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ORIGINAL ARTICLE

The Synthesis, Characterization, Crystal Structure and Photophysical Properties of a New Meso-BODIPY Substituted Phthalonitrile

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Abstract A new highly fluorescent difluoroboradipyrromethene (BODIPY) dye (**4**) bearing an phthalonitrile group at meso-position of the chromophoric core has been synthesized starting from 4-(4-meso-dipyrromethene-phenoxy)phthalonitrile (**3**) which was prepared by the oxidation of 4-(2-meso-dipyrromethane-phenoxy)phthalonitrile (**2**). The structural, electronic and photophysical properties of the prepared dye molecule were investigated. The final product exhibit noticeable spectroscopic properties which were examined by its absorption and fluorescence spectra. The original compounds prepared in the reaction pathway were characterized by the combination of FT-IR, ^{1}H and ^{13}C NMR, UV–vis and MS spectral data. It has been calculated; molecular structure, vibrational frequencies, ^{1}H and ^{13}C NMR chemical shifts and HOMO and LUMO energies of the title compound by using B3LYP method with 6-311++G(dp) basis set, as well. The final product (**4**) was obtained as single crystal which crystallized in the triclinic space group P-1 with a=9.0490 (8) Å, b=10.5555 (9) Å, c=11.7650 (9) Å, α=77.024 (6)°, β=74.437 (6)°, γ=65.211 (6)° and Z=2. The crystal structure has intermolecular C—H···F weak hydrogen bonds. The singlet oxygen generation ability of the dye (**4**) was also investigated in different solvents to determine of using in photodynamic therapy (PDT).

Keywords Bodipy · Synthesis · Crystal structure · Phthalonitrile · Fluorescence · Electronic spectra · photodynamic therapy

Introduction

The advancement of emissive dyes for applications in organic fluorescent areas is steadily growing in recent years. Boradiazaindacenes (BODIPY dyes, BDPs, difluoroboradipyrromethenes, etc.) are well known fluorescent dyes with many distinctive and desirable properties. They have high molar absorption coefficients which emit relatively sharp fluorescence peaks with high quantum yield and long excited singlet state life time [1]. Among the large variety of known highly fluorescent organic compounds BODIPY derivatives have been recognised as very convenient fluorophores in many applications such as fluorescent labeling of biomolecules [2], energy transfer cassettes [3], photosensitizer in photodynamic therapy [4], fluorescence probes as chemosensors for the selective and efficient detection of chemically and biologically important ionic species [5], fluorescent switches [6] and drug delivery agents [7]. Because of these fluorescence properties, various BODIPY dyes are also commercially available for protein labelling [8].

So far, several reviews were published explaining most of the knowledge about BODIPY dyes [9]. A BODIPY

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chromophore is composed of two units of pyrrole which are connected by a methene bridge in the 2-position and a boron atom which is coordinated by the heteroatoms.

Small modifications in the chromophoric core of these dyes enable tuning of their spectroscopic / photophysical properties in the way of altering of electron releasing / withdrawing groups on the pyrrole core [10], central meso position [11] and the boron substituents [12] of BODIPY framework. This kind of substitutions can have a strong influence on the position of the absorption and emission maxima which range from at about 500 nm to over 700 nm depending on their location on the BODIPY core [13, 14].

In this study, we report the synthesis and characterization of new meso-substituted BODIPY derivative. We have also studied the absorption, fluorescence spectroscopic properties and the singlet oxygen production capacity of the fluorophore which is the fluorescence materials. The crystal structure of the prepared BODPY dye was also investigated.

Experimental

Materials and Measurements

Pyrrole, 4-hydroxybenzaldehyde was purchased from Sigma-Aldrich Company. The deuterated chloroform ($CDCl_3$) for NMR spectroscopy and the following chemicals were obtained from Sigma-Aldrich; TEA, TFA, benzene, hexane, MeOH, THF, DMSO, AcOH, CH_2Cl_2 (DCM), Chloroform ($CHCl_3$), 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), BF_3-OEt_2 and $FeCl_3.6H_2O$. All other reagents and solvents were reagent grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [15] and the solvents stored over molecular sieves (4A°). K_2CO_3 were dried over 120 °C and used as anhydrous. 4-nitrophthalonitrile was prepared according to literature procedure [16]. Oxygen free inert atmosphere was supplied by argon through dual-bank vacuum-gas manifold system. Thin-Layer chromatography (TLC) was performed using silica gel 60 HF_{254} as an adsorbent. Column chromatography was performed with silica gel (Merck grade 60).

Melting points (m.p.) were determined using a Barnstad-Electrotermel 9200 apparatus and are uncorrected. Electronic spectra were recorded on a Shimadzu's UV-2700 with quartz cell of 1 cm. Infrared spectra were recorded on a Perkin Elmer Spectrum two FT-IR spectrophotometer equipped with Perkin Elmer UATR-TWO diamond ATR and corrected by applying the atr-correction function of Perkin Elmer Spectrum software. ^1H and ^{13}C NMR spectra were recorded a Varian Mercury Plus 300 MHz spectrometer. Fluorescence spectra were measured using a Varian Eclipse spectrofluorometer using 1 cm path length cuvettes at room temperature. Photo-irradiations for singlet oxygen determination were measured using a General Electric quartz line lamp (300 W). A 600 nm glass cut off filter (Schott) and a water filter were used to filter off ultraviolet and infrared radiations respectively. An interference filter (Intor, 700 nm with a bandwidth of 40 nm) was additionally placed in the light path before the sample. Light intensities were measured with a POWER MAX5100 (Mol electron detector incorporated) power meter. Mass spectra were recorded on a AB SCIEX 4000 QTRAP LC-MS/MS spectrometer and Waters SYNAPT MS system HRMS (High Resolution Mass Spectrometer) in electrospray positive ion mode. The elemental analyses were performed on a Costech ECS 4010 instrument.

Computational Procedure

The molecular structure of BODIPY in the ground state (in vacuo) is computed by performing the density functional theory (DFT) by a hydrid functional B3LYP functional (Becke's three parameter hybrid functional using the LYP correlation functional) methods [17, 18] at 6-311++G(d,p) level. The optimized geometrical structure, IR spectra, ^1H and ^{13}C NMR chemical shifts and HOMO and LUMO energies of BODIPY in this study are carried out by using Gauss-View molecular visualization program [19] and Gaussian 09 W program package [20]. Additionally, harmonic vibrational frequencies for the title compound are calculated with these methods and then scaled by 0.9615 [21] and these results were compared with the experimental data.

Synthesis

*4-(4-formylphenoxy) Phthalonitrile (**1**)*

4-nitrophthalonitrile (1.00 g, 5.78 mmol) and 4-hydroxybenzaldehyde (0.71 g, 5.78 mmol) were dissolved in N,N-dimethylformamide (15 mL) and degassed with argon in a dual-bank vacuum-gas manifold system. After stirring for 15 min, finely ground anhydrous potassium carbonate (2 g, 14.45 mmol) was added portion-wise within 2 h period with the efficient stirring. The progress of the reaction was monitored by TLC using DCM / hexane (3/1) solvent system. The stirring of the suspension was maintained at room temperature for further 24 h. The resulting mixture was poured into an iced-water/acetone mixture (5/1: v/v). The occured precipitate was collected by filtration, washed several times with ethanol and dried in vacuo. The desired pure compound (**1**) was obtained as a yellowish powder in sufficient purity. Yield 1.30 g, 90 %. m.p. 154 °C. FT-IR (PIKE MIRacle^{TM} ATR) ν max/ cm^{-1}: 3105-3041(Ar, C-H), 2805–2764 (OC-H), 2237 (C≡N), 1691 (C=O), 1587–1506 (Ar, C=C), 1489–1309 (C-C), 1255 (Ar-O-Ar), 1209, 1155, 1111, 1087, 950, 858, 839, 821. ^1H-NMR ($CDCl_3$) δ (ppm) : 10.03 (s, 1H, OCH)), 8.01 (d, 2H,

ArH), 7.81 (d, 1H, ArH), 7.41–7.34(m, 2H, ArH), 7.23 (d, 2H, ArH). ^{13}C-NMR ($CDCl_3$) δ (ppm): 190.7, 160.3, 159.1, 135.9, 134.1, 132.6, 123.0, 122.9, 120.59, 118.2, 115.3, 114.9, 110.6.

*4-(4-meso-dipyrromethane-phenoxy)phthalonitrile (**2**)*

4-(4-formylphenoxy)phthalonitrile (**1**) (1.00 g, 4.03 mmol) was dissolved in freshly distilled pyrrole (7 mL, 0.10 mol). The mixture was degassed by bubbling with Ar for 15 min. TFA (30.8 μL, 0.40 mmol, 0.1 equiv based on the benzaldehyde) was added to the solution and the mixture was stirred under Ar for 25 min. at room temperature until no starting aldehyde detected by TLC (THF/Hexan-1/3). The mixture was diluted with dichloromethane (50 mL) and than washed with 0.1 M NaOH solution (50 mL) and sufficient amount of water, respecively. The organic phase was dried with Na_2SO_4, filtered and the solvent was evaporated under reduced pressure. Column chromatography (on silica gel, THF/ hexane/ TEA-25/75/1) was applied to yield 0.90 g (61 %) of pure dipyrromethane **2**, m.p. 93 °C. FT-IR (PIKE MIRacle^{TM} ATR) ν max/cm^{-1}: 3381 (N-H), 3101–3039 (Ar, C-H), 2961–2855 (Alip. C-H), 2231 (C≡N), 1685 (C=N), 1607–1500 (Ar, C=C), 1484–1421 (C-C), 1248 (Ar-O-Ar), 1088, 717. ^{1}H-NMR ($CDCl_3$) δ (ppm): 8.03 (br, 2H, NH), 7.71 (d, 1H, ArH), 7.32–7.23 (m, 4H, ArH), 7.02 (d, 2H, ArH), 6.74-6.72 (m, 2H, PyrH), 6.19-6.16 (m, 2H, PyrH), 5.92-5.89 (m, 2H, PyrH), 5.51 (s, 1H, AlipH). ^{13}C-NMR (CDCl3) δ (ppm): 161.9, 152.5, 140.8, 135.7, 132.2, 130.8, 121.7, 121.7, 120.9, 117.9, 117.8, 115.7, 115.2, 109.0, 108.8, 107.7, 43.6.

*4-(4-meso-dipyrromethene-phenoxy)phthalonitrile (**3**)*

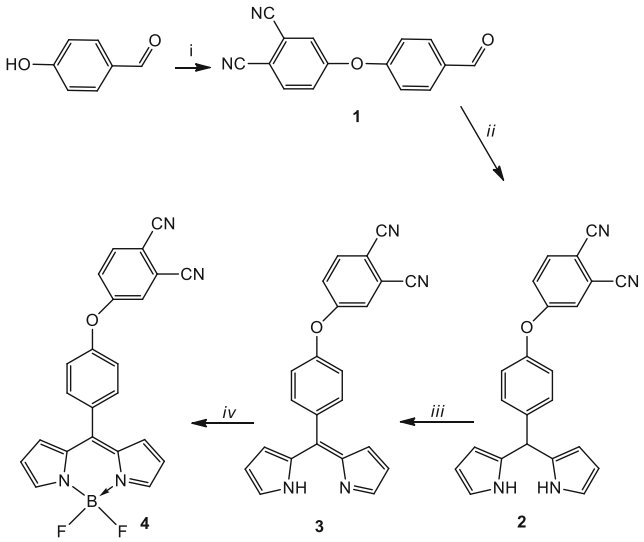
4-(4-meso-dipyrromethane-phenoxy) phthalonitrile **2** (0.75 g, 2.05 mmol) was dissolved in benzene (10 mL). A solution of DDQ (0.58 mg, 2.5 mmol) dissolved in benzene (10 mL) was added and the mixture stirred for 1 h at room temperature until no starting molecule was detected by TLC (THF/Hexan-1/3). The black precipitate formed during the reaction was filtered-off, washed with benzene and the filtrate was purified by column chromatography (silica gel, THF/hexane/TEA-25/75/1) to give **3** as orange solid (0.55 g, 72 %), m.p. 180 °C. FT-IR (PIKE MIRacle^{TM} ATR) ν max/cm^{-1}: 3286 (N-H), 3106–3035 (Ar, C-H), 2232 (C≡N), 1679 (C=N), 1591–1500 (Ar, C=C), 1485–1354 (C-C), 1247 (Ar-O-Ar), 1209, 726. ^{1}H-NMR ($CDCl_3$) δ (ppm) : 8.38 (d,1H, ArH), 8.30 (s, 1H, NH), 7.81–7.59 (m,3H, ArH), 7.41 (d, 1H, ArH), 7.37–7.15 (m, 3H, PyrH), 6.98 (s, 1H, PyrH), 6.62–6.43 (m, 2H, PyrH). ^{13}C-NMR ($CDCl_3$) δ (ppm): 163.5, 162.0, 156.2, 145.4, 135.4, 134.4, 133.36, 131.2, 128.1, 123.4, 123.4, 122.5, 121.8, 119.82, 118.3, 117.4, 115.8, 115.5, 112.1, 108.9, 107.9.

*4-(4-meso-BOBIPY-phenoxy)phthalonitrile (**4**)*

A solution of 4-(4-meso-dipyrromethene-phenoxy)phthalonitrile **3** (0.40 g, 1.02 mmol) in toluene (15 mL) was purged with Ar. To the solution, 10 equiv of TEA (1.45 mL, 10.2 mmol) was added and heated to 70 °C for 0.5 h. Then, 15 equiv of BF_3-OEt_2 (2 mL, 15.3 mmol) was added and the reaction mixture was heated to reflux temperature for 3.5 h. After completion of the reaction the reaction mixture was cooled to room temperature, washed with 0.1 M NaOH solution (3×25 mL) and the layers were separated off. The organic layer was dried with anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel eluting with THF/ Hexan-2/3 to obtain pure BODIPY derivative **4** (0.35 g, 74 %). m.p., 205 °C. FT-IR (PIKE MIRacle^{TM} ATR) ν max/cm^{-1}: 3115–3038 (Ar, C-H), 2232 (C≡N), 1685 (C=N), 1590–1537 (Ar, C=C), 1481–1386 (C-C and C-H def.), 1250 (Ar-O-Ar), 1110 (N-B), 1077 (B-F), 977, 777. ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.97 (s, 2H, ArH), 7.83 (d, 1H, ArH), 7.69 (d, 2H, ArH), 7.43–7.37 (m, 2H, ArH), 7.27–7.25 (m, 2H, PyrH), 6.97 (d, 2H, PyrH), 6.60 (d, 2H, PyrH). ^{13}C-NMR ($CDCl_3$) δ (ppm): 160.7, 159.2, 145.6, 144.9, 135.9, 135.02, 133.1, 131.7, 122.5, 122.6 120.4, 119.2, 119.1, 118.2, 115.4, 115.01, 110.2.

Table 1 Crystal data and structure refinement for the title compound

Chemical formula	$C_{23}H_{13}BF_2N_4O$
Color/shape	Firebrick/prism
Crystal system	Triclinic
Space group	$P-1$
Temperature	296 K
Unit cell dimensions	a=9.0490(8) Å
	b=10.5555(9) Å
	c=11.7650(9) Å
	α=77.024(6)°
	β=74.473(6)°
	γ=65.211(6)°
Volume	974.70(15) Å^3
Z	2
Density (calculated)	1.398 Mg m^{-3}
Wavelength	0.71073 Å
Reflections collected	10,815
Independent reflections	4041
Absorption correction	Integration X-RED
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.17, −0.25
S	1.01
R_{int}	0.046
θ range for data collection (°)	2.1≤θ≤26.5
Absorbtion coefficient (μ)	0.10 mm^{-1}
Final R indices [I>2r(I)]	R_1=0.050, wR_2=0.121
h/k/l	−10, 11/ −13, 13/ −14, 14



Scheme 1 *Reagent and conditions*: (*i*). 4-nitrophthalonitrile, DMF, K_2CO_3, (90 %); (*ii*). freshly distilled pyrrole, TFA, rt, 20 min., (61 %); (*iii*). benzene, DDQ, rt, 1 h, (72 %); (*iv*). Toluene, TEA, BF_3-OEt_2, rt→ 70 °C→130 °C, 2,5 h, (74 %)

Electronic Spectra Measurements

The absorption spectra of compound **4** were recorded in different solvents altering from non-polar to polar. The stock solutions were prepared in DCM, $CHCl_3$, THF, EtOH, DMF and DMSO at around 1×10^{-4} M concentration depending of the weights. The prepared solutions were stored in dark, and diluted to 1×10^{-7} M concentration for the measurements. The freshly diluted solutions were used for absorption, excitation and emission measurements. The molar absorptivity coefficients presented in Table 6 were calculated from the related recorded absorption maxima and given as Log ε. Correspondingly, the excitation and emission wavelengths were listed in the table, as well. The Stokes shifts were calculated as the differences from the recorded absorption and emission bands. The concerned results were discussed in the results part.

X-ray Crystal Structure Determination

A firebrick single crystal sized $(0.17\times0.36\times0.49)$ mm^3 was chosen and mounted on a glass fiber then carefully mounted on goniometer of a STOE IPDS II diffractometer and used for the structure determination for the crystallographic study. All difraction measurements were collected on an Stoe IPDS II diffractometer with graphite monochromatized Mo Kα radiation (λ=0.71073 Å) using the ω scan method. A total of 11, 130 independent reflections were collected, among which 2599 reflections were considered as observed [$I>2\sigma(I)$] and used for the structure refinement. Usual Integration X-RED 32 absorption corrections were applied. All diffraction measurements were performed at 296 K using monochromated Mo Kα radiation.

Data Collection

Single-crystal X-ray data were collected on a Stoe IPDS II [22] single crystal diffractometer using monochromated MoKα radiation at 296 K. For the title compound (**4**) data colleciton: X-AREA; cell refinement: X-AREA [22]; data reduction: X-RED32 [18, 23]. The structure was solved by direct methods followed by fourier synthesis using SHELXS-

Table 2 Experimental and theoretical vibrational bands of the BODIPY compound

Assigments	FT-IR	B3lyp		Assigments	FT-IR	B3lyp	
	Freq	Freq	Intensity	Freq	Freq	Freq	Intensity
υS(CH)	3115–3038	3151	2.601	υ(C=C)	1590–1537	1582	2.866
υS(CH)		3150	4.554	υ(C=C)		1567	272.6
υAS(CH)		3138	1.844	υ(C=C)		1552	121.3
υAS(CH)		3137	3.608	υ(C=C)		1536	173.9
υAS(CH)		3126	3.554	υ(C=C)		1529	379.2
υAS(CH)		3125	4.577	υ(C=C)+β(CH)	1481–1386	1485	111.6
υS(CH)		3099	1.270	υ(C=C)+β(CH)		1471	154.9
υAS(CH)		3097	0.606	υ(C=C)+β(CH)		1457	4.183
υS(CH)		3092	2.390	υ(C=C)+β(CH)		1391	24.95
υAS(CH)		3084	3.306	υ(C=C)+β(CH)		1376	229.2
υAS(CH)		3081	3.089	υ(CO)	1250	1218	406.5
υAS(CH)		3072	3.857	υ(NB)	1110	1107	350.8
υAS(CH)		3068	8.813	υ(BF)	1077	1034	192.7
υ(C≡N)	2232	2188	6.705	υ(BF)	977	933	165.1
υ(C≡N)		2184	31.21	υ(BF)	777	764	18.78
υ(C=N)	1685	1456	55.01				

2014 [19, 24] and refined on F2 by full-matrix least-squares methods using SHELXL-2014 [24] and molecular figures: ORTEP-3 for Windows version 2014.1 implemented in WinGX 2014 [25–27] program suit. The general-purpose crystallographic tool PLATON [28] were used for the structure analysis and used to prepare material for publication. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated geometrically and allowed to ride on their parent carbon atoms. All H atoms attached to C atoms were fixed geometrically and treated as riding with C—H= 0.93 Å and Uiso(H)=1.2 Ueq(C). Details of the data collection conditions and parameters of refinement process are given in Table 1.

Result and Discussion

Synthesis

The synthetic route used to obtain BODIPY derivative (**4**) is presented in Scheme 1.

The meso-substituted BODIPY dye (**4**) was obtained as purple crystaline solid from a serial reaction described as follows. The reaction of 4-hydroxybenzaldehyde and 4-nitrophthalonitrile using K_2CO_3 as catalyst in DMF with stirring at room temperature for 24 h gave 4-(4-formylphenoxy) phthalonitrile (**1**). The dipyrromethane derivative **2** was prepared in 61 % yield by the condensation of the benzaldehyde derivative **1** with 25 equivalent of freshly distilled pyrrole in the presence of catalytic amount of trifluoroacetic acid (TFA) at room temperature as described by Lindsey for meso-substituted dipyrromethane [29]. The subsequent oxidation was applied in benzene with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) at room temperature to yield (72 %) dipyrromethene derivative **3** as orange solid. The complexation of compound **3** with triethylamine and boron trifluoride etherate in refluxing toluene gave the chelated product **4** as purple solid after isolating by the column chromatography (silica gel, eluent: THF/Hexan-2/3) in 74 % yield.

Characterization of the products was carried out by a combination of methods including FT-IR, ^{1}H NMR, ^{13}C-NMR, melting point, UV–vis and Mass spectroscopy. All the spectral data are in accordance with the proposed structures.

When compared the FT-IR spectra of p-hydroxybenzaldehyde and **1**, the disappearance of –OH

Table 3 Theoretical and experimental ^{13}C and ^{1}H isotropic chemical shifts with respect to TMS all values in ppm

Atoms	Experimental	B3LYP	Atoms	Experimental	B3LYP
1H			13C		
H37	7.97	7.15	C1	160.7	162.07
H30		7.14	C13	159.2	157.3
H8	7.83	6.77	C35	145.6	147.6
H16	7.69	6.71	C29		146.9
H19	7.43–7.37	6.57	C25	144.9	142.3
H9		6.53	C10	135.9	135.5
H17		6.46	C38	135.0	135.2
H18	7.27–7.25	6.07	C39		135.2
H34		5.72	C5	133.1	135.1
H7		5.71	C11		132.8
H28	6.97	5.64	C15	131.7	131.7
H36	6.60	5.58	C26	122.5	129.9
H30		5.52	C32		129.8
			C12	122.6	121.4
			C6	120.4	121.0
			C3	119.2	119.7
			C14	119.1	119.2
			C33	118.2	118.6
			C27		118.0
			C2	115.4	116.9
			C22	115.01	116.8
			C4	110.2	112.9

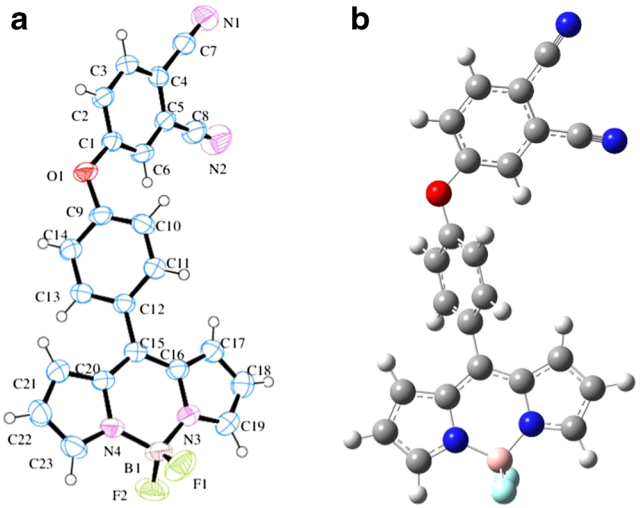


Fig. 1 **a** Theoretical calculated structure of title compound, **b** Ortep diagram of the title compound, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level

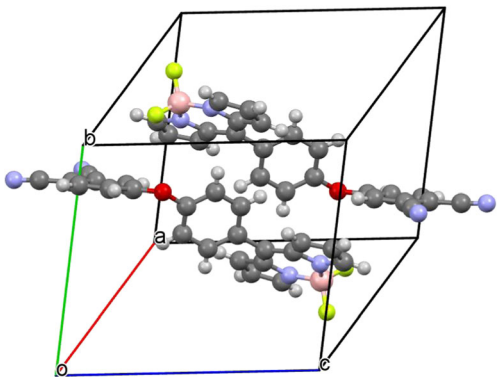


Fig. 2 Crystal packing diagram for the title molecule

Table 4 Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C23—H23···F1^{i}	0.93	2.45	3.348 (3)	163
C3—H3···F2^{ii}	0.93	2.35	3.189 (2)	150

Symmetry codes: (i) $-x+1, -y+2, -z$; (ii) $x+1, y-1, z+1$

vibration at 3158 cm^{-1} and the appearance of new absorption bands at 2237 and 1255 cm^{-1} belonging to the -C≡N and Ar-O-Ar respectively, clearly indicate the formation of **1**.

In the FT-IR spectrum of **2**, the C=O vibration at 1691 cm-1 and the aldehyde C-H vibrations at 2805–2764 cm^{-1} of compound **1** disappeared. However the existence of NH groups appeared at 3381 cm^{-1} was clearly indicated the formation of the compound **2**. The similar characteristics were observed in the FT-IR spectrum of **3** except the peak attributed to N-H stretching shifted to 3286 cm^{-1}. The formation of Boron-dipyrrin complex (**4**) with the complexation of free donor sites was confirmed by the lack of N-H vibration and the precence of B-F stretching band at 1077 cm^{-1}. The B-F band was calculated at: 1034 cm^{-1} using B3LYP method with 6-311++G(dp) basis set. In the rest of the spectrum, the stretching vibrations at 2232 cm^{-1} for -C≡N, between 1579 and 1537 cm^{-1} for aromatic -C=C-, and 1250 cm^{-1} for Ar-O-Ar were very similar to that of **3**. The other vibration bands of BODIPY given in Table 2.

The ^{1}H-NMR and ^{13}C-NMR data gave satisfactory information about the proposed structures. When compared the ^{1}H-NMR spectra of p-hydroxybenzaldehyde and **1,** the disappearances of OH proton signal of p-hydroxybenzaldehyde and the appearance of new peaks in aromatic region were the evidence of the formation of phthalonitrile derivative **1** has occurred. The ^{1}H-NMR spectrum of **2** was very obvious in the view of conversion of aldehyde group of compound **1** to the dipyrromethane, which was relevant to the disappearance of aldehyde proton at 10.03 ppm and the appearance of NH protons of pyrrole groups at 8.03 ppm. Similarly, in ^{1}H-NMR spectrum of **3,** the appearance of NH protons of pyrrole groups at 8.30 ppm was attributed to conversion of dipyrromethane to dipyrromethene. On the other hand, the disappearance of this NH proton at the ^{1}H-NMR spectrum of **4** showed that the chelation was occurred, as well. Also in this study, the ^{1}H and ^{13}C NMR spectra were calculated using B3LYP method with 6-311++G(dp) basis set, given in Table 3.

In the ^{13}C-NMR spectrum of **1,** the presence of the signals at 115.3 and 114.9 ppm attributed to the nitrile carbon atoms is the obvious difference from p-hydroxybenzaldehyde. However, the ^{13}C NMR data accord with the expected structures of **2**, **3** and the Boron-dipyrrin complex **4** exhibit symmetric carbon signals in their spectra.

Description of the Crystal Structure

Theoretical calculated structure of the title compound, meso-BOBIPY substituted phthalonitrile (**4**) is presented at Fig. 1b. The calculated molecular structure was compared with molecular shape obtained from the collected X-ray data and presented as the ortep diagram in Fig. 1a. Both molecules were matched for bond angles and bond distances.

Table 5 Some experimental and theoretical bond distances and angles (Å, deg) of the BODIPY molecule

	Exp.	B3LYP		Exp.	B3LYP
C1—O1	1.368 (2)	1.365	C12—C15	1.474 (3)	1.485
C4—C7	1.437 (3)	1.427	B1—F2	1.368 (3)	1.411
C7—N1	1.136 (3)	1.155	B1—F1	1.391 (3)	1.433
C8—N2	1.137 (3)	1.154	B1—N4	1.533 (3)	1.603
C9—O1	1.388 (2)	1.392	B1—N3	1.539 (3)	1.604
O1—C1—C2	115.29 (17)	115.97	F2—B1—N4	110.7 (2)	111.70
O1—C1—C6	123.41 (18)	123.72	F1—B1—N4	109.58 (19)	107.92
N1—C7—C4	177.6 (3)	178.4	F2—B1—N3	110.7 (2)	107.96
N2—C8—C5	178.6 (3)	178.05	F1—B1—N3	109.8 (2)	111.72
C14—C9—O1	115.81 (19)	120.19	N4—B1—N3	106.54 (16)	106.97
C10—C9—O1	122.73 (19)	118.45	C1—O1—C9	121.28 (15)	120.54
F2—B1—F1	109.46 (19)	110.36	N4—B1—N3—C19	−169.2 (2)	−148.09
O1—C1—C2—C3	−178.72 (18)	−178.97	N4—B1—N3—C16	7.6 (3)	18.65
O1—C9—C10—C11	172.98 (19)	176.41	F1—B1—N4—C23	−62.6 (3)	−25.54
C20—C15—C16—C17	172.3 (2)	161.18	N3—B1—N4—C23	178.7 (2)	148.13
C12—C15—C16—C17	−5.5 (3)	−10.42	F2—B1—N4—C20	−130.6 (2)	−159.96
F2—B1—N3—C19	−48.8 (3)	−25.54	F1—B1—N4—C20	108.6 (2)	78.50
F1—B1—N3—C19	72.2 (3)	95.9	N3—B1—N4—C20	−10.2 (3)	−18.48

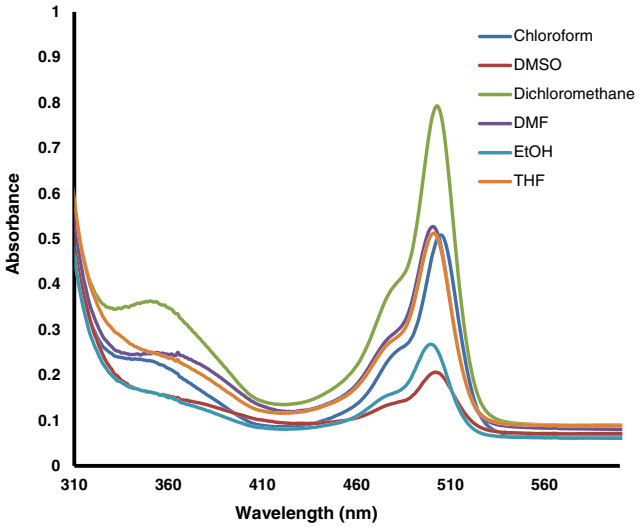


Fig. 3 UV–vis spectra of compound **4** in different solvents. Concentration: 1×10^{-7} M

The molecular structure, an ORTEP-III [27] and the theoretical geometry views of which are shown Fig. 1, crystallizes in the Triclinic space group P −1 with two molecules in the unit cell. The crystal structure analysis shows that the title molecule contain a 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY), a phthalonitrile and a dioxolane segments in the asymmetric unit. Figure 1a shows the molecular structure of the title compound with the atomic numbering scheme. The title compound (**4**) contains two phenyl rings (ring A: C1/C2/C3/C4/C5/C6 and ring B: C9/C10/C11/C12/C13/C14) with two acetonitrile group (C7/N1 and C8/N2) substituted at C4, C5 in ring A, and one BODIPY group C15/C16/C17/18/C19/N3/B1/F1/F2/N4/C20/C21/C22/C23,

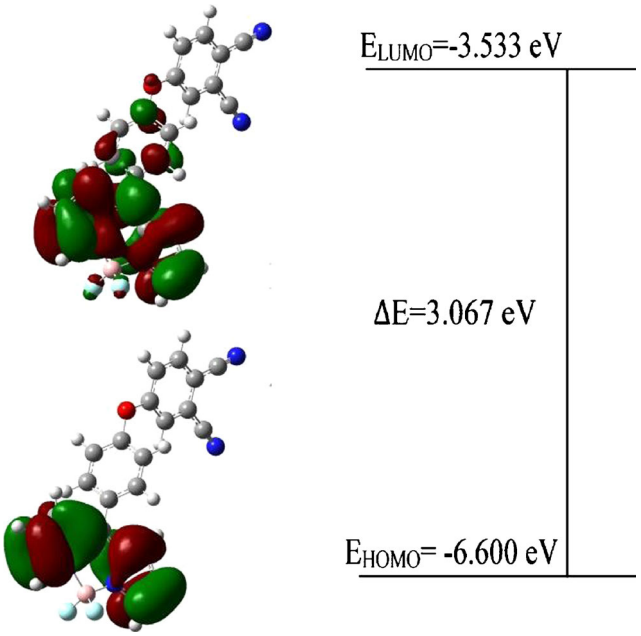


Fig. 4 The HOMO and LUMO orbitals of the BODIPY molecule

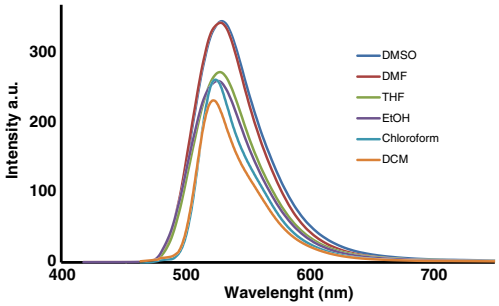


Fig. 5 Emission spectra of compound **4** in different solvents. Concentration: 1×10^{-5} M

respectively. BODIPY group substituted at C15 phenyl ring with phthalonitrile group at O1, respectively. Phenyl rings are essentially planar but BODIPY group is non planar. All rings are not coplanar. The maximum deviation of the A ring and the B ring from planarity are 0.167 Å for atom C4 and 0.0067 Å for atom C12, respectively. The plane of the phenolate ring makes dihedral angles of 67.365 (0.062) with the planes of rings A.

In the title compound (**4**), while the B—F bond distances are 1.391 (3) Å for B1—F1 and 1.368 (3) Å for B1—F2 and this bond calculated at: 1.433 and 1.411 Å, using B3LYP method with 6-311++G(dp) basis set, respectively. The B—N bond distances are found at: 1.539 (3) Å for B1—N3 and 1.533 (3) Å for B1—N4, this bond were calculated at: 1.604 and 1.603 Å, respectively. The F1—B1—N3, F1—B1—N4 and F1—B1—F2 bond angles are found at: 110.7 (2)°, 109.58 (19)° and 109.46 (19)°, respectively. These bond angles are calculated at: 111.72°, 107.92° and 110.36° using B3LYP method with 6-311++G(dp) basis set, respectively. These bond distances and bond angles are consistent with the literature [30, 31, 36]. For the aromatic rings, the C—C bond distances range from 1.375 (3) Å to 1.399 (3) Å and the aromatic rings belong to molecule are essentially planar (r.m.s. deviations are 0.0122 Å for ring A and 0.0044 Å for ring B).

The phthalonitrile group exhibits normal geometry and is planar. The two cyano groups deviate from this plane by 0.0870(15) and −0.0711(17) Å at atoms N1 and N2,

Table 6 Fluorescence properties of **4** in $CHCl_3$, CH_2Cl_2, DMSO, DMF, THF and EtOH

Solvent	$S_0\rightarrow S_1$ $\lambda_{max.}$(nm)	Excitation $\lambda_{Ex.}$ (nm)	Emission $\lambda_{Em.}$ (nm)	Stokes shift Δ_{Stokes} (nm)	Φ_F
THF	501	501	528	27	0.124
DMF	501	501	528	27	0.170
DMSO	502	502	530	28	0.166
EtOH	499	499	525	26	0.121
DCM	503	503	523	20	0.271
$CHCl_3$	505	505	524	10	0.369

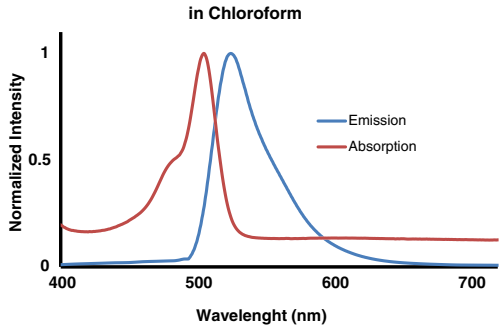


Fig. 6 Absorption and emission spectra of compound **4** in $CHCl_3$

respectively. The C≡N bond lengths [N1≡C7=1.136(3) Å and N2≡C8=1.137(3) Å] bonds show N≡C triple bond character and are in good agreement with the literature compare values reported in the literature [32–35]. At the same time, the C≡N bond lengths have been calculated using B3LYP method with 6-311++G(dp) basis set and this bonds were found as: 1.155 Å and 1.154 Å, respectively. If the cyano groups are considered in the molecule, the C—C—N bond angles can be seen that near-linear. As expected, the N—C—C angles [N1—C7—C4=177.6(3)° and N2—C8—C5=178.6(3)°] are almost linear and in a good agreement with previously reported values by [36–39]. In our calculation these angles were calculated as 178.4° and 178.05 for using B3LYP method, respectively.

The crystal packing (Fig. 2) of the title compound (**4**) is stabilized by one intermolecular C23—H23···F1 and one C3—H3···F2 hydrogen bonds with the geometric parameters 2.45 Å, 3.348(3) Å, 162.9° and 2.35 Å, 3.489(2) Å, 150.4°, respectively. The geometric parameters belong to these hydrogen in Table 4. Some selected optimized geometric parameters (bond lengths, bond angles and dihedral angles) of the title compound are listed in Table 5.

Electronic Spectral Characterization

The ground state electronic absorption spectra and emission spectra of the compound **4** have been recorded in different solvents such as DCM, $CHCl_3$, THF, EtOH, DMF and DMSO at 1×10^{-7} M concentration. Generally, BODIPYs

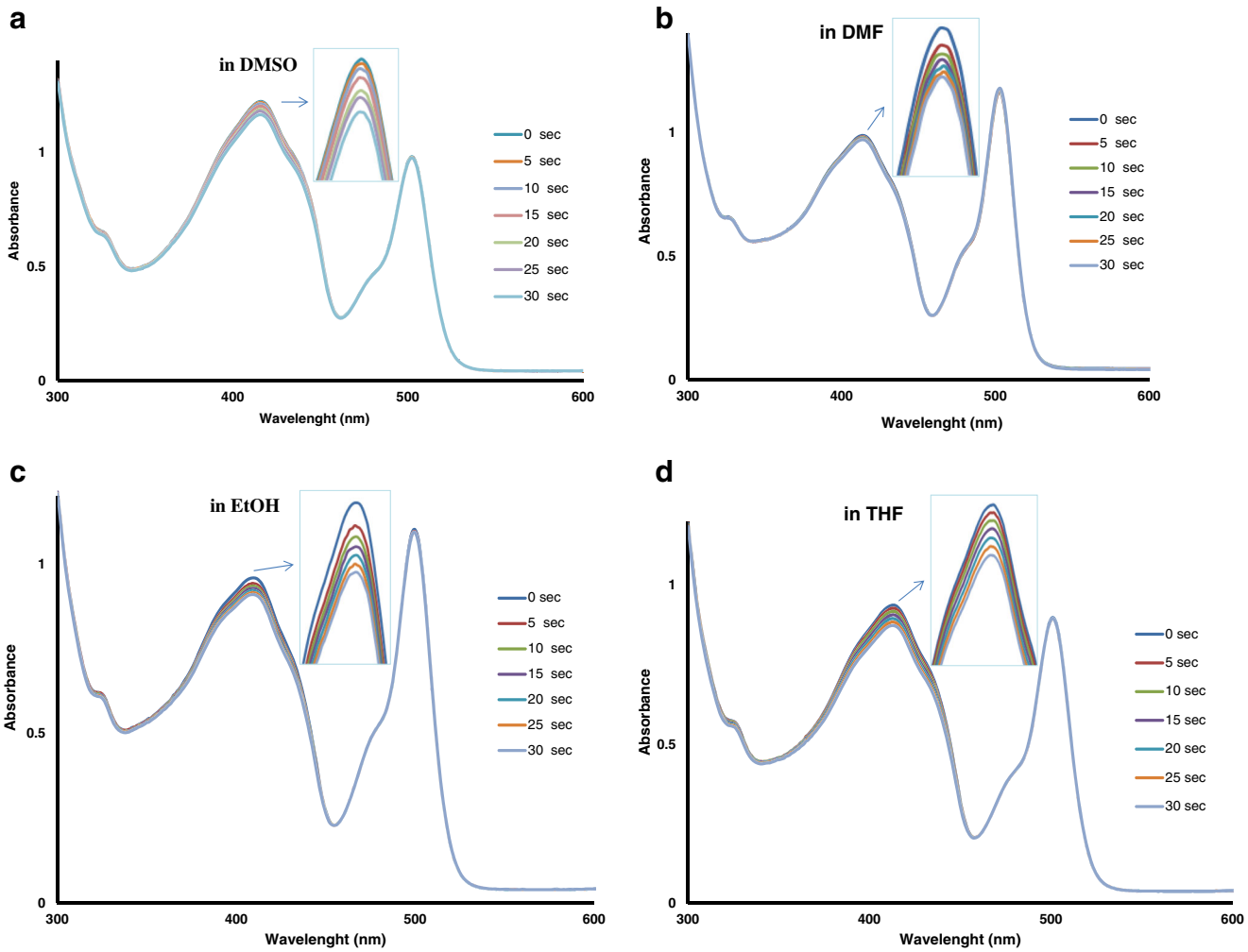


Fig. 7 Typical spectra for the determination of singlet oxygen quantum yield of the complex **4** in different solvents

exhibit one intense visible $S_0 \rightarrow S_1$ absorption band at ~500 nm [39]. Figure 3 shows the absorption spectra of the compound **4** in the mentioned solvents for examining of their spectroscopic properties. It is clearly understood from the absorption spectra that the BODIPY compound **4** has a sharp strong band at the range of 499–505 nm. From the comparison of electronic spectra of the Bor-Dipyrrin derivative fluorophore (**4**), the shortest wavelength absorption was observed in EtOH solution and the longest wavelength absorption in Chloroform solution. The highest occupied molecular orbital (HOMO, −6.600 eV) and the lowest unoccupied molecular orbital (LUMO, −3.533 eV) are the main orbital taking part in chemical reaction. The HOMO energy characterizes the ability of electrongiving, the LUMO characterizes the ability of electron accepting, and the gap between HOMO and LUMO characterizes the molecular chemical stability [40]. Theenergy gap(ΔE=3.067 eV) is calculated as seen Fig. 4.

Photophysical and Photochemical Studies

Fluorescence Quantum Yields

Fluorescence quantum yields (Φ_F) were determined by comparative method [41], Eq. (1)

$$\Phi_F = \Phi_{F(Std)} \frac{F.A_{Std}.n^2}{F_{Std}.A.n^2_{Std}} \quad (1)$$

where F and F_{Std} are the areas under the fluorescence curves of the BODIPY derivative (**4**) and the reference, respectively. A and A_{Std} are the absorbances of sample and reference at the excitation wavelength, and n^2 and n^2_{Std} are the refractive indices of solvents (n_{DCM} :1.424, $n_{chloroform}$:1.445, n_{THF} : 1.407, n_{DMSO}:1.480, n_{DMF} :1.430, n_{EtOH}:1.361) used for the sample and the reference measurements, respectively . Fluorescein was used as a standard; =0.79 in ethanol [30]. The sample and the standard were excited at the same relevant wavelength. The solvent effect on the quantum yield was studied for DCM, $CHCl_3$, THF, DMSO, DMF and EtOH and the emission spectra of compound **4** in these solvents were also compared with the reference under the same conditions (Fig. 5). The calculated quantum yields (Φ_F) in the used solvents are different from each other; in DMSO 0.166, in DMF 0.170, in THF 0.124, in DCM 0.271,in $CHCl_3$ 0.369 and in EtOH 0.121 (Table 6), respectively. Comparing these results, the highest value obtained in $CHCl_3$ (Fig. 6) and the yields in all solvents are lower than the fluorescein quantum yield in ethanol.

Singlet Oxygen Generation

The singlet oxygen generation capability of the title compound **4** was determined using diphenylisobenzofuran (DPBF) as a quencher for singlet oxygen. Different solvents (DMSO, DMF, THF and EtOH) were also used for comparison. The absorption bands of compound **4** in all solvents did not show any changes when the absorption band of DPBF at 416 nm reduced by light irradiation (Fig. 7). These results indicate that compound **4** did not decompose during singlet oxygen studies under irradiation. The compound **4** in THF and EtOH produced more singlet oxygen compared to DMSO and DMF. The singlet oxygen generation spectra of **4** in DMSO, DMF, THF and EtOH were given in Fig. 6.

Conclusion

BODIPY derivative **4** is important in relation to the synthesis of novel and useful fluorescent material that there are some possible application such as fluorescent labeling of biomolecules [2] and fluorescent probes for as selective sensor [42] which was the motivation of this work. In the present study, we have reported the synthesis of a BODIPY class dye with a phthalonitrile subunit as the core compound (**4**) and characterized by standard methods (FT-IR, ^{1}H and ^{13}C-NMR spectroscopy, electronic spectroscopy and mass spectra). The single crystal X-ray structure of the title compound was predicted and its structural properties were also studied and reported in the present work. The theoretical calculations were also performed to confirm the proposed structure.

The absorption, the fluorescence and singlet oxygen generation properties of **4** were investigated. Increased singlet oxygen production was investigated for **4** in DMSO, DMF, THF and EtOH. This feature may be useful for PDT application of these dyes.

The title compound (**4**) is also open to prepare further BODIPY substituted oligomeric molecules via on it. As the phthalonitrile substituted derivative of the dye class, compound **4** may be helpful in fundamental research for the synthesis of BODIPY substituted phthalocyanines because of the key starting compound of this oligomeric class. This is one of the pioner reports in the field and we have attempted to fill this gap in the literature.

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