Dalton Transactions

PAPER

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2014, **43**, 7561

A first archetype of boron dipyrromethene-phthalocyanine pentad dye: design, synthesis, and photophysical and photochemical properties

Cem Göl, Mustafa Malkoç, Serkan Yeşilot and Mahmut Durmuş*

Received 7th February 2014,
Accepted 9th March 2014

DOI: 10.1039/c4dt00406j

www.rsc.org/dalton

A novel type of phthalocyanine pentad containing four boron dipyrromethene (**BODIPY**) units at peripheral positions of the phthalocyanine framework has been designed and synthesized for the first time. The Sonogashira coupling reaction between 4,4′-difluoro-8-(4-ethynyl)-phenyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (**Ethynyl-BODIPY**) and 2(3),9(10),16(17),23(24)-tetrakis(iodo) zinc(II) phthalocyanine (**Iodo-Pc**) has been used for the synthesis of the target compound. The BODIPY-phthalocyanine pentad dye (**BODIPY-Pc**) has been fully characterized by ^{1}H NMR, MALDI-TOF mass, FT-IR and UV-Vis spectroscopic techniques and elemental analysis as well. The photoinduced energy transfer process for this dye system was explored in tetrahydrofuran solution. The singlet oxygen generation capability and photodegradation behaviours of this **BODIPY-Pc** pentad dye were also investigated in DMSO for the determination of the usability of this new type of dye system as a photosensitizer in PDT applications.

Introduction

Photodynamic therapy (PDT) is a cancer treatment technique that uses nontoxic light-sensitive compounds called photosensitizers, along with harmless light having a long wavelength to damage cancer cells.[1] Recently, phthalocyanine (Pc) compounds have been mostly used in photodynamic therapy (PDT) as photosensitizers[2,3] besides being utilized in many fields such as industrial,[4] technological[5,6] and other biomedical applications.[7,8] Phthalocyanine compounds are considered to be ideal candidates for PDT of cancer due to their suitable properties such as long wavelength absorption (near IR), capability for efficient singlet oxygen generation and having nontoxic effects in the absence of light.[9] BODIPY (4-difluoro-4-borata-3a-azonia-4a-aza-s-indacene) derivatives have also been studied as a new class of photosensitizers[10,11] besides using them in light harvesting systems,[12] logic gates,[13] chemical sensors[14] and energy transfer cassettes.[15]

Although there are many individual examples of BODIPY and phthalocyanine compounds, only a few studies about compounds containing these two groups on the same molecule are known in the literature. Most of these molecules contain BODIPY groups as axial substituents on the boron subphthalocyanines or silicon phthalocyanines.[16–19] Only one study published by Torres and co-workers was devoted to the asymmetrical phthalocyanine derivative and this compound bears one BODIPY group at the peripheral position.[20]

The target compound in this study is a pentad dye system that contains four BODIPY groups on the phthalocyanine framework. To the best of our knowledge, there is no report about symmetrical BODIPY-substituted phthalocyanines in the literature. Although both types of compounds (BODIPY and phthalocyanine) have been investigated as photosensitizers themselves in PDT of cancer, there is no report about the investigation of the photosensitizing properties of BODIPY substituted phthalocyanines. In order to check whether this type of photosensitizer is a good candidate or not, the photophysical and photochemical properties were evaluated in the present work.

The aim of the present study is to synthesize a new type of dye system containing both BODIPY and phthalocyanine units. It exhibits all the advantages of two different unique groups (BODIPY and phthalocyanine) present on a single molecule and might be a good candidate in many application areas such as light harvesting systems and PDT.

Experimental

Materials

Tetrahydrofuran (THF), triethylamine (TEA), dichloromethane (DCM), pentanol and toluene were dried as described by Perrin and Armarego[21] before use. Zinc(II) chloride, zinc(II) acetate, trifluoroacetic acid (TFA), 2-dimethylaminoethanol

Gebze Institute of Technology, Department of Chemistry, P.O. Box 141, 41400 Gebze, Kocaeli, Turkey. E-mail: durmus@gyte.edu.tr; Fax: (+)90(262)605 31 01

(DMAE), K_2CO_3, copper(I) iodide, bis(triphenylphosphine)-palladium(II) chloride, dichloro dicyano benzoquinone (DDQ), trimethylsilylacetylene (TMSA), $BF_3{\cdot}OEt_2$, 4-iodophthalonitrile and unsubstituted zinc phthalocyanine were purchased from Aldrich. 1,3-Diphenylisobenzofuran (DPBF) was purchased from Fluka. Column chromatography was performed on silica gel 60 (0.04–0.63 mm). 4,4′-Difluoro-8-(4-iodo)-phenyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (**Iodo-BODIPY**),[22] 4,4′-difluoro-8-(4-ethynyl)-phenyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (**Ethynyl-BODIPY**),[23] and 2(3),9(10),16(17),23-(24)-tetrakis(iodo) zinc(II) phthalocyanine (**Iodo-Pc**)[24] were synthesized and purified according to literature procedures.

Equipment

Absorption spectra in the UV-visible region were recorded using a Shimadzu 2101 UV spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm pathlength cuvettes at room temperature. The FT-IR spectrum was recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Positive ion and linear mode MALDI-MS spectra of BODIPY-phthalocyanine pentad dye (**BODIPY-Pc**) were obtained in dihydroxybenzoic acid (as a MALDI matrix) using a Bruker Microflex LT MALDI-TOF mass spectrometer. The ^{1}H-NMR spectrum was recorded on a Varian 500 MHz spectrometer in $CDCl_3$ solution.

The light source was a General Electric quartz line lamp (300 W). A 600 nm glass cutoff filter (Schott) and a water filter were used to filter off ultraviolet and infrared radiation, respectively. An interference filter (Intor, 670 nm with a bandwidth of 40 nm) was additionally placed in the light path before the sample. Light intensities were measured using a POWER MAX5100 (Molectron Detector Incorporated) power meter.

Photophysical parameters

Fluorescence quantum yields. Fluorescence quantum yield (Φ_F) of **BODIPY-Pc** was determined by the comparative method using eqn (1):[25,26]

$$\Phi_F = \Phi_F(\mathrm{Std})\frac{FA_{\mathrm{Std}}n^2}{F_{\mathrm{Std}}An_{\mathrm{Std}}{}^2} \quad (1)$$

where F and F_{Std} are the areas under the fluorescence emission curves of **BODIPY-Pc** and the standard, respectively. A and A_{Std} are the respective absorbances of **BODIPY-Pc** and the standard at the excitation wavelengths, respectively. n^2 and $n_{\mathrm{Std}}{}^2$ are the refractive indices of solvents used for **BODIPY-Pc** and the standard, respectively. Unsubstituted ZnPc (Φ_F = 0.20 in DMSO)[27] was employed as the standard. Both the samples and the standard were excited at the same wavelength. The absorbance of the solutions at the excitation wavelength ranged between 0.04 and 0.05.

Photochemical parameters

Singlet oxygen quantum yield. Singlet oxygen quantum yield (Φ_Δ) of **BODIPY-Pc** was carried out using the experimental set-up described in the literature.[28–30] Typically, a 3 mL portion of **BODIPY-Pc** solution ($C = 1 \times 10^{-5}$ M) containing the singlet oxygen quencher was irradiated in the Q band region with the photo-irradiation set-up described in ref. 28–30. Singlet oxygen quantum yield (Φ_Δ) was determined in air using the relative method in DMSO with unsubstituted ZnPc as a reference. DPBF was used as a chemical quencher for singlet oxygen in DMSO. Eqn (2) was employed for the calculations:

$$\Phi_\Delta = \Phi_\Delta^{\mathrm{Std}}\frac{RI_{\mathrm{abs}}^{\mathrm{Std}}}{R^{\mathrm{Std}}I_{\mathrm{abs}}} \quad (2)$$

where $\Phi_\Delta^{\mathrm{Std}}$ is the singlet oxygen quantum yield for the standard unsubstituted ZnPc ($\Phi_\Delta^{\mathrm{Std}}$ = 0.67 in DMSO).[31] R and R^{Std} are the DPBF photobleaching rates in the presence of **BODIPY-Pc** and the standard, respectively. I_{abs} and $I_{\mathrm{abs}}^{\mathrm{Std}}$ are the rates of light absorption by **BODIPY-Pc** and the standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen,[32] the concentration of the quencher (DPBF) was lowered to $\sim 3 \times 10^{-5}$ M. Solutions of the sensitizer and the standard ($C = 1 \times 10^{-5}$ M) containing DPBF were prepared in the dark and irradiated in the Q band region using the photoirradiation setup. DPBF degradation at 417 nm was monitored. A light intensity of 6.7×10^{15} photons s^{-1} cm^{-2} was used for Φ_Δ determinations.

Photodegradation quantum yield. Photodegradation quantum yield (Φ_d) measurement of **BODIPY-Pc** was carried out using the experimental set-up described in the literature.[28–30] Photodegradation quantum yield was determined using eqn (3):

$$\Phi_d = \frac{(C_0 - C_t)VN_A}{I_{\mathrm{abs}}St} \quad (3)$$

where C_0 and C_t are **BODIPY-Pc** concentrations before and after irradiation respectively, V is the reaction volume, N_A is Avogadro's constant, S is the irradiated cell area and t is the irradiation time. I_{abs} is the overlap integral of the radiation source light intensity and the absorption of **BODIPY-Pc**. A light intensity of 2.24×10^{16} photons s^{-1} cm^{-2} was employed for Φ_d determinations.

Synthesis

4-[4,4′-Difluoro-8-(4-ethynyl)-phenyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene]phthalonitrile (BODIPY-Pht). 4-Iodophthalonitrile (33 mg, 0.13 mmol), **Ethynyl-BODIPY** (46 mg, 0.13 mmol), $PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol) and CuI (4 mg (0.022 mmol) were added to a Schlenk tube equipped with a magnetic stir bar. A solvent system of THF : Et_3N 5 : 2 was well-degassed under argon for 30 min prior to its addition to the reaction mixture. The reaction was quenched with a saturated solution of NH_4Cl after 24 h. The organic layer was then diluted with CH_2Cl_2 and washed with water and saturated

NH_4Cl. The organic layers were dried over anhydrous $MgSO_4$, filtered, and the solvent was removed from the filtrate *in vacuo* to afford the crude product, which was purified by column chromatography (silica gel 4 : 1 hexane : CH_2Cl_2). Yield: 53 mg (86%). UV/Vis ($CHCl_3$) λ_{max}/nm (log ε): 333 (4.44), 504 (4.80). FT-IR [ATR ν_{max}/cm^{-1}]: 3106 (aromatic-CH), 2959–2858 (aliphatic-CH), 2234 (–C≡N–), 2213 (–C≡C–), 1610 (–C═N), 1541 (C═C), 1508, 1468. ^{1}H-NMR ($CDCl_3$): δ, 7.87 (s, 1H, Ar-CH), 7.79 (d, 1H, Ar-CH), 7.75 (d, 1H, Ar-CH), 7.63 (d, 2H, Ar-CH), 7.30 (d, 2H, Ar-CH), 5.87 (s, 2H, CH), 2.48 (s, 6H, CH_3), 1.35 (s, 6H, CH_3). Calc. for $C_{29}H_{21}BF2N_4$: MALDI-TOF-MS *m*/*z*: calc. 474.3; found 474.2 $[M]^+$.

2(3),9(10),16(17),23(24)-Tetrakis-[4,4′-difluoro-8-(4-ethynyl)-phenyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene phthalocyaninato]zinc(II) (BODIPY-Pc). *Method A*: **BODIPY-Pht** (40 mg, 0.084 mmol) and anhydrous zinc(II) acetate (31 mg, 0.168 mmol) were heated at reflux temperature in pentanol (4 mL) for 6 h in the presence of DBU (0.1 mL, 0.07 mmol) under an argon atmosphere. After cooling, the solution was dropped into the hot *n*-hexane. The dark green solid product was precipitated and collected by filtration and washed with *n*-hexane. The green crude product was purified by column chromatography (silica gel CH_2Cl_2 to 50 : 1 CH_2Cl_2 : THF). Yield: 2.6 mg (6.3%).

Method B: **Iodo-Pc** (24 mg, 0.022 mmol), **Ethynyl-BODIPY** (75 mg, 0.22 mmol), $PdCl_2(PPh_3)_2$ (6 mg, 0.0085 mmol) and CuI (2 mg, 0.0105 mmol) were added to a Schlenk tube equipped with a magnetic stir bar. A solvent system of THF : Et_3N 2 : 1 was well-degassed under an argon atmosphere for 30 min prior to its addition to the reaction mixture. The reaction was quenched with a saturated solution of NH_4Cl after 16 h. The organic layer was then diluted with CH_2Cl_2 and washed with water and saturated NH_4Cl. The organic layers were dried over anhydrous $MgSO_4$, filtered, and the solvent was removed from the filtrate *in vacuo* to afford the crude product, which was then purified by column chromatography (silica gel CH_2Cl_2 to 50 : 1 CH_2Cl_2 : THF). Yield: 36 mg (83%). UV/Vis (DMSO) λ_{max}/nm (log ε): 372 (4.84), 502 (5.18), 698 (5.04). FT-IR [ATR ν_{max}/cm^{-1}]: 3063 (aromatic-CH), 2956–2851 (aliphatic-CH), 2209 (–C≡C–), 1610 (–C═N), 1510 (C═C), 1468, 1408. ^{1}H-NMR ($CDCl_3$): δ, ppm 8.34 (m, 4H, Pc-H), 7.99 (m, 16H, BODIPY-H), 7.47 (m, 8H, Pc-H), 6.01 (br, 8H, CH), 2.54 (s, 12H, CH_3), 1.89 (s, 12H, CH_3), 1.50 (s, 12H, CH_3), 1.18 (s, 12H, CH_3). Calc. for $C_{116}H_{84}B_4F_8N_{16}Zn$: C 70.90, H 4.31, N 11.42%; found: C 71.67, H 4.81 N 11.21%. MALDI-TOF-MS *m*/*z*: calc. 1962.67; found 1943.58 $[M - F]^+$ and 1962.35 $[M]^+$.

Results and discussion

Synthesis and characterization

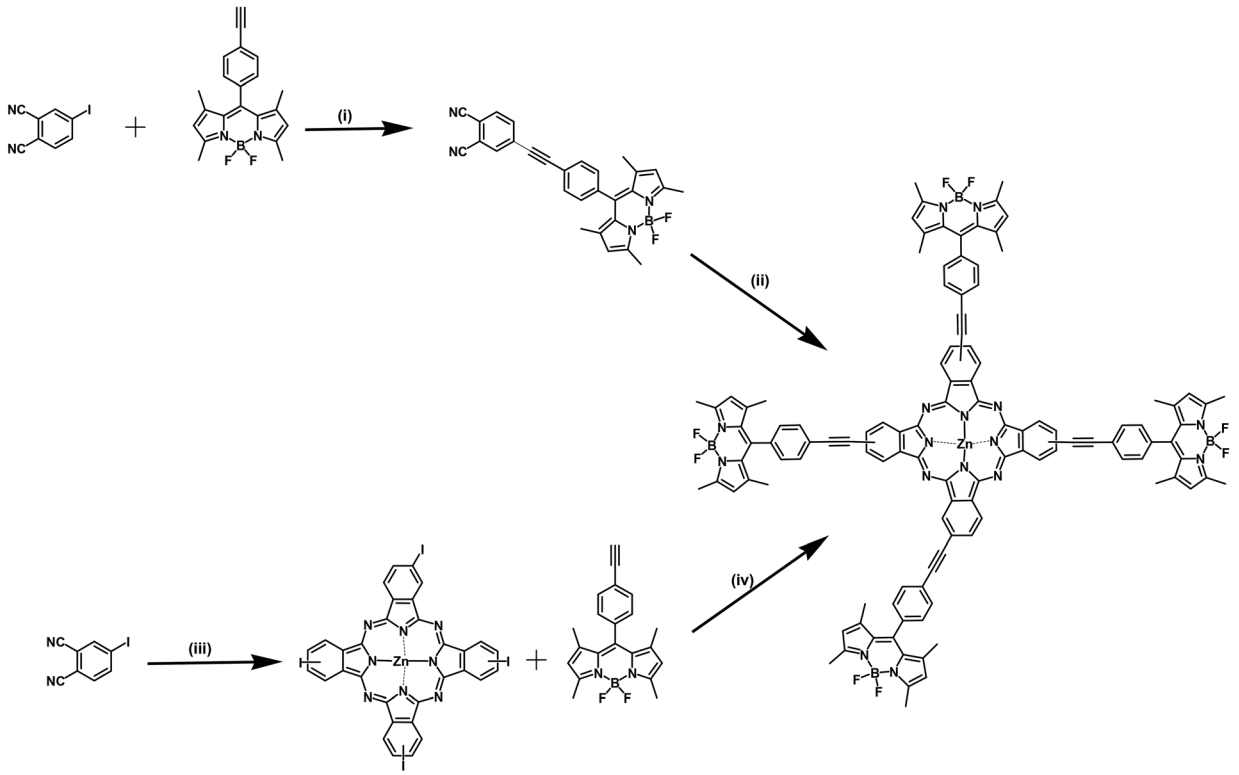
In this study, two different synthesis strategies have been employed for the synthesis of the target BODIPY-zinc(II) phthalocyanine pentad dye (**BODIPY-Pc**). The first strategy is the base catalyzed cyclotetramerization of BODIPY substituted phthalonitrile (**BODIPY-Pht**) which is generally used for the synthesis of phthalocyanine compounds but the target **BODIPY-Pc** was obtained in very low yield (6%) in this synthesis strategy (Scheme 1). It could be due to the decomposition of the BODIPY units under cyclotetramerization conditions such as high temperature. The other strategy is the synthesis of the novel target **BODIPY-Pc** *via* a Pd-catalyzed Sonogashira coupling reaction between 4,4′-difluoro-8-(4-ethynyl)-phenyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (**Ethynyl-BODIPY**) and 2(3),9(10),16(17),23(24)-tetrakis(iodo) zinc(II) phthalocyanine (**Iodo-Pc**) (Scheme 1). The synthesis of the targeted novel **BODIPY-Pc** was achieved through this coupling reaction in high yield (83%). We concluded that this synthesis strategy is a suitable way for substitution of the phthalocyanine derivatives *via* an ethynyl bond. The synthesized tetra-BODIPY substituted Zn(II) phthalocyanine (**BODIPY-Pc**) was obtained as a statistical mixture of four regioisomers (D_{4h}, C_{4h}, C_{2v} and C_s) because the starting compound (**Iodo-Pc**) bears four iodine substituents in various possible positions relative to one another with respect to each other.[33] In general, phthalocyanine compounds are hardly ever soluble in most organic solvents; however, introduction of BODIPY substituents in the phthalocyanine ring increased the solubility and the target **BODIPY-Pc** exhibited excellent solubility in the most common organic solvents (DMSO, acetone, ethyl acetate, DMF, toluene, benzene, chloroform and THF).

The novel **BODIPY-Pc** was fully characterized by general spectroscopic methods (UV-Vis, FT-IR, ^{1}H-NMR and MALDI-TOF mass) and elemental analysis as well. In the FT-IR spectrum of **BODIPY-Pc**, the aromatic and aliphatic CH stretchings were observed at 3063 cm^{-1} and 2956–2851 cm^{-1}, respectively. The characteristic vibrations were observed at ~1510 cm^{-1} for C═C groups, 2209 cm^{-1} for –C≡C– groups and 1610 cm^{-1} for –C═N groups. The ^{1}H NMR spectrum of **BODIPY-Pc** showed complex patterns due to the isomer mixture. This compound was found to be pure by ^{1}H NMR with all the substituents and ring protons observed in their respective regions. The resonances for the phthalocyanine ring protons were observed between 8.34 ppm and 7.47 ppm as multiplets. The aromatic protons for benzene groups on BODIPY units were observed at 7.99 ppm as multiplets. The CH protons on the BODIPY units were observed at 6.01 ppm as a broad peak. The CH_3 protons on the BODIPY units were observed at 2.54 ppm, 1.89 ppm, 1.5 ppm and 1.18 ppm as singlets. The mass spectrum of **BODIPY-Pc** was obtained by the MALDI-TOF-MS technique and the molecular ion peaks of this compound were found at *m*/*z* 1962.35 as $[M]^+$ and 1943.58 as $[M - F]^+$ (Fig. 1).

The elemental analysis results were also consistent with the predicted structure of **BODIPY-Pc** as shown in Scheme 1.

Ground state electronic absorption and fluorescence spectra

Fig. 2 shows the normalized absorption spectra of **Ethynyl-BODIPY**, **Iodo-Pc** and **BODIPY-Pc** in THF. The former two compounds were used as references. The electronic spectrum of the newly synthesized **BODIPY-Pc** shows a panchromatic behaviour (Fig. 2) which appears in the absorption over a broad spectral region and is able to using an efficient light-harvesting system. This spectrum contains three main characteristic



Scheme 1 Synthesis route of **BODIPY-Pc** pentad dye. Reagents and conditions: (i) THF/NEt_3, [$Pd(PPh_3)_2Cl_2$], CuI, rt, 24 h; (ii) pentanol, $Zn(OAc)_2$, reflux, 6 h; (iii) DMAE, $ZnCl_2$, reflux, 18 h (iv) THF/NEt_3, [$Pd(PPh_3)_2Cl_2$], CuI, rt, 16 h.

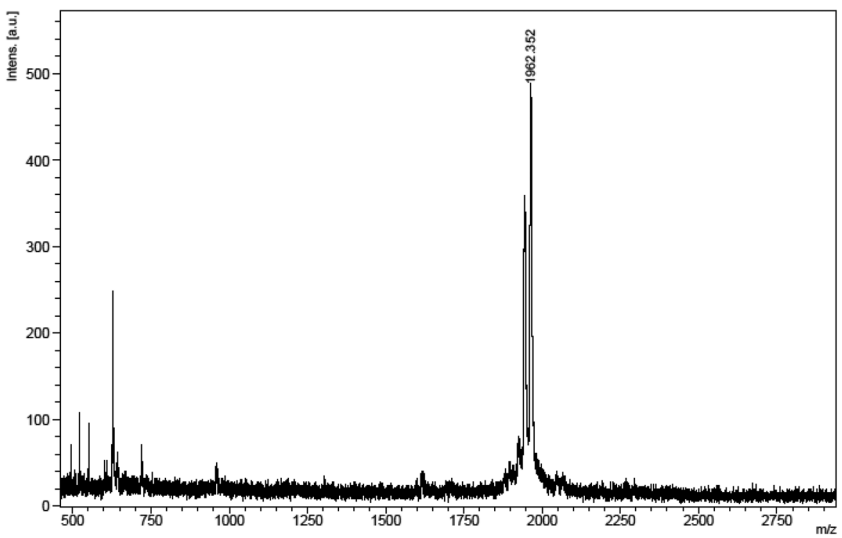


Fig. 1 MALDI-TOF spectrum of **BODIPY-Pc** pentad dye.

bands related to the phthalocyanine core (698 nm, ε = 110 571 and 370 nm, ε = 68 714) and a BODIPY unit (502 nm, ε = 151 386). The observed single (narrow) Q band at 698 nm is typical for non-aggregated metallophthalocyanine complexes.[34] The B-band is broad due to the superimposition of the B_1 and B_2 bands in *ca.* 370 nm regions (Fig. 2). The effect of the BODIPY substitution on the phthalocyanine skeleton is also clearly apparent on inspection of the UV-Vis absorption spectrum of this pentad dye (Fig. 2). For instance, the Q band based phthalocyanine unit is 18 nm red-shifted when substituted with BODIPY groups. This observed red-shifted Q band indicates that two chromophores (BODIPY and Pc) possess significant ground-state electronic interactions.

The aggregation behaviour of **BODIPY-Pc** was investigated in the most common organic solvents (acetone, ethyl acetate, DMF, toluene, benzene, chloroform, THF, and dichloro-

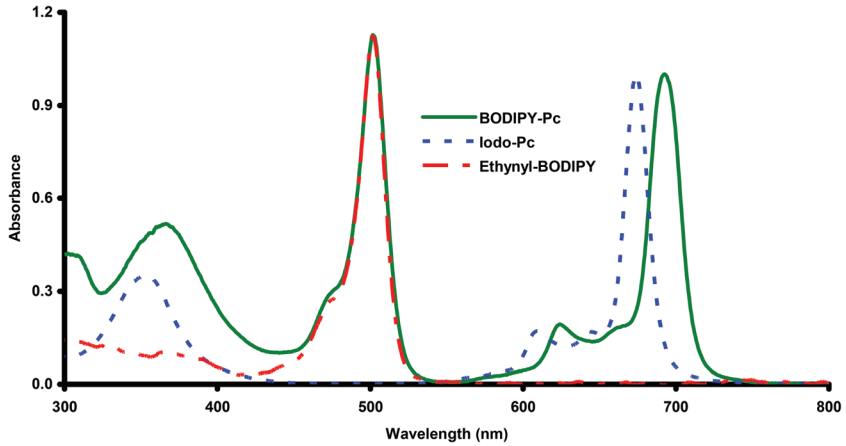


Fig. 2 Normalized UV-Vis absorption spectra of BODIPY reference (**Ethynyl-BODIPY**), zinc phthalocyanine reference (**Iodo-Pc**) and target **BODIPY-Pc** pentad dye in THF.

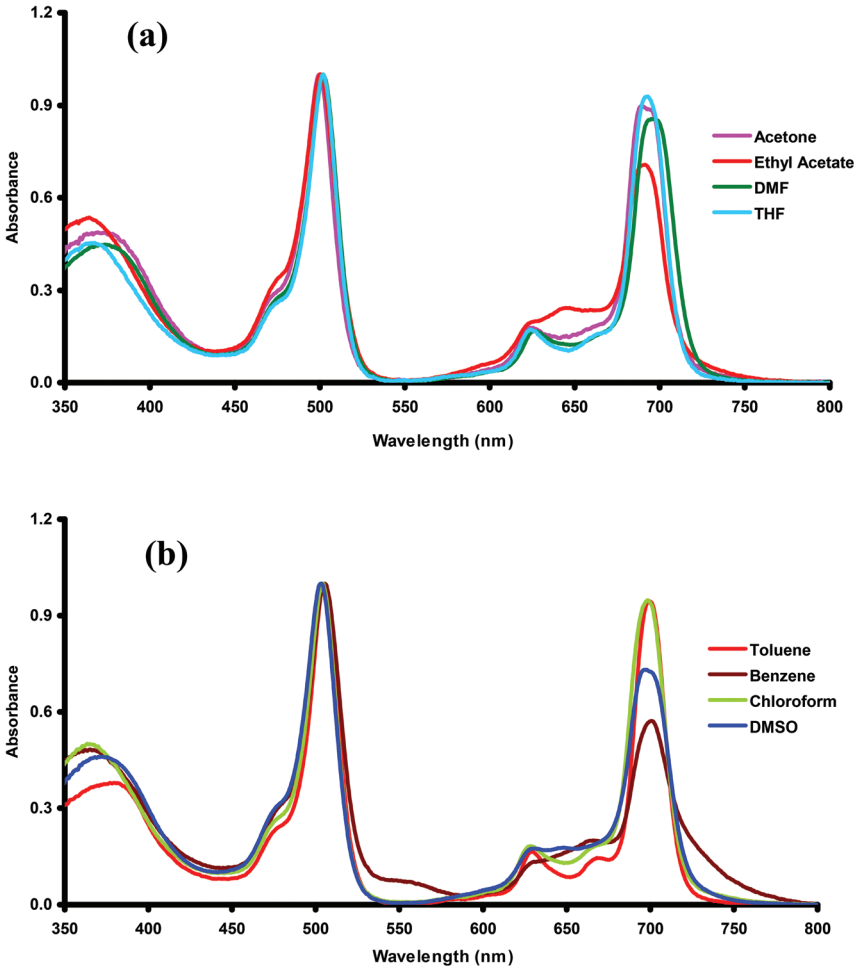


Fig. 3 UV-Vis absorption spectra of **BODIPY-Pc** pentad dye in (a) acetone, ethyl acetate, DMF, THF and (b) toluene, benzene, chloroform, DMSO (normalized according to the BODIPY absorption maxima) *C*: ~6.6 × 10^{-6} M.

methane) (Fig. 3) to determine a suitable solvent for further studies such as singlet oxygen generation and photodegradation studies. DMSO was selected for these studies because this pentad dye did not form any aggregated species in this solvent. On the other hand, DMSO is one of the most suitable solvents for biological studies because this solvent is not toxic

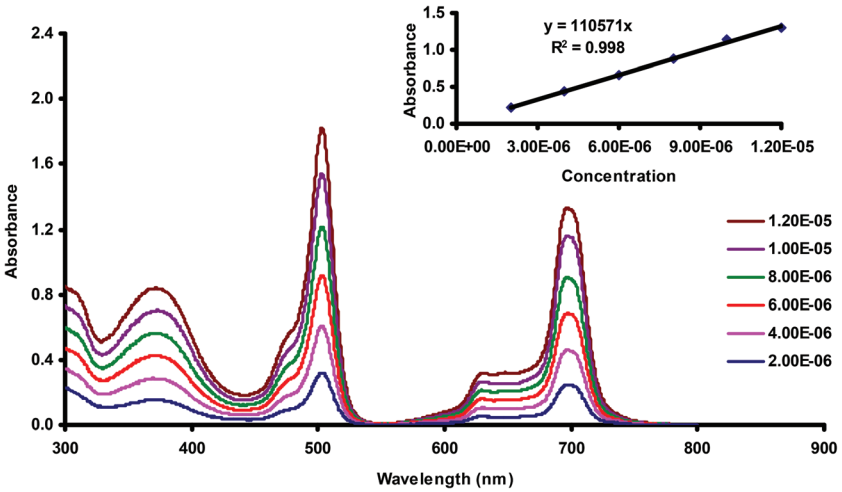


Fig. 4 UV-Vis absorption spectra of **BODIPY-Pc** pentad dye in DMSO at different concentrations. (Inset: plot of absorbance *versus* concentration.)

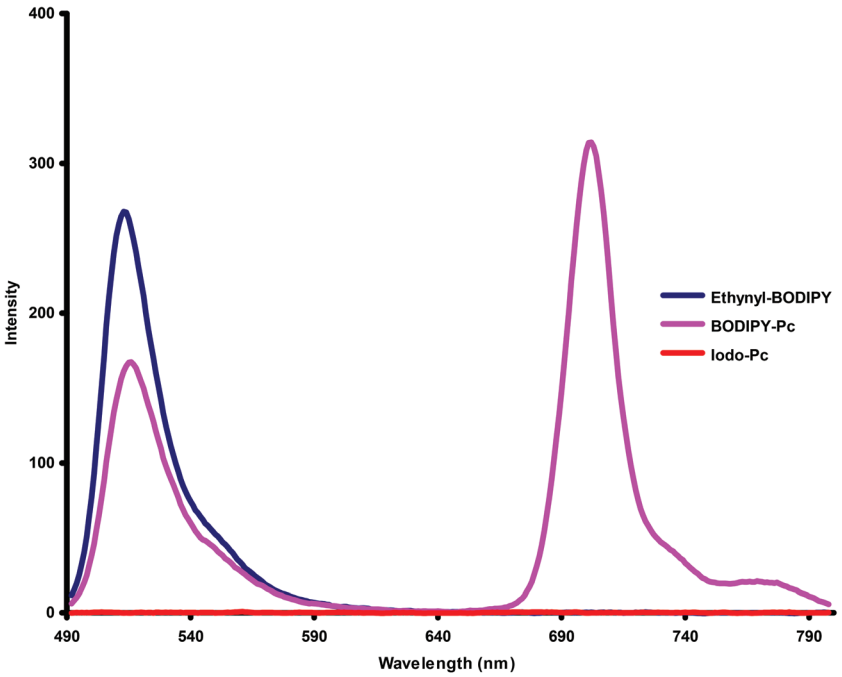


Fig. 5 Emission spectra of BODIPY reference (**Ethynyl-BODIPY**), zinc phthalocyanine reference (**Iodo-Pc**) and target BODIPY substituted phthalocyanine (**BODIPY-Pc**) in THF. Excitation wavelength: 480 nm.

at low concentrations. Moreover, the UV-Vis spectra of this newly synthesized **BODIPY-Pc** were also recorded at different concentrations (ranging from 1.2×10^{-5} to 2×10^{-6} M) in DMSO (Fig. 4). The studied concentration range obeyed the Beer–Lambert law for the studied **BODIPY-Pc**, and 1.0×10^{-5} M was decided as the working concentration.

The fluorescence emission peak maximum was observed at 710 nm for **BODIPY-Pc** when excited at 666 nm. Furthermore, when this pentad dye was excited from the donor part (at 480 nm), two fluorescence emission peaks were observed at 516 and 710 nm. However, **Iodo-Pc** did not show any fluorescence emission peak when excited at 480 nm in THF as expected since there is no absorption at this wavelength (Fig. 5).

Energy transfer study

Ethynyl-BODIPY showed a strong fluorescence emission band at 516 nm when it was excited at 480 nm. However, this band virtually decreased when excited at the same excitation wavelength for **BODIPY-Pc**. Instead, an additional emission band was observed at 710 nm, which is due to the phthalocyanine part of this dye. The **Iodo-Pc** compound did not show any emission band when excited at 480 nm at the same concentration because this compound does not show any absorption

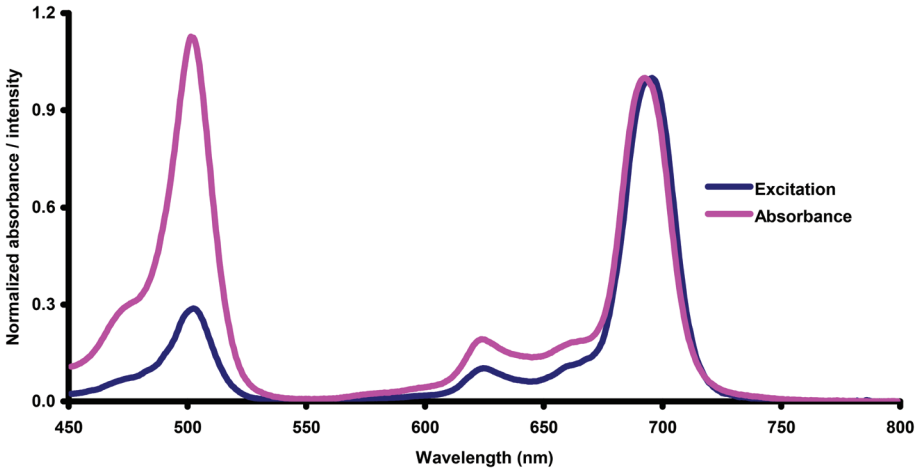


Fig. 6 Normalized absorption and excitation spectra of **BODIPY-Pc** pentad dye in THF. 710 nm was used as the emission wavelength for the excitation spectrum.

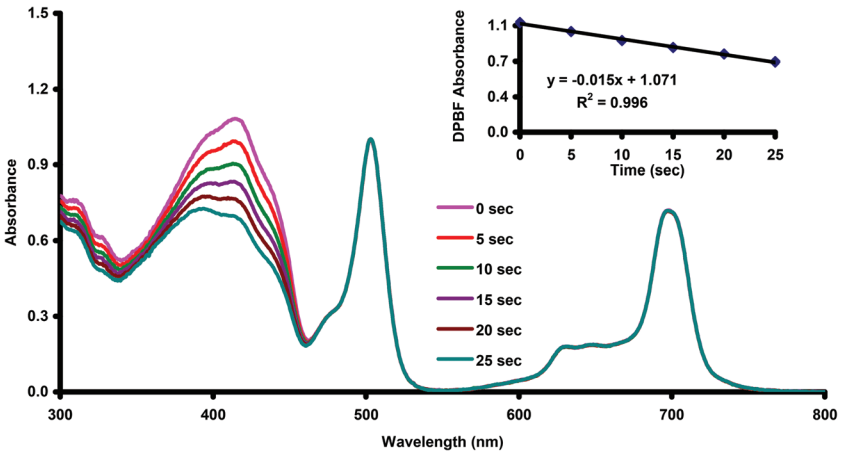


Fig. 7 Absorbance changes during the determination of singlet oxygen quantum yield for **BODIPY-Pc** pentad dye in DMSO at a concentration of 1.0×10^{-5} M. (Inset: plots of DPBF absorbance *versus* time.)

in this region. All these investigations indicate that an efficient singlet–singlet energy transfer process in **BODIPY-Pc** from the excited BODIPY part to the phthalocyanine unit has occurred. This energy transfer process is also confirmed by the excitation spectrum of **BODIPY-Pc** which is similar to the absorption spectrum of this dye in THF (Fig. 6). It is concluded that the Dexter model which occurs through covalent bonds is the mechanism responsible for energy transfer from donor BODIPY units to the acceptor phthalocyanine core.[35]

The fluorescence quantum yield (Φ_F) for **Ethynyl-BODIPY** in THF is 0.55,[22] while that for the BODIPY part of **BODIPY-Pc** is greatly reduced to 0.08. According to the equation $\Phi_{ENT} = 1 - \Phi_{F(pentad)}/\Phi_{F(donor)}$[36,37] where Φ_{ENT} is the energy transfer quantum yield, $\Phi_{F(pentad)}$ and $\Phi_{F(donor)}$ are the fluorescence quantum yields of the pentad dye (**BODIPY-Pc**) excited to the donor part (480 nm) and the donor (**Ethynyl-BODIPY**), respectively. The Φ_{ENT} value was found to be 0.86, showing that this is an efficient energy transfer process for **BODIPY-Pc**.

Singlet oxygen generation study

The singlet oxygen generation potential of a photosensitizer is very important and should be determined for PDT applications because singlet oxygen formation is very noxious and damages the tumor cells. In this study, the singlet oxygen generation was firstly examined for **BODIPY-Pc** systems. The singlet oxygen quantum yield (Φ_Δ) value was determined in DMSO by photochemical methods using diphenylisobenzofuran (DPBF) which is a singlet oxygen quencher (Fig. 7). No changes were observed in the BODIPY and Pc absorption band intensities of the **BODIPY-Pc** during the Φ_Δ determinations (Fig. 7) when using 30 V light irradiation, indicating that this dye was not degraded under this light irradiation during singlet oxygen determinations. The Φ_Δ value of **BODIPY-Pc** was estimated as 0.69 in DMSO which is higher than that of the starting **Iodo-Pc** compound (Φ_Δ = 0.54).[38] The substitution of iodine atoms with BODIPY units on the phthalocyanine framework has led

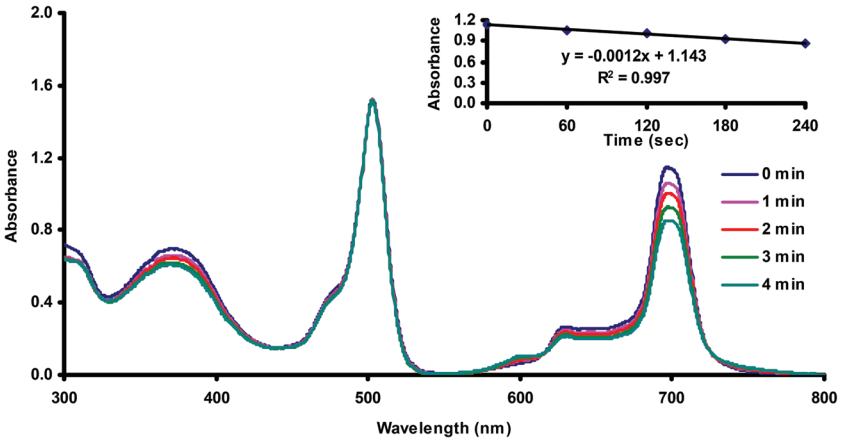


Fig. 8 Absorption changes of **BODIPY-Pc** pentad dye in DMSO during irradiation within 1 min intervals. (Inset: plot of Q band absorbance *versus* time.)

to an increase in the singlet oxygen generation efficiency which might be derived from the energy transfer from BODIPY units to the phthalocyanine moiety.

Photodegradation study

Find out the degradation rate of a photosensitizer is crucial because its excretion degree from the body after PDT activation should be known. The degradation of the molecules under light illumination is quantified as photodegradation quantum yield (Φ_d). The spectral change during photodegradation is given in Fig. 8. As indicated in this figure, it is worth emphasizing that the absorbance changes of BODIPY units (at 502 nm) for **BODIPY-Pc** remain stable, while the Q band absorbance of the Pc unit decreases during light irradiation (100 V) because this compound was irradiated by 670 nm close to the Q band region of phthalocyanine. The Φ_d value of **BODIPY-Pc** was found to be 5.14×10^{-4} which is a moderate value (10^{-6} to 10^{-3}).[39] As a result, this pentad dye showed appropriate stability for biological applications such as PDT.

Conclusions

In this study, a novel symmetrical BODIPY-zinc phthalocyanine pentad dye bearing four BODIPY units connected to the phthalocyanine core *via* an ethynyl linkage at peripheral positions (**BODIPY-Pc**) was synthesized with a high yield for the first time and this pentad dye was fully characterized by various spectroscopic techniques such as ^{1}H-NMR, FT-IR, UV-Vis, fluorescence, MALDI-TOF spectra and elemental analysis as well. The newly synthesized **BODIPY-Pc** showed light absorption over a broad spectral region due to the panchromatic behaviour and this pentad dye exhibited efficient energy transfer from the excited BODIPY units to the phthalocyanine core. The photodynamic therapy potential of this pentad dye system was also revealed by determination of singlet oxygen generation capability and the stability against light irradiation in DMSO solution. The **BODIPY-Pc** produced efficiently singlet oxygen and it showed moderate stability which is very important for photocatalytical applications. As a result, this newly designed **BODIPY-Pc** system is able to using efficient light-harvesting systems and it could also be a good candidate as a photosensitizer in PDT applications for cancer treatment.

Acknowledgements

This study was supported by the Scientific and Technological Research Council of Turkey (TUBITAK) (project no. TBAG-111T066).

References

1 S. B. Brown, E. A. Brown and I. Walker, *Lancet Oncol.*, 2004, **5**, 497.
2 R. Bonnet, *Chem. Soc. Rev.*, 1995, **24**, 19.
3 J. F. Lovell and P. C. Lo, *Theranostics*, 2012, **9**, 815.
4 P. Gregory, *J. Porphyrins Phthalocyanines*, 2000, **4**, 432.
5 K. Daimon, K. Nukada, Y. Sakaguchi and R. Igarashi, *J. Imaging Sci. Technol.*, 1996, **40**, 249.
6 A. Tracz, T. Makowski, S. Masirek, W. Pisula and Y. H. Geerts, *Nanotechnology*, 2007, **18**, 485303.
7 S. A. Priola, A. Raines and W. S. Caughey, *Science*, 2000, **287**, 1503.
8 E. Ben-Hur and W. S. Chan, in *The Porphyrin Handbook*, ed. K. Kadish, K. M. Smith and R. Guilard, Academic Press, Boston, 2003, vol. 19, p. 1.
9 M. Durmuş, Photochemical and Photophysical Characterization, in *Photosensitizers in Medicine, Environment, and Security*, ed. T. Nyokong and V. Ahsen, Springer, New York, 2012, p. 135.
10 S. G. Awuahab and Y. You, *RSC Adv.*, 2012, **2**, 11169.
11 A. Kamkaew, S. H. Lim, H. B. Lee, L. V. Kiew, L. Y. Chung and K. Burgess, *Chem. Soc. Rev.*, 2013, **42**, 77.
12 M. D. Yilmaz, O. A. Bozdemir and E. U. Akkaya, *Org. Lett.*, 2006, **8**, 2871.

13 A. Coskun, E. Deniz and E. U. Akkaya, *Org. Lett.*, 2005, **7**, 5187.
14 O. A. Bozdemir, F. Sozmen, O. Buyukcakir, R. Guliyev, Y. Cakmak and E. U. Akkaya, *Org. Lett.*, 2010, **12**, 1400.
15 A. Harriman, G. Izzet and R. Ziessel, *J. Am. Chem. Soc.*, 2006, **128**, 10868.
16 J. Y. Liu, H. S. Yeung, W. Xu, X. Li and D. K. P. Ng, *Org. Lett.*, 2008, **10**, 5421.
17 J. Y. Liu, E. A. Ermilov, B. Röder and D. K. P. Ng, *Chem. Commun.*, 2009, 1517.
18 E. A. Ermilov, J. Y. Liu, D. K. P. Ng and B. Röder, *Phys. Chem. Chem. Phys.*, 2009, **11**, 6430.
19 J. Y. Liu, Y. Huang, R. Menting, B. Röder, E. A. Ermilov and D. K. P. Ng, *Chem. Commun.*, 2013, **49**, 2998.
20 Y. Rio, W. Seitz, A. Gouloumis, P. Vazquez, J. L. Sessler, D. M. Guldi and T. Torres, *Chem. – Eur. J.*, 2010, **16**, 1929.
21 D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 2nd edn, 1989.
22 X. Yin, Y. Li, Y. Zhu, X. Jing, Y. Li and D. Zhu, *Dalton Trans.*, 2010, **39**, 9929.
23 J. Godoy, G. Vives and J. M. Tour, *Org. Lett.*, 2010, **12**, 1464.
24 E. M. Maya, P. Haisch, P. Vazguez and T. Torres, *Tetrahedron*, 1998, **54**, 4397.
25 S. Fery-Forgues and D. Lavabre, *J. Chem. Ed.*, 1999, **76**, 1260.
26 D. Maree, T. Nyokong, K. Suhling and D. Phillips, *J. Porphyrins Phthalocyanines*, 2002, **6**, 373.
27 A. Ogunsipe, J. Y. Chen and T. Nyokong, *New J. Chem.*, 2004, **28**, 822.
28 J. H. Brannon and D. Madge, *J. Am. Chem. Soc.*, 1980, **102**, 62.
29 A. Ogunsipe and T. Nyokong, *J. Photochem. Photobiol., A: Chem.*, 2005, **173**, 211.
30 I. Seotsanyana-Mokhosi, N. Kuznetsova and T. Nyokong, *J. Photochem. Photobiol., A: Chem.*, 2001, **140**, 215.
31 N. Kuznetsova, N. Gretsova, E. Kalmkova, E. Makarova, S. Dashkevich, V. Negrimovskii, O. Kaliya and E. Luk'yanets, *Russ. J. Gen. Chem.*, 2000, **70**, 133.
32 W. Spiller, H. Kliesch, D. Wöhrle, S. Hackbarth, B. Roder and G. Schnurpfeil, *J. Porphyrins Phthalocyanines*, 1998, **2**, 145.
33 M. Durmuş, S. Yeşilot and V. Ahsen, *New J. Chem.*, 2006, **30**, 675.
34 M. J. Stillman and T. Nyokong, in *Phthalocyanines: Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH Publishers, New York, 1989, vol. 1, ch. 3.
35 B. Albinsson and J. Martensson, *J. Photochem. Photobiol. C: Photochem. Rev.*, 2008, **9**, 138.
36 K. K. Jensen, S. B. van Berlekom, J. Kajanus, J. Mårtensson and B. Albinsson, *J. Phys. Chem. A*, 1997, **101**, 2218.
37 K. Kilsa, J. Kajanus, J. Martensson and B. Albinsson, *J. Phys. Chem. B*, 1999, **103**, 7329.
38 X.-F. Zhang and H.-J. Xu, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 3347.
39 T. Nyokong, *Coord. Chem. Rev.*, 2007, **251**, 1707.