered off and the solvent was evaporated under reduced pressure. The residue was dissolved in CH₂Cl₂, the organic phase washed twice with water and dried with anhydrous Na₂SO₄ following standard procedures. The crude material was purified by preparative TLC using CH₂Cl₂ as eluent, to give a reddish brown solid in 81% yield from the second upper fraction. The full structural characterization is presented in Figs. S26–S31, Supplementary Information.

Synthesis of compound 9. Under nitrogen atmosphere 5.75 mg (0.0051 mmol) of 5 and 11.5 mg (0.0185 mmol) of 7 were dissolved in 6 mL of THF. 20 mg of K₂CO₃ were added and the resulting mixture was refluxed for 28 h. Upon reaction completion (monitored by TLC) the white precipitate was filtered off and the solvent was evaporated under reduced pressure. The residue was dissolved in CH₂Cl₂, the organic phase washed twice with water and dried with anhydrous Na₂SO₄ following standard procedures. The crude material was purified by preparative TLC using THF:hexane (3:2) as the eluent, to give a reddish brown solid in 40% yield. The full structural characterization is presented in Figs. S32–S40, Supplementary Information.

3. Results and DISCUSSION

8-(4-hydroxyphenyl)-1,3,5,7-tetramethyl BODIPY, herein abbreviated as **BODIPY-OH**, was elected as the fluorophore in our study due to its high fluorescence and appropriate nucleophilicity with respect to cyanuric chloride [32]. BODIPY-OH was synthesized in 21% yield by the mechanochemical method described by Laramine et al. [65] exploring the green chemistry concept. Diphenylamine was chosen as the auxiliary group, which is expected to modify the chemical and physical properties of the triad with particular emphasis on the solubility. Ultimately two porphyrins derived from the well-studied 5,10,15, 20-tetrakis(pentafluorophenyl)porphyrin (TPPF₂₀) [61] containing one or four ethylenediamine branches, respectively 4 and 5, were synthesized (Scheme 1) to complete the triads 8 and 9 presented in Scheme 2. Two-carbon chains separate the porphyrin core from the terminal amino group to minimize the steric interference towards the nucleophilic substitution reaction over the chlorine atom of the triazine intermediate 7.

Synthesis of the ethylenediamine substituted fluorophenylporphyrins 4 and 5.

The synthetic access to the amine porphyrins 4 and 5 involved, in both cases, the reaction of 5,10,15,20-tetrakis(pentafluorophenyl) porphyrin (TPPF₂₀) with the mono-protected Boc-ethylenediamine 1, prepared according to literature [62], followed by the amine deprotection step (Scheme 1).

The nucleophilic substitution of one or four para fluorine atoms in



 $TPPF_{20}$ was controlled by the number of equiv. of the amino derivative 1 and the reactions were performed in toluene at reflux in the presence of potassium carbonate [62,66]. The mono-N-Boc protected ethylene diamine porphyrin 2 was isolated in 68%, after 24 h of reaction of TPPF₂₀ with 1 equiv. of amine 1, while the tetra-substituted porphyrin 3 was obtained in 63% after 72 h of reaction using 4 equiv. of the amine. The evolution of both reactions was controlled by TLC and were stopped after verifying the almost consumption of the starting porphyrin accompanied by the formation of the desired main product. The structures of porphyrins 2 and 3 were confirmed by NMR, UV-vis and high-resolution mass spectrometry, see the Supplementary Information, Figs. S1–S8. The analysis of ¹H NMR spectra (Figs. S1 and S5) show in both cases the expected absorption at lower field of the eight β -pyrrolic protons of the porphyrin core. In the aliphatic region the resonances of the methylene protons from one alkyl or four alkyl chains appear with the expected pattern - two triplets at $\delta \sim 3.8$ ppm and $\delta \sim 3.6$ ppm. The resonances of the Boc protons appear as a singlet at $\delta \sim 1.45$ ppm and of the two nitrogen internal protons at $\delta \sim -2.9$ ppm as a broad singlet. The analysis of ¹⁹F NMR spectra confirms also the expected loss of one p-fluorine atom in the case of porphyrin 2 and of four p-fluorine atoms in porphyrin 3 (Figs. S2 and S6). In the ¹³C NMR spectra the carbon resonances of the Boc methyl groups are located at $\delta \sim 29.7$ ppm and those due to the remaining methylene carbons are found at $\delta \sim$ 47.1 ppm and δ \sim 40.9 ppm. The deprotection of the amino group or groups in porphyrins 2 and 3 in the presence of trifluoroacetic acid (TFA) afforded after the work up the desired porphyrins 4 and 5 in 82 and 87% yields, respectively. The structures of porphyrins 4 and 5 were unambiguously confirmed by 1D, and 2D NMR studies and their molecular formulas by HRMS. In these spectra, the ion peak [M+H]⁺ at 1015.12537 for 4 and



Scheme 2. Synthetic pathway for BODIPY-Porphyrin conjugates 8 and 9.

at 1135.31798 for **5** confirmed the successful cleavage of the *N*-Boc group(s) (Figs. S12 and S16). Moreover, in the aliphatic region of their ¹H NMR spectra is patent the absence of the signal due to the Boc protons and the presence of two triplets corresponding to the methylene hydrogens at $\delta \sim 3.7$ and 3.1 ppm; a broad singlet due to the resonance of *N*H of the ethylenediamine fragment(s) appear(s) for porphyrin **4** at $\delta \sim$ 5 ppm and for porphyrin **5** at $\delta \sim 6.5$ ppm). The resonances of the β -pyrrolic protons as a singlet at δ 9.2 ppm for **5** and as the two doublets at δ 8.9 and 8.8 ppm for porphyrin **4** is on line with the substitution degree (Figs. S9 and S13).

3.1. Synthesis of triazine-BODIPY-porphyrin triads

The initial step for the synthesis of the triads 8 and 9 exhibited in Scheme 2 involves the reaction of cyanuric chloride with diphenylamine in the presence of sodium carbonate at 0 °C in dry acetone [64]. Specifically, the choice of this amine as the first group to be connected to the triazine ring is due to its poor nucleophilicity, affording the known intermediate 6 without scrambling with poly-substituted products. Compound 6 was conveniently collected in 64% yield after column chromatography and its mono-substitution pattern confirmed by MS. In the subsequent step, it was performed the replacement of a chlorine atom of 6 using the equivalent amount of BODIPY-OH in the presence of sodium carbonate in dry acetone at 35 °C. In the course of the reaction, a new fluorescent orange spot related with the product was observed in the TLC plates (CH₂Cl₂:hexane 2:1) after 2 h, along with a considerable amount of 6. In our case, the consumption of 6 only took place after 27 h of stirring, and this is significantly longer than the 2 h period reported in the literature for similar conditions (see references [31,32,64,67] as examples). The crude reaction mixture was passed through a chromatography column affording the new compound 7 in 56% yield. In the HRMS-ESI spectrum, the ion peak of 7 [M+H]+ at 621.21247 unequivocally confirms that one BODIPY unity was introduced into compound 6.

Moreover, the presence of a resonance for two β -pyrrolic protons (δ = 5.98 ppm), two sets of resonances for two methyl groups each (δ = 2.56 ppm and 1.27 ppm) and three sets of resonance for a total of fourteen aryl protons (δ = 7.16–7.39 ppm) in the ¹H NMR spectrum, and the characteristic signal at δ = -142.35 in the ¹⁹F NMR spectrum corresponding to the BF₂ group, corroborate the expected structure (see the complete NMR assignments in the Supplementary Information).

Single-crystal X-ray diffraction was also used to fully elucidate the structural features of compound 7 and to unequivocally prove the success of the nucleophilic substitution of 6 with BODIPY-OH. Compound 7 crystallizes in the centrosymmetric P21/n space group, with the asymmetric unit being composed of a whole molecular unit as depicted in Fig. 2. The close packing of individual molecular units is mainly driven by the need to effectively fill the available space. A number of weak supramolecular contacts are present within the crystal structure, mainly C–H…F hydrogen bonding interactions [between two methyl groups (positions 1 and 7 of the BODIPY system) and F1, and one o-phenyl carbon with F2]: dC…F distances found in the 3.187(4)-3.361(4) Å range with the corresponding <(CHF) interaction angles in the range 117-145°. Despite the presence of several aromatic rings, no structurally relevant π … π contacts were found.

The last step to achieve triads **8** and **9** consisted in the nucleophilic substitution of the mono- and tetra-amine porphyrins **4** and **5**, respectively, over intermediate **7**.

The protocol that has been used by many authors when aminoporphyrins are the nucleophile over cyanuric chloride derivatives makes use of DIPEA as the HCl acceptor [42,43,45,68].

In our experiments, DIPEA reacted as expected in the synthesis of the mono-adduct **8**, but represented a persistent contaminant in the synthesis of the tetra-adduct **9** and so due to that it was replaced by K_2CO_3 . In both cases a 10% excess of **4** and **5** was added and the reactions were followed by TLC until the stage when a minimum amount of **BODIPY**-



Fig. 2. Schematic representation of the molecular unit present in the crystal structure of **7**. Non-hydrogen atoms are represented as thermal ellipsoids drawn at the 50% probability level and hydrogen atoms as small spheres with arbitrary radii.

OH was detected. Mono-adduct **8** was isolated in 81% yield by preparative TLC (CH₂Cl₂) after 5 h in refluxing THF, while completing the total of four substitutions on tetra-adduct **9** required a longer time (28 h). The latter product was isolated from preparative TLC (THF:hexane 3:2) in 40% yield. In addition to the losses inherent to the TLC purifications of multi substitution reactions, the lower yield of **9** compared to **8** could be attributed to BODIPYs partially substituted porphyrins, whose isolation was not the focus of this work. The structural identities of **8** and **9** were confirmed by ESI- HRMS, ¹H, ¹³C and ¹⁹F NMR spectroscopy and the respective spectra are depicted in Supplementary Information (Figs. S26–S40). For each compound, the major peak in the ESI-HRMS spectrum appeared as half the calculated molecular weight in agreement with the double-charged [M+2H]²⁺ species.

In the ¹H NMR spectrum of **8**, the porphyrin core shows a set of resonances for the eight asymmetric β -pyrrolic protons around $\delta = 9$ ppm and one resonance for two inner NH protons at $\delta = -2.92$ ppm. The resonances due to the ethylenediamine fragment appear as a set of signals between $\delta = 3.90$ –3.65 ppm for the four ethylene protons and as two broad peaks for the two NH protons at δ = 5.16 and 4.72 ppm. The BODIPY moiety of 8 showed the same pattern of signals as its precursor 7 and similar chemical shifts. One difference, however, is that the two methyl groups at positions 1 and 7 of the BODIPY system in compound 8 are split into two resonances at $\delta = 1.25$ and 1.23 ppm, denoting slightly different environments. The tetra-substitution pattern in compound 9 is confirmed, for example, by the 1:4 ratio in the number of inner NH hydrogens of the porphyrin centre (2H, $\delta = -2.89$ ppm) and the peripheral BODIPY β -pyrrolic protons (8H, = 5.90 ppm). Highlighted assignments are: a resonance at $\delta = 2.52$ ppm for twenty four methyl protons (positions 3 and 5 of the BODIPY system), two sets of resonance at $\delta = 1.24$ and $\delta = 1.20$ ppm for twelve methyl protons each (positions 1 and 7) and a set of resonance in the range $\delta = 7.09-7.35$ ppm relative to fifty six aryl protons.

The most distinct feature in the characterization of triads 8 and 9 is

observed in the ¹⁹F NMR spectra (Fig. 3). In compound **8** the two fluorine atoms of BF₂ give rise to a resonance centred at $\delta = -142.77$ ppm, which is consistent with the integral ratio of the fluoroporphyrin system: six *ortho*-F, six *meta*-F, three *para*-F, two *ortho*'-F and two *meta*'-F. On the other hand, the symmetric compound **9** has a simpler spectrum showing a resonance centred at $\delta = -142.66$ ppm for a total of eight fluorine atoms of four BF₂ groups, in agreement with the integral ratio of eight *ortho*-F and eight *meta*-F of the fluoroporphyrin moiety.

The UV–Vis absorption and fluorescence emission spectra of the triazine-BODIPY-porphyrin triads are compared with those of the individual units in Fig. 4. Table 1 presents a summary of the optical properties of compounds **4**, **5**, **7**, **8** and **9**.

The ethylenediamine substituted fluorophenylporphyrins 4 and 5 show typical absorption spectra of meso-tetraarylporphyrins with the intense Soret band centred in the 410–430 nm region and being accompanied by less intense Q-bands between 550 and 650 nm (Fig. 4). The maximum molar extinction coefficient of the Soret band is 17.97 \times 10⁴ M⁻¹cm⁻¹ for 4 and 12.37 \times 10⁴ M⁻¹cm⁻¹ for 5 (Table 1). The BODIPY derivative 7 shows a narrow absorption band centred at 502 nm with molar absorptivity of 7.99 \times 10⁴ M⁻¹cm⁻¹ in good agreement with the UV–Vis absorption spectrum of the BODIPY fluorophore.

The absorption spectra of triads **8** and **9** show features of both porphyrin and BODIPY units in good agreement with the expected molar ratio. The molar extinction coefficient of the Soret band in the triads (15-16 × 10⁴ M⁻¹cm⁻¹) are similar to those of the isolated porphyrins, thus confirming the presence of one porphyrin unit per triad. The molar extinction coefficients of the green absorption of BODIPY in triad **8** (5.9 × 10⁴ M⁻¹cm⁻¹) is of the same order of magnitude of derivative **7**, thought it appears to be 30% lower. This band is nearly four times stronger in triad **9** than in triad **8**, thus confirming the tetra-substitution of the porphyrin core in triad **9**.

3.2. Steady-state emission

Two emission bands are observed at 660 and 706 nm for compound 4 and 660 and 714 nm for compound 5. The emission quantum yield Φ of the mono-substituted fluorophenylporphyrin 4 in DMSO ($\Phi = 3.8\%$) is slightly lower than that of the tetra-substituted derivative 5 ($\Phi = 7.4\%$). The quantum yield of the fluorophenylporphyrin is 2–3 times lower than that of the TPP standard used to estimate the quantum yield. This is a well-known effect of having the hydrogen atoms in the meso-aryl moieties replaced by fluorine, which leads to a larger distortion from planarity. In addition, the halogen atoms promote a spin-orbit coupling that decreases the radiative deactivation pathways while increasing the non-radiative pathways [69]. For compound 7, the emission of BODIPY is centred at 516 nm with a Stokes shift of only 14 nm and $\Phi = 65\%$, considerably higher than that of the porphyrin derivatives.

The photoluminescence spectra of the triads upon excitation at 470 nm feature a narrow band in the green (\approx 515 nm) and a doublet in the red (660/708 nm and 660/718 nm for 8 and 9) ascribed to the BODIPY and the porphyrin units, respectively. The peak positions of the emission bands in the triads are nearly coincident with those observed in the isolated components evidencing the lack of conjugation between the porphyrin and the BODIPY units. Emission in the green is exclusively due to direct excitation of the BODIPY. This is supported by the fact that the excitation spectra collected in the green (514 nm) shows only the typical BODIPY absorption band at 502 nm (dashed blue trace in Fig. 4). On the other hand, emission in the red is observed from either direct excitation of the porphyrin and excitation of the BODIPY followed by an efficient energy transfer from the BODIPY donor (D) to the porphyrin acceptor (A). The energy transfer process is supported by the fact that the excitation spectra of the triads recorded upon collection of the emission in the red (660 or 700 nm) overlaps perfectly with the absorption spectra (dashed green and red lines in Fig. 4). Furthermore, the good spectra overlap of both emission and excitation spectra of the triads with the spectra of the individual units excludes the formation of



Fig. 3. ¹⁹F NMR spectra of triads 8 and 9 with integral ratio and fluorine assignment. Optical properties of BODIPY-porphyrin triads.

emissive charge transfer complexes in both the ground and electronic excited state. This is further supported by the fact that the lifetime of the porphyrin moiety does not changes in the hybrid compared to the free porphyrin, which excludes a charge transfer dynamic quenching. The emission quantum yield of **8** is of the same magnitude order of the quantum yield of porphyrin **4** ($\Phi = 4.1\%$ and 4.7% upon excitation at 422 and 470 nm, respectively). The emission quantum yield of **9** is about twice higher than that of porphyrin **5** ($\Phi = 11.3\%$ and 15.9% upon excitation at 422 and 470 nm, respectively). A strong quenching of the BODIPY emission is observed in both triads while the porphyrin emission efficiency remains similar to that observed in the individual porphyrins **4** and **5**.

3.3. Fluorescence decay curves

The fluorescence decays were measured in DMSO and fitted with a sum of exponentials after convolution with the experimental response function. The average lifetimes $\overline{\tau} = \sum_{a_i} \frac{a_i \tau_i}{a_i}$ where a_i are the pre-exponential factors and τ_i the lifetimes from the fluorescence decay curves fitting, are collected in Table 1. The average lifetimes are 6.7 and 5.7 ns, respectively for 4 and 5. The BODIPY derivative 7 has a slightly lower emission lifetime of 4 ns The energy transfer in the triads results in a faster decay of the green emission of BODIPY (<1 ns) as compared with emission of derivative 7 (4 ns). As shown in Fig. S41 of the Supplementary Information, a very clear fast decay component is observed in the green emission of the triads is not so evident. Both hybrids show multiexponential red emission decays with average lifetimes in the same range of the individual porphyrins (5–7 ns).

Fig. 5 shows that at equimolar concentrations the red emission of the porphyrin upon excitation of the BODIPY unit at 470 nm is significantly stronger in the triads (8 and 9) than in the isolated porphyrins (4 and 5). This gives a clear evidence of efficient energy transfer from the BODIPY to the porphyrins in the triads. The energy transfer in the triads can be estimated as $E = 1 - \frac{\bar{\tau}_{DA}}{\bar{\tau}_D}$ where $\bar{\tau}_{DA}$ and $\bar{\tau}_D$ refers to the average lifetime of the donor emission measured in the presence (8 and 9) and absence (7) of the acceptor, respectively. An energy transfer efficiency of nearly 90% is estimated for both triads (92% for 8 and 88% for 9).

The transfer of excitation energy from an electronic excited molecule (donor) to another (acceptor) is possible if the emission spectrum of the donor partially overlaps with the absorption spectrum of the acceptor. For allowed donor and acceptor transitions, the dipole-dipole term of the expansion of the coulombic interaction is predominant for large donor to acceptor separations. In the limit of very weak coupling, the rate of energy transfer by a dipole-dipole interaction between an energy donor and an acceptor separated by a distance R is given by the Förster Equation (2) [70]:

$$k_{ET} = \frac{1}{\tau_D} \left(\frac{R_0}{R}\right)^6$$
(2)

where τ_D is the lifetime of the donor in the absence of acceptor and R₀ is the Förster radius at which the rate of energy transfer and decay of the excited donor are equally probable. The Förster radius can be calculated from spectroscopic data of the donor and acceptor molecules, following Equation (3) [71],:



Fig. 4. Normalized UV–Vis absorption, emission and excitation spectra of compounds **4**, **5**, **7**, **8** and **9** in DMSO. The absorption spectra in straight black trace, the emission spectra upon excitation at 422 nm and 470 nm in straight blue and green traces, respectively, and the excitation spectra recorded upon collection of emission at 514 nm, 660 nm and 700 nm are shown as dashed traces in blue, green and red, respectively.

Table 1

Summary of absorption and emission properties of the synthesized compounds: maximum absorption and emission wavelengths (λ_{abs} and λ_{em} , nm), photoluminescence emission quantum yields (Φ , %) and average lifetimes ($\overline{\tau}$, ns).

compound	absorption	Emission		
	$\lambda_{\rm max}/{\rm nm}~(\epsilon/10^4{\rm M}^{-1}{\rm cm}^{-1})$	$\lambda_{\rm max}/{\rm nm}$	Φ (%)	$\overline{\tau}$ (ns)
4	413 (17.97), 508 (1.84), 582 (0.60), 632 (0.31)	660, 706	3.8 ^a	6.7 ^c
5	421 (12.37), 514 (1.67), 547 (0.46), 586 (0.42)	660, 714	7.4 ^a	5.7 ^c
7	502 (7.99)	516	65.0 ^b	4.0 ^d
8	413 (16.3), 503 (5.9), 578 (0.48)	514, 660,	4.1 ^a	0.3^{d}
		708	4.7 ^b	4.1 [°]
9	426 (15.22), 502 (21.20), 548 (0.67),	514, 658,	11.3 ^ª	0.5 ^d
	588 (0.54)	718	15.9 ^b	7.2 ^c

^a Excitation at 422 nm.

^b Excitation at 470 nm.^c.

^c Emission collected in the red (700 nm).

 $^{\rm d}\,$ Emission collected in the green (514 nm).



Fig. 5. Fluorescence emission of equimolar concentration solutions of the BODIPY (7) and porphyrins compared with the corresponding triads in panel A (4, 7 and 8) and panel B (5, 7 and 9) upon excitation at 470 nm. The intensity of 4, 5, 8 and 9 are read on the left axes while that of derivative 7 is shown on the right axes.

$$R_o^6 = 8.79 \times 10^{-5} \left(\frac{\Phi_D \kappa^2}{n^4}\right) \int_0^\infty F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda$$
(3)

where Φ_D is the emission quantum yield of the donor, *n* is the refractive index of the medium, and the integral on the right side of Equation (3) is the overlap integral of the normalized donor emission spectra, $F_D(\lambda)$, with the absorption spectra of the acceptor, $\varepsilon_A(\lambda)$, and κ^2 is an orientation factor between the transition dipole moments of the donor and the acceptor molecules. A $R_0 = 43$ Å is estimated for the BODIPY-Porphyrin donor-acceptor pair in DMSO assuming an orientation factor $\kappa^2 = 2/3$ corresponding to freely rotating donor and acceptor dyes. The efficiency of Förster Resonance Energy Transfer (FRET) is given by,

$$E_{FRET} = \frac{k_{ET}}{\frac{1}{r_D} + k_{ET}} = \frac{1}{1 + (\frac{R}{R_0})^6}$$
(4)

which allows the estimation of the average distance between D and A. For an efficiency of 90%, estimated before from the decay times of the donor, a value of R ≈ 30 Å was calculated, which is larger than the distance estimated based on the molecular structure of the conjugates (≈ 20 Å depending on the conformation). The discrepancy in the R values is due to the fact that the donor and acceptor separation is not fixed, but varies with the conformation and Brownian motion of the triads, in which case a distribution of distance has to be considered and the separation R, when evaluated from equation (4), is an apparent separation. Furthermore, the donor and acceptor molecules are not point dipoles and the rotation of the donor and acceptor is not completely free, which introduces uncertainty in the Förster radius, R₀.

Electronic structure calculation of the lowest energy electronic transition of triad **8** and the isodensity surfaces of the frontier molecular orbitals involved (Fig. S42) confirm that the mechanism behind the quenching of the emission of BODIPY is a FRET process. The lowest energy transitions involve orbitals localized in the porphyrin fragment (from H or H-1 to L and L+1), orbitals delocalized between this fragment and the triazine bridge (from H-3 to L or L+1), or orbitals localized in the

BODIPY fragment (from H-2 to L+2). The lack of orbital overlap between the porphyrin and the BODIPY fragments supports the assignment of the energy transfer process to a through space dipole – dipole interaction (FRET) rather than through-bond Dexter process.

3.4. Nonlinear NIR excitation

The nonlinear emission properties of the triads where studied in the 710–930 nm region. Typical nonlinear two-photon absorption (TPA) cross section of BODIPY and porphyrins in this spectral region have been reported to be below 20 GM [72–74]. The triazine core has also been explored as an electron acceptor unit in the design of small molecules and polymers for upconverted emission based on TPA [75,76]. Triazines have been used in the construction of NIR antenna polymers for two-photon activated volumetric data storage based on energy transfer to photochromic acceptor units [77,78].

The TPA and the upconverted emission spectra of 4, 7 and 8 are shown in Fig. 6. The corresponding results for 5 and 9 are shown in Fig. S43 and follow the same trend as for 4 and 8.

The TPA cross-section was determined by two-photon induced fluorescence using well-known TPA cross-section standards as explained in detail in the experimental section. The maximum TPA of porphyrin is observed at shorter wavelengths (40-70 GM at 730 nm). Both 4 and 5 show TPA cross-sections that are at least twice higher than those reported for the isolated porphyrin units in the 710–930 nm region. In line with earlier reports, the BODIPY derivative 7 has only a modest TPA cross-section in this wavelength range with the highest value observed at longer wavelengths (5 GM at 930 nm). Noteworthy, the peak of the TPA band of 7 should lay just outside our observation window at 1030 nm (2 \times 516 nm). In the triads the TPA spectra are dominated by the contribution of the porphyrin unit, with maximum TPA cross-sections laying in the same range as those observed for the porphyrins monomer and also peaking at shorter wavelengths. The high TPA crosssections observed for the triads at 730 nm (36 and 65 GM for triad 8 and 9, respectively) are in good agreement with the values observed for

the porphyrin monomers (40-70 GM). In Fig. 4, we showed that the emission spectra upon one-photon excitation depends on the excitation wavelength. The same is true for two-photon induced emission. Nevertheless, the emission should have no memory on the nature of the excitation process, meaning that as long as we introduce the same amount of energy in the system the order of the photon interaction should not affect the nature of final excited state nor its dynamics. Thus, the nonlinear emission spectrum induced at a given excitation wavelength should be equal to the linear emission spectrum at half that wavelength. Indeed, Fig. 6(F) shows that the upconverted emission upon two-photon excitation at 930 nm is equal to the down-converted emission spectrum collected upon one-photon excitation at half that wavelength (470 nm). Both the green emission of BODIPY and the red emission of porphyrins are observed under 930 nm excitation. The separation of \approx 400 nm between NIR excitation and emission in the green can be useful for application in sensing and imaging. On the other hand, excitation in the NIR and emission in the far red might also be of value for applications requiring non-invasive introduction of a certain amounted of energy within scattering media. The inserts in Fig. 6 show that for all the compounds the fluorescence emission upon NIR excitation depends quadratically on the excitation power ($\log F_2$ vs log P with a slope of 2), thus confirming that the upconverted emission is due to a two-photon excitation process.

4. Conclusion

We synthesized two triads connecting a BODIPY derivative **7** to mono- and tetra-ethylenediamine substituted porphyrins **4** and **5** via a triazine linker. Triad **8** has a linear D-A structure with one BODIPY and one porphyrin unit bridged by the triazine and triad **9** is a branched A-D₄ structure with the porphyrin core linked to four BODIPY units. The structure and optical properties of the triads were evaluated by different techniques namely NMR (¹H, ¹⁹F, ¹³C), HRMS, UV–vis and fluorescence. The nonlinear upconverted emission properties of the triads were studied by two-photon excitation in the NIR (710–930 nm). The



Fig. 6. Nonlinear two-photon absorption and emission spectra of 4, 7 and 8: TPA (red symbols) and one-photon absorption (OPA, black line) spectra in panels A, C and E on the left and two-photon emission excited at 930 nm (red symbols) and one-photon emission excited at 470 nm (black line) in B, D and F on the right. The inserts show the log-log plot of the NIR excited fluorescence intensity as a function of the excitation power showing a quadratic dependence (linear fit with a slope of \approx 2).

synthesized triads exhibit linear and nonlinear optical properties shaped by the efficient energy transfer from the BODIPY to the porphyrin. We observed both green and red emission upon excitation in the NIR at 930 nm featuring a large separation between excitation and emission wavelengths that can be of value for application in sensing and imaging.

Contribution

Marcos C. de Souza: Project administration, Investigation Writing-review-and editing.

José A. S. Cavaleiro; Maria da Graça P. M. S. Neves: Supervision, Investigation.

Carla I. M. Santos; Inês Mariz: Methodology.

Ermelinda Maçôas; José M. G. Martinho: Investigation, Writing-review.

Filipe A. A. Paz; Ricardo F. Mendes: Methodology, Formal analysis. Leandro F. Pedrosa; Bruno da S. Marques; Luana A. Machado: Investigation, Methodology.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Authors are grateful to University of Aveiro, Instituto Superior Técnico (IST, Portugal) and FCT/MCTES (Fundação para a Ciência e Tecnologia/Ministério da Ciência e Tecnologia, Portugal) for funding, the research units: QOPNA (FCT UID/QUI/00062/2019), LAQV-REQUIMTE (UIDB/50006/2020), CICECO-Aveiro Institute of Materials (Ref.UID/CTM/50011/2020), (UID/CTM/50011/2019) and (UID/ NAN/50024/2019); the projects: (UID/EMS/00481/2013), (PTDC/FIS-NAN/4662/2014), (PTDC/NAN-MAT/29317/2017), (PTDC/QUI-QFI/ 29319/2017), (LISBOA-01-0145-FEDER-029319) and (UIDB/00100/ 2020) through national funds and, where applicable, co-financed by European Union, FEDER, QREN, and COMPETE within the PT2020 Partnership Agreement, and to the Portuguese NMR Network. RFM acknowledges FCT for his Junior Research Position (CEECIND/00553/ 2017) and C. I. M. Santos for her research contract (REF.IST-ID/95/ 2018). Authors also thank the Departamento de Química Orgânica of Universidade Federal Fluminense (UFF-Brazil), Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro-FAPERJ (grants 101.125/2018, 211.119/2019 and 201.754/2018) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior-CAPES.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2021.109137.

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