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Synthesis of covalently linked boron–dipyrromethene–chromophore conjugates using 3-bromo boron–dipyrromethene as a key precursor

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ABSTRACT

3-Bromo boron dipyrromethene (3-bromo BODIPY) has been used as key synthon to prepare one ethynyl bridged and six ethynylphenyl bridged BODIPY–chromophore conjugates using mild Pd(0) coupling conditions. The chromophores possessing very distinct features, such as anthracene, BODIPY, terpyridine, porphyrin, Zn(II)porphyrin, 21,23-dithiaporphyrin and thiasapphyrin were connected at 3-position of boronboron–dipyrromethene dye by coupling of 3-bromo BODIPY with ethynyl or ethynylphenyl chromophore in toluene/triethylamine in the presence of catalytic amount of $AsPh_3/Pd_2(dba)_3$ at 40 °C followed by column chromatographic purification. The spectral studies indicated that the interaction is stronger in ethynyl bridged BODIPY–chromophore conjugate compared to ethynylphenyl bridged BODIPY–chromophore conjugates. The steady-state fluorescence indicated that in ethynyl bridged BODIPY–anthracene conjugate, the BODIPY unit act as energy acceptor and showed a possibility of energy transfer from donor anthracene unit to acceptor BODIPY unit on selective excitation of anthracene unit. However, in ethynylphenyl bridged BODIPY–porphyrin conjugates, the BODIPY unit act as energy donor and exhibited a possibility of singlet-singlet energy transfer from BODIPY unit to porphyrin unit.

1. Introduction

4,4-Difluoro-4-bora-3a,4a-diaza-*s*-indacene dyes popularly known as BODIPY dyes are known for their sharp bands in the absorption spectra, large molar absorption coefficients, high fluorescence quantum yields, reasonably long excited singlet state lifetimes, excellent chemical and photochemical stability in both solution and solid states and versatile charge-transfer properties.[1] BODIPY dyes have good solubility in most common organic solvents and are resistant towards aggregation in solution. BODIPY dyes are amenable to structural modifications so that their spectroscopic properties can be fine tuned by introducing suitable substituents at the right positions on BODIPY core.[1] BODIPY dyes have numerous applications that include light-harvesting arrays,[2] biological probes,[3] supramolecular fluorescent gels,[4] fluorescent switches and sensors,[5] among others. In recent past, dual chromophore systems containing BODIPY along with another chromophore are receiving attention from several viewpoints.[6–10] These kinds of systems can be used to study photoinduced intercomponent electron and/or energy transfer processes, possibly leading to valuable functions, such as charge separation and/or energy migration. There are several BODIPY–chromophore conjugates reported in literature in which chromophores, such as porphyrin,[6] pyrene,[7] anthracene,[8] BODIPY,[9] Zn (II)/Ru(II) bis-terpyridine,[10] etc. complexes were connected covalently to BODIPY and explored their properties. However, in most of these systems, the chromophores were connected via the *meso*-aryl group. Since the *meso*-aryl group and the chromophore are perpendicular to each other, electronic conjugation between two moieties is weak. Recently, there are some reports on BODIPY–chromophore conjugates in which the chromophores are connected directly at α- or β-pyrrole positions of BODIPY ring.[11] In these systems, BODIPY and chromophore units interact very strongly and influence each others properties. For example, Akkaya and co-workers synthesized BODIPY tetrad in which two BODIPY units are covalently linked at 3,5-positions of another BODIPY via styryl linker, which in turn linked to the fourth BODIPY through *meso*-phenyl.[11b] Very recently Ziessel and co-workers reported panchromatic BODIPY dyes in which five BODIPY units are covalently linked in an iterative fashion.[9c] In both these novel cases, the singlet state energy levels of BODIPY units are arranged in cascade manner for efficient intramolecular energy flow from BODIPY units that are at high energy to the BODIPY units that are at lower in energy. Akkaya and co-workers also reported BODIPY–bipyridine/terpyridine conjugates in which bipyridine/terpyridine units are covalently linked at β-pyrrole positions and used for synthesis of metal complexes.[11c] Although, some interesting reports on strongly coupled BODIPY–-chromophore conjugates have been appeared, there is a need for

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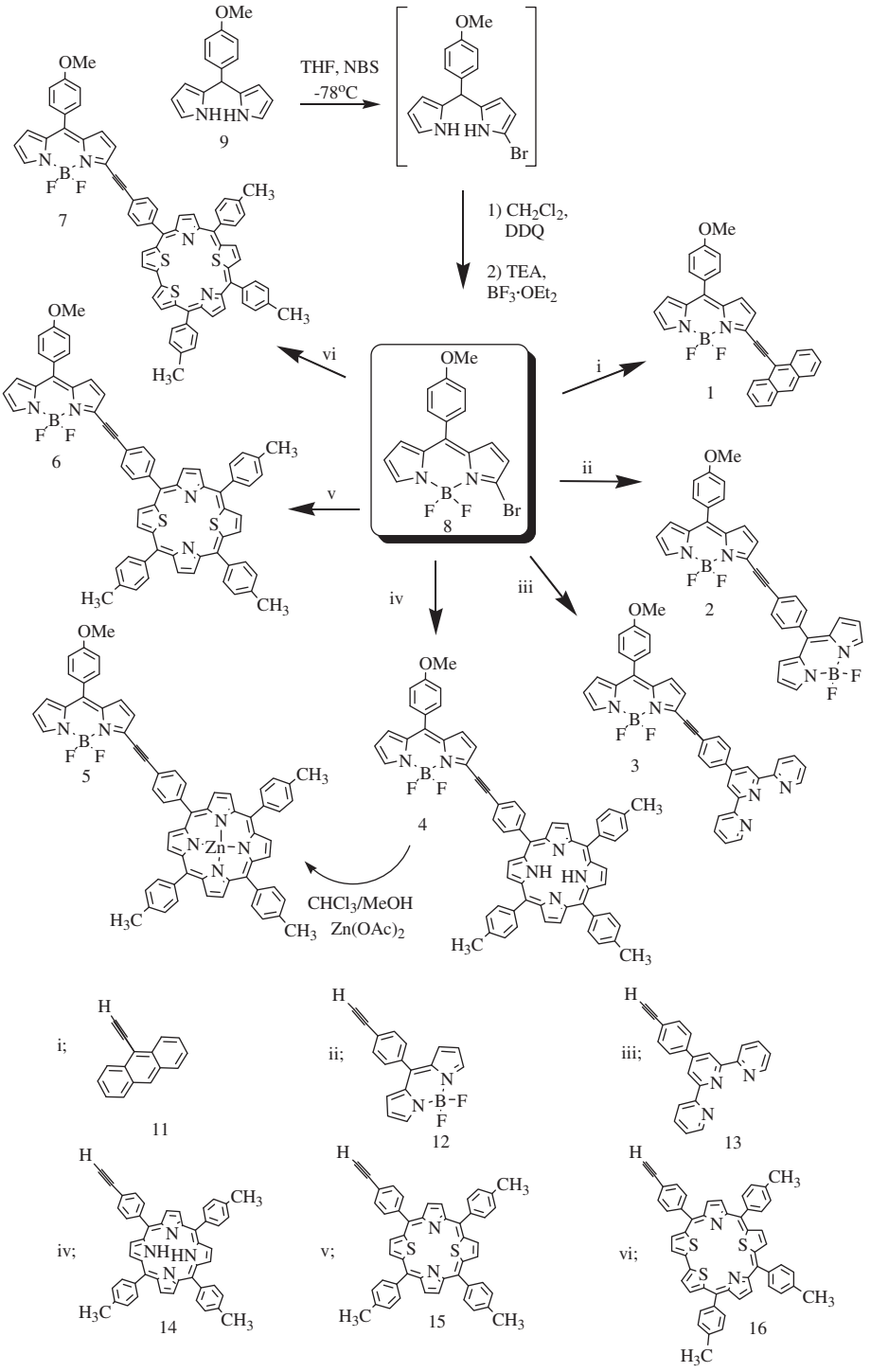
more such systems for understanding electronic communication between the BODIPY and the chromophore for their potential use in photonic devices. Furthermore, bichromophoric systems containing two different chromophores possessing different absorption properties and ground state/excited state redox potentials could function in parallel in solar energy conversion schemes. We herein report the synthesis of series of covalently linked BODIPY–chromophore conjugates **1**–**7** in which the chromophores, such as anthracene, terpyridine, BODIPY, porphyrin, thiaporphyrin and expanded porphyrin are connected at α-position of BODIPY unit by ethyne bridge under mild Pd(0) coupling conditions. The absorption, electrochemical and fluorescence properties of some of these compounds are also described.

2. Results and discussion

To synthesize the BODIPY–chromophore conjugates **1**–**7**, we need an access to α-bromo boron–dipyrromethene[12] **8**, which was prepared over sequence of steps. The *meso*-anisyl dipyrromethane **9** was prepared by treating 1 equiv of *p*-anisaldehyde with



Scheme 1. Synthetic scheme for the preparation of BODIPY–chromophore conjugates **1**–**7**. Reaction conditions used were $Pd_2(dba)_3/AsPh_3$, toluene/TEA, 35–60 °C.

25 equiv of pyrrole under standard Lindsey's dipyrromethane forming conditions.[13] The compound **8** was then prepared by treating **9** with 1 equiv of *N*-bromosuccinimide at −78 °C in THF for 1 h and the resulted compound was oxidized with DDQ in CH_2Cl_2 and complexed with $BF_3{\cdot}OEt_2$. The compound **8** was confirmed by HR-MS mass spectrum and characterized by ^1H, ^{19}F and ^{11}B NMR spectroscopic techniques. The absorption spectrum of compound **8** showed typical BODIPY absorption band and exhibited slight red shift (8–10 nm) compared to *meso*-tolyl boron–dipyrromethene **10**.[14]

The compound **8** was used to prepare a series of BODIPY–chromophore conjugates **1**–**7** as shown in Scheme 1. The other required precursors, such as 9-ethynylanthracene **11**,[15] 4,4-difluoro-8-(4-ethynylphenyl)-4-bora-3a,4a-diaza-*s*-indacene **12**,[8a] 4′-(4-ethynyl phenyl)-2,2′:6′,2″-terpyridine **13**,[16] 5-(4-ethynylphenyl)-10,15,20-tri(*p*-tolyl)porphyrin **14**,[17] 5-(4-ethynylphenyl)-10,15,20-tri(*p*-tolyl) dithiaporphyrin **15**[18] and 5-(4-ethynylphenyl)-10,15,20-tri(*p*-tolyl)-25,27,29-trithiasapphyrin **16**[19] were prepared by following the literature procedures. The compounds **1**–**7** except compound **5** were prepared by coupling of **8** with appropriate ethynyl functionalized chromophore in the presence of $Pd_2(dba)_3/AsPh_3$ in toluene/triethylamine[20] (5:1) at 45–60 °C for 2–6 h depending on the chromophore followed by column chromatographic purification. For example, the BODIPY-conjugates **1**, **2** and **7** were prepared by coupling **8** with corresponding ethynyl chromophore **11**, **12** and **16**, respectively, in the presence of catalytic amount of $Pd_2(dba)_3/AsPh_3$ in toluene/triethylamine at 40 °C for 2 h. Similarly, the BODIPY-conjugates **3**, **4** and **6** were prepared by coupling of **13**, **14** and **15**, respectively, under similar reaction conditions using longer reaction time (~6 h) and at slightly higher temperature (50–60 °C).

The compound **5** was obtained by treating compound **4** with $Zn(OAc)_2$ in $CHCl_3/CH_3OH$ at reflux temperature for 2 h. All compounds were purified by column chromatography using either silica or alumina and confirmed by mass spectral analysis. The compounds **1**–**7** are freely soluble in chlorinated solvents and characterized by ^1H, ^{13}C, ^{19}F and ^{11}B NMR spectroscopic techniques. In couple of cases, we recorded $^1H-^1H$ COSY to identify the proton signals of BODIPY core, such as H_d, the adjacent pyrrole proton of BODIPY unit where the chromophore is connected.

The resonances of BODIPY–chromophore conjugates were assigned on the basis of the spectra observed for the two monomers; the BODIPY monomer and chromophore monomer, taken independently.

A comparison of ^1H, ^{19}F and ^{11}B NMR spectra of compounds **1** and **2** are shown in Fig. 1a–c, respectively; $^1H-^1H$ COSY spectrum for compound **2** in Fig. 2 and the relevant NMR data of compounds

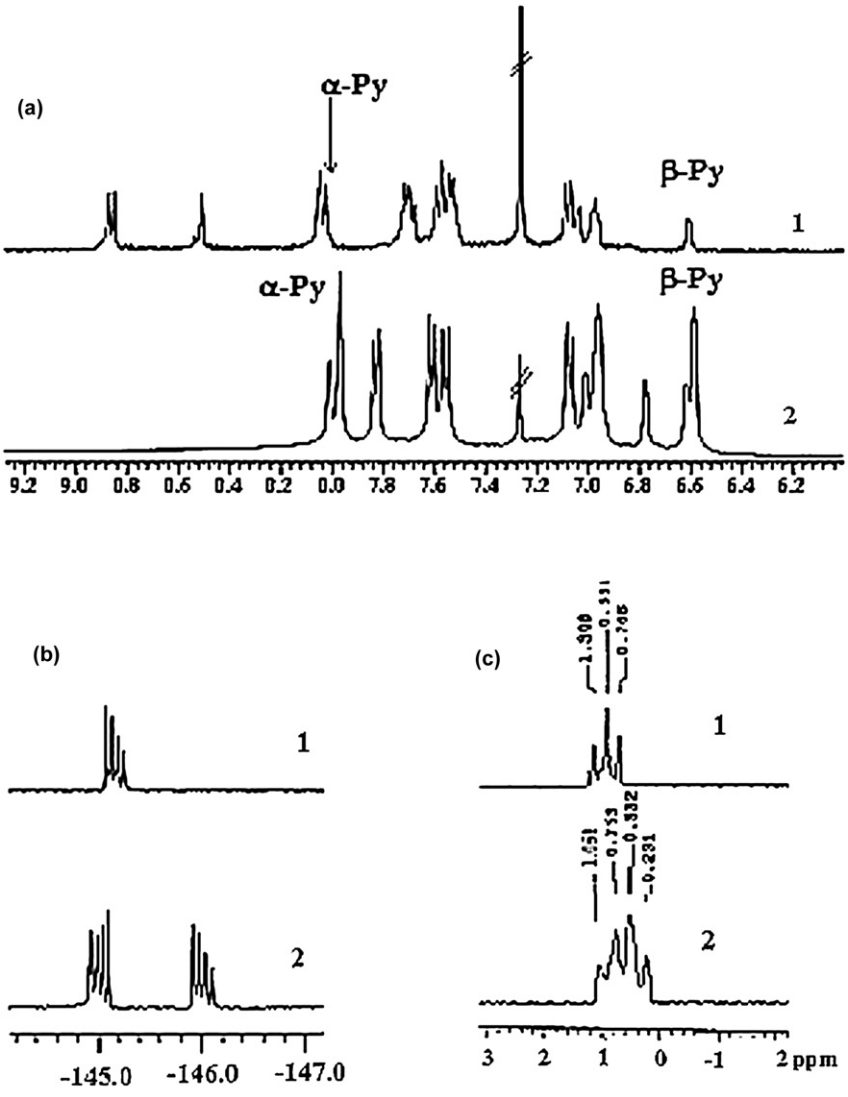


Fig. 1. Comparison of (a) ^1H, (b) ^{19}F and (c) ^{11}B NMR spectra of compounds **1** and **2** in selected region recorded in $CDCl_3$.

1–**7** along with reference BODIPY **10**[14] is presented in Table 1. In compound **1**, the anthracene moiety is connected to BODIPY unit at α-position by ethynyl bridge, whereas in compounds **2**–**7**, the chromophores are connected to BODIPY at α-position by ethynylphenyl bridge. Thus, in compound **1**, the BODIPY and anthracenyl moiety interacts more strongly compared to the other conjugates **2**–**7**, which is reflected in their NMR studies. For example, in ^{1}H NMR, the H_d proton of BODIPY unit experiences 0.42 ppm downfield shift, whereas compounds **2**–**7** experiences 0.20–0.32 ppm shift compared to **10**. Similarly, the downfield shifts were observed in ^{19}F and ^{11}B NMR for all compounds **1**–**7** compared to reference BODIPY **10** and maximum downfield shift was observed for compound **1** in ^{11}B NMR indicating the strong interaction between the BODIPY and anthracenyl units. Some interesting observations were

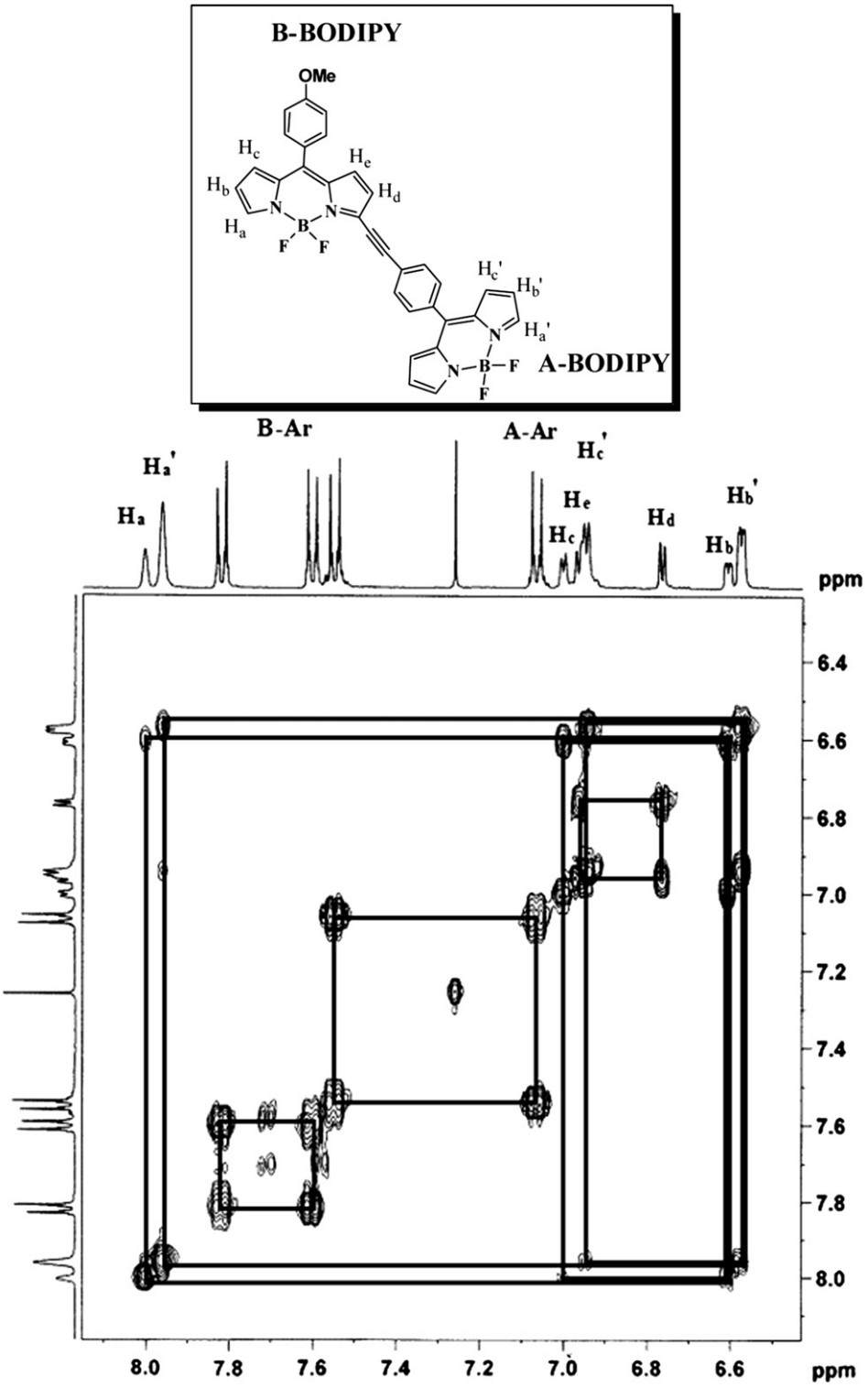


Fig. 2. ^{1}H–^{1}H COSY NMR spectrum of compound **2** in selected region recorded in $CDCl_3$.

Table 1
Comparison of ^{1}H, ^{11}B and ^{19}F NMR chemical shift values (in ppm) of compounds **1**–**7** along with **10** recorded in $CDCl_3$

Compound	^{1}H NMR H_d	^{19}F NMR	^{11}B NMR
10	6.55	−145.27	0.50
1	6.97	−145.34	0.99
2	6.79	−145.12 −146.08	0.75
3	6.75	−146.17	0.77
4	6.84	−145.85	0.91
5	6.86	−145.92	0.69
6	6.85	−146.07	0.89
7	6.87	−146.04	0.91

made for compound **2** in ^{19}F and ^{11}B NMR compared to the other BODIPY–chromophore conjugates.

In general, BODIPY–chromophore conjugates **1** and **3**–**7** showed a triplet in ^{11}B NMR at 0.50 ppm and a single quartet in ^{19}F NMR spectrum because of coupling to ^{11}B (I=3/2, J=32 Hz) and resonances approximately at −146 ppm. However, in compound **2**, due to the presence of two BODIPY moieties, we observed two sets of quartets at −145.12 and −146.08 ppm corresponding to BODIPY A and BODIPY B, respectively. Similarly, in ^{11}B NMR spectrum of compound **2**, the two triplets of two BODIPY moieties A and B merged and appeared as a quartet. This kind of observations were made earlier in other systems containing two or more BODIPY units.[9]

The absorption properties of conjugates **1**–**7** were studied in toluene at room temperature and the data are tabulated in Table 2. The absorption spectra of conjugates **1**–**7** depend on the chromophore, that is, connected to BODIPY unit. In all these conjugates, the absorption bands corresponding to BODIPY unit as well as the chromophore are present with alteration in peak maxima and intensity. In compound **1**, the strong band at 616 nm along with a shoulder at 575 nm corresponding exclusively to BODIPY unit along with the small ill-defined bands in 350–450 nm region, which are due to both BODIPY and anthracene units are present (Fig. S29). The large red shift of absorption band (~115 nm) of BODIPY unit in **1** compared to the reference BODIPY **10**[14] indicates that the BODIPY and anthracenyl moieties in **1** interact strongly. Furthermore, Burgess and co-workers[8a] reported BODIPY–anthracene conjugates in which the anthracenyl moiety is connected at β-pyrrole position of BODIPY core using the same ethynyl bridge exhibited BODIPY absorption band only at 540 nm. This indicates that the anthracenyl moiety present at α-position involves in stronger interaction with BODIPY core compared to anthracenyl group present at the β-position of BODIPY unit.

Table 2
Absorption and fluorescence data of BODIPY–chromophore conjugates **1**–**7** along with **10** in toluene

Compound	λ_{abs} nm (log ε)	ϕ^{Donor}	Donor (%Q)[a]
10	502 (4.68)	0.05	—
1	354 (sh), 375 (sh), 401 (4.18), 424 (4.26), 575 (sh), 616 (4.59)	<0.0003[b]	98%
2	423 (3.32), 509 (3.64), 562 (3.67)	<0.0001[c]	99%
3	299 (4.17), 328 (4.22), 422 (3.91), 529 (sh), 563 (4.53)	0.32[c]	—
4	421 (4.99), 519 (sh), 564 (4.19), 650 (3.29)	<0.0001[c]	99%
5	425 (4.98), 563 (4.26), 597 (3.79)	0.003[c]	83%
6	438 (5.00), 515 (4.18), 567 (4.41), 633 (3.34), 699 (4.32)	0.010[c]	70%
7	515 (4.46), 560 (3.78), 627 (sh), 689 (3.75), 782 (2.54), 884 (3.0)	—	—

[a] (%Q) denotes percentage of quenching of fluorescence quantum yield.
[b] Anthracene unit.
[c] BODIPY unit.

The absorption spectrum of BODIPY–BODIPY conjugate **2** showed two strong bands at 509 and 562 nm with almost equal intensity (Fig. 3a). The red shifted absorption band at 562 nm corresponds to BODIPY unit B to which ethynylphenyl group is connected at α-position and the absorption band at 506 nm is due to the BODIPY unit A.[14] This indicates that the two BODIPY units A and B in conjugate **2** exhibit quite different absorption properties. In BODIPY–terpyridine **3**, a strong band at 563 nm corresponds to BODIPY unit along with small bands of terpyridinyl unit in 300–400 nm region are present (Fig. S30).

The BODIPY-N_4 porphyrinyl conjugate **4** showed absorption bands at 421, 564, 650 nm along with a shoulder band at 519 nm (Fig. 3b). In general, porphyrin shows four well defined Q-bands in 700-450 nm region and one strong Soret band at ~420 nm.[17] However, the conjugate **4** did not exhibit typical Q-bands of porphyrin because of BODIPY unit whose strong absorption band at 564 nm was merged with the Q-bands of porphyrin unit. Thus, the bands at 421 and 650 nm were exclusively due to porphyrin unit and the band at 564 nm was mainly due to BODIPY unit.

In conjugate **5**, the absorption bands at 425 and 597 nm are mainly due to ZnTTP and a strong band at 563 nm is due to both ZnTTP and BODIPY units (Fig. S31). The BODIPY–N_2S_2 porphyrin conjugate **6** showed characteristic 21,23-dithiaporphyrin[18] absorption bands at 438, 515, 633 and 699 nm (Fig. S32). The band at 567 nm is highly intense compared to other Q-bands due to the absorption of BODIPY unit in the same region. In BODIPY–sapphyrin conjugate, the BODIPY absorption was observed as strong band at 560 nm and the bands at 515, 627, 689, 782 and 884 nm are due to sapphyrin[19] unit (Fig. S33).

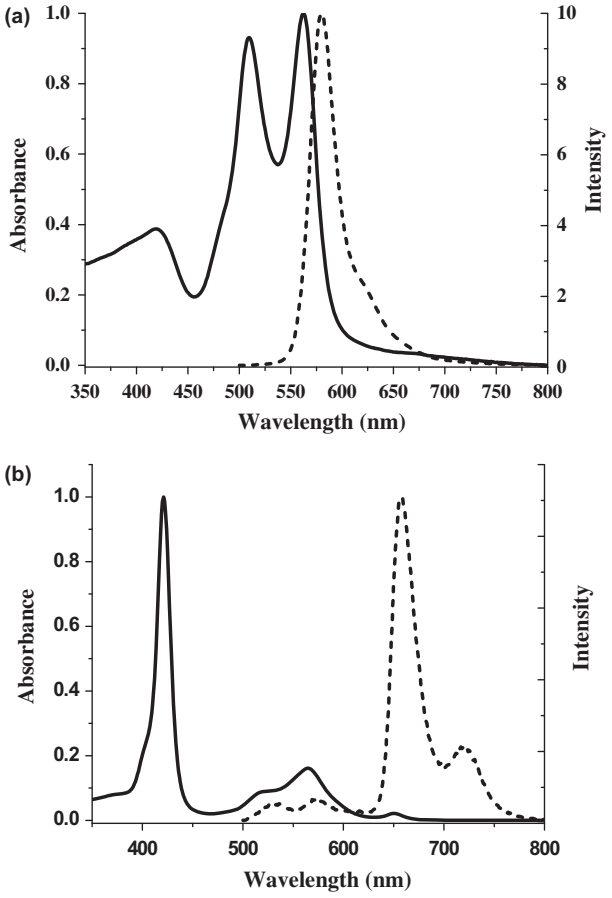


Fig. 3. Normalized absorption (—) and emission spectra (– – – –) of compounds (a) **2** and (b) **4** recorded in toluene.

Thus, the absorption study clearly indicated that in compounds **2**–**7**, the absorption band of BODIPY unit experienced significant red shift compared to *meso*-tolyl BODIPY **10** due to the presence of ethynylphenyl group at α-position, whereas the chromophores connected to BODIPY unit which contains *meso*-phenyl group did not show any shift in their respective absorption bands. However, in compound **1**, due to the presence of direct ethynyl bridge between the two chromophores, the BODIPY unit showed more red shift compared to other conjugates.

The redox potentials of conjugates **1**–**7** were measured in CH_2Cl_2 by cyclic voltammetry at a variable scan rate (50–150 mV/s) using tetrabutylammonium perchlorate as the supporting electrolyte. A comparison of reduction wave of BODIPY unit in conjugates **1**–**5** is shown in Fig. 4 and the data are presented in Table 3. Bard and co-workers showed that the *meso*-aryl substituted BODIPYs exhibit one reversible oxidation and one reversible reduction.[21] In all conjugates, the BODIPY unit showed one reversible or quasi-reversible reduction and did not show any well defined oxidation wave. In compound **2**, because of two BODIPY units, the reduction of both BODIPY units were overlapped and appeared as one broad reduction wave in cyclic voltammetry (Fig. 4b).

However, using differential pulse voltammetric (DPV) studies, we identified the reduction corresponding to each BODIPY unit in compound **2**. Furthermore, the chromophores in compounds **1** and **3**–**7** showed their respective oxidation and reductions with slight shifts in their potentials. The redox potentials of BODIPY–chromophore conjugates **1**–**7** were assigned on the basis of the redox potential data of their corresponding independent chromophores. For example, the conjugate **7** showed a reduction at −0.47 V, which corresponds exclusively to BODIPY unit and two other reductions at −1.12 and −1.37 V were mainly due to sapphyrin unit (Fig. S34).

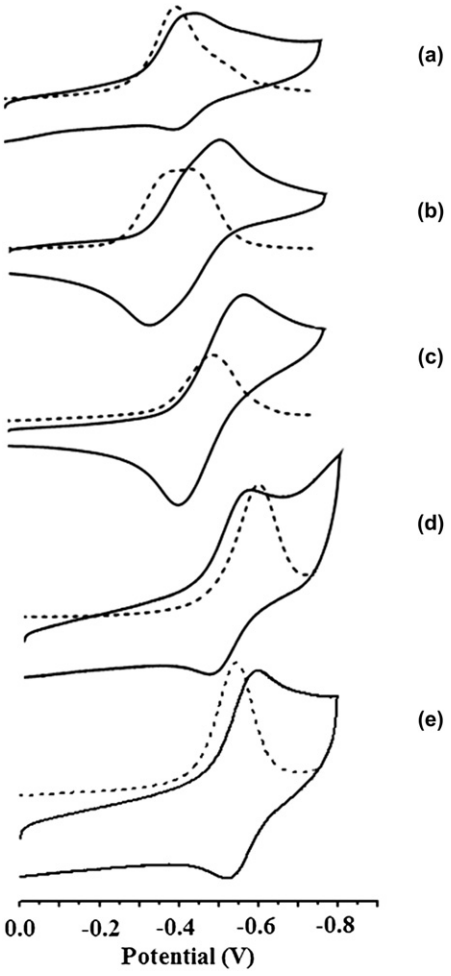


Fig. 4. Comparison of reduction waves of cyclic voltammograms along with differential pulse voltammograms of (a) **1**, (b) **2**, (c) **3**, (d) **4** and (e) **5** in dichloromethane containing 0.1 M TBAP as supporting electrolyte recorded at 50 mV/s scan speed.

Table 3
Electrochemical redox data (V) of compounds **1**–**7** along with **10** in dichloromethane containing 0.1 M TBAP as supporting electrolyte

Compound	BODIPY	Chromophore			
	$E^{red}_{1/2}V(\Delta E_p,\ mV)$	$E^{ox}_{1/2}(\Delta E_p,\ mV)$		$E^{red}_{1/2}(\Delta E_p,\ mV)$	
		I	II	I	II
10	−1.15 (94)	1.17 (92)			
1	−0.41, −0.46[a]	—	—	−1.24[a]	−1.58[a]
2	−0.49 (175)	—	—	−1.16[a]	—
3	−0.52 (145)	0.99[a]	—	−1.36[a]	—
4	−0.59 (96)	1.11[a]	1.57[a]	−1.09 (86)	−1.43 (100)
5	−0.52 (85)	0.91 (153)	1.21 (180)	−1.18[a]	−1.57 (70)
6	−0.64[a]	1.34[a]		−0.90[a]	−1.13[a]
7	−0.47 (84)	—	—	−1.12[a]	−1.37 (167)

[a] Obtained from DPV.

In all conjugates, the BODIPY unit showed one reversible reduction, which appeared at less negative potential (−0.40 to −0.65 V) compared to **10** (−1.15 V) indicating that the BODIPY unit in conjugates **1**–**7** is easily reducible. The fluorescence properties of conjugates **1**–**7** were studied in toluene using different excitation wavelengths.

The fluorescence properties of conjugates **1**–**7** are dependent on BODIPY as well as chromophore units. In these conjugates, the BODIPY unit is acting either as energy donor or as energy acceptor, which depends on the chromophore that is attached to it. In conjugate **1**, the anthracene unit acts as energy donor and BODIPY unit acts as energy acceptor. On excitation at 350, 420 and 488 nm, the emission was mainly observed at 650 nm corresponding to the BODIPY unit with negligible emission from anthracene unit. The 1:1 mixture of the corresponding monomers (**8** and **11**) of compound **1**, on excitation at 350 nm showed mainly emission coming from anthracene unit (Fig. S29). The excitation spectrum recorded at 680 nm matches with its absorption spectrum. These observations indicate a possibility of singlet-singlet energy transfer from anthracene to BODIPY unit in compound **1**. In BODIPY–BODIPY conjugate **2**, the BODIPY unit B, which contains ethynylphenyl group at α-position absorbs at lower energy, whereas the BODIPY unit A absorbs at higher energy. This is clearly reflected in its absorption spectrum (Fig. 3a). Thus, on excitation of BODIPY unit at 488 nm, the emission was exclusively observed from the BODIPY unit, which contains ethynylphenyl group at α-position and no emission was noticed from the donor BODIPY unit due to the energy transfer from BODIPY unit A to BODIPY unit B in conjugate **2**. The BODIPY–terpyridine conjugate **3**, on excitation at 488 nm, the emission from BODIPY unit was observed with quantum yield of 0.32 (Fig. S30). The conjugate **4** containing N_4 porphyrin and BODIPY units, on excitation at BODIPY unit at 488 nm, the emission was mainly observed from N_4 porphyrin unit because of singlet–singlet energy transfer from BODIPY unit to N_4 porphyrin (Fig. 3b). However, in conjugate **5** (Fig. S31) and **6** (Fig. S32), on excitation of BODIPY unit, the emission was observed from both BODIPY and porphyrin units. In these two cases, the energy transfer from BODIPY unit to porphyrin unit was not very efficient hence emission was also observed from the donor BODIPY unit. The conjugate **7** is almost non-fluorescent indicating that the thiasapphyrin unit connected at α-position of BODIPY unit enhances the non-radiative

decay channels. Although, the quenching of donor emission in conjugates was mainly attributed to singlet-singlet energy transfer from donor to acceptor unit, we did not rule out the possibility of some contribution from electron transfer for quenching the donor emission. A detailed time-resolved studies are required to understand the photophysical properties of these novel conjugates.

3. Conclusions

In conclusion, we used 3-bromo BODIPY as a synthon to prepare one ethynyl bridged BODIPY–anthracene conjugate and six ethynylphenyl bridged BODIPY–chromophore conjugates, such as BODIPY-BODIPY, BODIPY–terpyridine, BODIPY–porphyrin, BODIPY–Zn(II)porphyrin, BODIPY–21,23-dithiaporphyrin and BODIPY–thiasapphyrin by coupling with chromophores containing ethynyl or ethynylphenyl functional group under mild Pd(0) coupling conditions. The spectral studies indicated that the interaction between the two chromophores is stronger in ethynyl bridged BODIPY–anthracene conjugate compared to the ethynylphenyl bridged BODIPY–chromophore conjugates. We showed that, in these conjugates, the BODIPY can act as either energy donor or energy acceptor depending on the type of chromophore to which it is linked. Furthermore, the chromophores connected at α-position of BODIPY would exhibit different trends in properties compared to the reported BODIPY–chromophore conjugates in which the chromophores are connected at β-position. We are presently exploring a detailed photodynamics of novel BODIPY–chromophore conjugates in our laboratory.

4. Experimental section

4.1. Chemicals

THF and toluene were dried over sodium benzophenone ketyl and chlorofom, ethyl-acetate, methanol, acetonitrile dried over calcium hydride prior to use. $BF_3{\cdot}OEt_2$ and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) obtained from Spectrochem (India) were used as obtained. All other chemicals used for the synthesis were reagent grade unless otherwise specified. Column chromatography was performed on silica (60–120 mesh) or alumina.

4.2. Instrumentation

^{1}H NMR spectra (δ in ppm) were recorded using Varian VXR 300, 400 MHz and Bruker 400 MHz spectrometer. ^{13}C NMR spectra were recorded on Bruker operating at 100.6 MHz ^{19}F NMR spectra were recorded on Varian spectrometer operating at 282.2 MHz ^{11}B NMR spectra were recorded on Varian spectrometer operating at 96.3 MHz. TMS was used as an internal reference for recording ^{1}H (of residual proton; δ 7.26) and ^{13}C (δ 77.0 signal) in $CDCl_3$. Absorption and steady-state fluorescence spectra were obtained with Perkin–Elmer Lambda-35 and PC1 Photon Counting Spectrofluorometer manufactured by ISS, USA instruments, respectively. Fluorescence spectra were recorded at 25 °C in a 1 cm quartz fluorescence cuvette. The fluorescence quantum yields (Φ_f) were estimated from the emission and absorption spectra by comparative method at the excitation wavelength of 488 nm using Rhodamine 6G (Φ_f=0.88).[22] Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) studies were carried out with electrochemical system utilizing the three electrode configuration consisting of a glassy carbon (working electrode), platinum wire (auxillary electrode) and saturated calomel (reference electrode) electrodes.[22b] The experiments were done in dry dichloromethane using 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. Half wave potentials were measured using DPV and also calculated manually by taking the average of the cathodic and anodic peak potentials. All potentials were calibrated versus saturated calomel electrode by the addition of ferrocene as an internal standard, taking $E_{1/2}$ (Fc/Fc^+)=0.42 V, versus SCE.[23] The ES-MS mass spectra were recorded with a Q-Tof micro mass spectrometer. High-resolution mass spectrum was obtained from Q-TOF instrument by electron spray ionization (ESI) technique.

4.3. 3-Bromo-4,4-difluoro-8-(4-methoxyphenyl)-4-bora-3a,4a-diaza-*s*-indacene (8)

This compound was prepared in sequence of steps in one pot reaction. *meso*-(*p*-Methoxyphenyl)-dipyrromethane **9** (500 mg, 2.12 mmol) was treated with 1 equiv of *N*-bromosuccinimide (377 mg, 2.12 mmol) in dry THF (50 mL) at −78 °C under nitrogen for 1 h. The reaction mixture was brought to room temperature. The reaction mixture was subjected to flash column chromatography using CH_2Cl_2, concentrated on rotary evaporator, dissolved in CH_2Cl_2 and DDQ (483 mg, 2.12 mmol) was added. The reaction mixture was stirred for 1 h at room temperature and then neutralized with triethylamine (10.49 mL, 75.4 mmol) and treated with $BF_3{\cdot}Et_2O$ (13.44 mL, 107.0 mmol) at room temperature for additional 1 h. The reaction mixture was washed successively with 0.1 M NaOH solution and water. The organic layers were combined, dried over Na_2SO_4, filtered and evaporated. The crude compound was subjected to silica gel column chromatography and the required α-bromo derivative of BODIPY **8** was collected as second band using of petroleum ether/dichloromethane (90:10). The solvent was removed on rotary evaporator under vacuo and afforded pure **8** as orange powder (250 mg, 33% yield). R_f (25% pet. ether/CH_2Cl_2) 0.70; IR (KBr, cm^{-1}) 737, 780, 837, 970, 1076, 1106, 1178, 1251, 1338, 1382, 1542, 1571, 1602, 2840, 2924; ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 3.91 (3H, s, OMe), 6.53 (2H, m, Py), 6.57 (2H, m, Py), 6.84 (2H, d, J=4.28 Hz, py), 6.93 (2H, d, J=3.70 Hz, py), 7.38 (2H, d, J=7.95 Hz, Ar), 7.44 (2H, d, J=7.95 Hz, Ar). ^{19}F NMR (282.2 MHz, $CDCl_3$, δ in ppm): −146.34 (q, J_{B-F}=56.5 Hz). HR-MS: calcd for ($C_{16}H_{13}BBrF_2N_2$) 377.0272 found 377.0271.

4.4. General procedure for the synthesis of BODIPY–chromophore conjugates 1–7

3-Bromo-4,4-difluoro-8-(4-methoxyphenyl)-4-bora-3a,4a-diaza-*s*-indacene **8** and appropriate chromophore containing ethynyl or ethynylphenyl functional group **11**–**16** were dissolved in dry toluene/Et_3N (6 mL, 5:1) in a 25 mL, two-necked, round-bottomed flask fitted with a reflux condenser, gas inlet and gas outlet tubes for nitrogen purging. The reaction vessel was placed in an oil bath preheated to 35 °C. After purging the flask with nitrogen for 15 min, $AsPh_3$ (3.5 equiv) and $Pd_2(dba)_3$ (0.44 equiv) were added, and the reaction mixture was stirred at 35 °C for 4 h. TLC analysis of the reaction mixture indicated the appearance of a dark new spot apart from the two minor spots corresponding to starting precursors. The solvent was removed under reduced pressure, and the crude compound was purified by silica gel column chromatography. The excess $AsPh_3$ and the small amounts of unreacted starting precursors were removed with petroleum ether and the required pure BODIPY–chromophore conjugate was then collected with petroleum ether/CH_2Cl_2.

*4.4.1. BODIPY–anthracene conjugate **1**.* Alumina column (petroleum ether/dichloromethane 95:5) R_f (5% pet. ether/CH_2Cl_2) 0.42; 42% yield; IR (KBr, cm^{-1}) 669, 768, 929, 1014, 1071, 1128, 1216, 1261, 1528, 1604, 2179, 2400, 2854, 2927, 3019, 3272; ^{1}H NMR (400 MHz, $CDCl_3$): 3.92 (3H, s, OMe), 6.61 (1H, m, β-Py), 6.97 (1H, m, β-Py), 7.03–7.08 (2H, m, β-Py), 7.53–7.59 (6H, m), 7.67–7.71 (2H, m), 8.02 (1H, s, α-Py), 8.04 (2H, s), 8.50 (1H, s), 8.84 (2H, d, J=8.2 Hz). ^{13}C NMR

(100 MHz, $CDCl_3$, δ in ppm): 55.74, 77.3, 94.28, 99.93, 114.29, 116.31, 118.74, 124.08, 126.15, 126.67, 127.17, 127.68, 128.87, 129.03, 129.90, 130.92, 131.09, 131.33, 132.64, 133.70, 136.46, 137.30, 144.01, 162.14. ^{19}F NMR (282.2 MHz, $CDCl_3$, δ in ppm): −145.49 (q, J_{B-F}=56.5 Hz). ^{11}B NMR (96.3 MHz, $CDCl_3$, δ in ppm): 0.991 (t, J_{B-F}=30.5 Hz). HR-MS calcd for ($C_{32}H_{21}BF_2N_2O$): 499.1793 found: 499.1813.

4.4.2. BODIPY–BODIPY conjugate ***2***. Alumina column (petroleum ether/dichloromethane 75:25) R_f (25% pet. ether/CH_2Cl_2) 0.30; 40% yield; IR (KBr, cm^{-1}) 769, 754, 849, 928, 1021, 1081, 1119, 1218, 1527, 1604, 1672, 1965, 2400, 2855, 2927, 3020; ^1H NMR (400 MHz, $CDCl_3$): 3.94 (3H, s, OMe), 6.59 (2H, m, β-Py), 6.63 (1H, s, β-Py), 6.79 (1H, m, β-Py), 6.97 (2H, m, β-Py), 7.07 (2H, d, J=8.2 Hz, Ar), 7.56 (2H, d, J=8.24 Hz, Ar), 7.61 (2H, d, J=8.24 Hz, Ar), 7.72 (2H, m, β-Py), 7.83 (2H, d, J=7.9 Hz, Ar), 7.98 (2H, s, α-Py), 8.02 (1H, s, α-Py). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 55.75, 65.73, 85.0, 100.0, 114.32, 18.98, 119.33, 123.32, 129.00, 130.74, 131.08, 131.57, 132.23, 132.46, 132.66, 134.88, 144.60, 144.96, 149.0, 162.0, 166.0, 167.89. ^{19}F NMR (282.2 MHz, $CDCl_3$, δ in ppm): −145.12 (q, J_{B-F}=56.4 Hz), −146.08 (q, J_{B-F}=56.4 Hz). ^{11}B NMR (96.3 MHz, $CDCl_3$, δ in ppm): 0.753 (m). ES-MS calcd for ($C_{33}H_{22}B_2F_4N_4O$): 588.19 found: 569.26 $[M-19]^+$. HR-MS calcd for ($C_{33}H_{22}B_2F_3N_4O$): 569.1932 found 569.1945.

4.4.3. BODIPY–terpyridine conjugate ***3***. Alumina column (petroleum ether/dichloromethane 40:60) R_f (60% pet. ether/CH_2Cl_2) 0.45; 50% yield; IR (KBr, cm^{-1}) 710, 758, 887, 983, 1023, 1081, 1121, 1216, 1527, 1604, 1965, 2201, 2855, 2926, 3018; ^1H NMR (400 MHz, $CDCl_3$): 3.94 (3H, s, OMe), 6.59 (1H, m, β-Py), 6.75 (1H, d, J=3.97 Hz, β-Py), 6.95 (2H, m, β-Py), 7.33–7.39 (4H, m, pyridyl+BDP-Ar), 7.47 (2H,d, J=7.9 Hz, BDP-Ar), 7.69 (2H, d, J=8.2 Hz, Tpy-Ar), 7.80 (2H, d, J=7.6 Hz, Tpy-Ar), 7.88–7.96 (2H, m, pyridyl), 8.0 (1H, s, α-Py), 8.67 (2H, d, J=7.63 Hz, pyridyl), 8.75 (4H, d, J=3.97 Hz, pyridyl). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 55.56, 114.10, 118.76, 121.42, 123.40, 123.95, 127.36, 130.63, 132.47, 132.79, 136.94, 145.00, 149.18, 156.11. ^{19}F NMR (282.2 MHz, $CDCl_3$, δ in ppm): −146.17 (q, J_{B-F}=56.4 Hz). ^{11}B NMR (96.3 MHz, $CDCl_3$, δ in ppm): 0.769 (t, J_{B-F}=25.9 Hz). HR-MS calcd for ($C_{39}H_{27}BF_2N_5O$): 631.2355 found: 631.2367.

4.4.4. BODIPY–porphyrin conjugate ***4***. Silica column (petroleum ether/dichloromethane 60:40) R_f (40% pet. ether/CH_2Cl_2) 0.55; 40% yield; IR (KBr, cm^{-1}) 710, 758, 888, 983, 1023, 1081, 1121, 1216, 1286, 1507, 1604, 1965, 2201, 2855, 2926, 3018, 3320; ^1H NMR (400 MHz, $CDCl_3$): −2.7 (1H, s), 2.70 (9H, s), 3.9 (3H, s), 6.59 (1H, s, BDP-β-Py), 6.84 (1H, d, J=3.9 Hz, BDP-β-Py), 6.99–7.02 (2H, m, BDP-β-Py), 7.04 (2H, d, J=8.7 Hz, BDP-Ar), 7.54–7.58 (8H, m), 8.03 (1H, s, α-Py), 8.05–8.10 (8H, m, Ar), 8.24 (2H, d, J=8.2 Hz), 8.86–8.89 (8H, m, β-py). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 21.69, 55.69, 65.76, 70.74, 84.09, 102.00, 113.97, 114.28, 118.89, 120.55, 120.70, 121.85, 123.49, 126.55, 127.32, 127.62, 128.90, 129.60, 130.73, 130.90, 131.09, 131.25, 131.70, 132.21, 132.50, 132.64, 134.21, 134.40, 134.68, 134.87, 135.72, 136.20, 137.09, 137.57, 139.37, 139.42, 141.91, 143.89, 144.32, 144.32, 145.20, 162.19. ^{19}F NMR (282.2 MHz, $CDCl_3$, δ in ppm): −145.85 (q, J_{B-F}=56.4 Hz). ^{11}B NMR (96.3 MHz, $CDCl_3$, δ in ppm): 0.912 (t, J_{B-F}=28.99 Hz). HR-MS calcd for ($C_{65}H_{48}BF_2N_6O$): calculated 977.3951 found: 977.3906.

4.4.5. BODIPY–Zn(II)porphyrin conjugate ***5***. A solution of **4** (20 mg, 0.02 mmol) and $Zn(OAc)_2$ (64.5 mg, 1.33 mmol) in dichloromethane/methanol (3:1, 20 mL) was stirred at room temperature for 2 h. The crude compound was purified by silica gel column chromatography using petroleum ether/dichloromethane (60:40) as eluent, and the desired porphyrin **5** was collected as a violet solid in 85% yield; R_f (40% pet. ether/CH_2Cl_2) 0.30; IR (KBr, cm^{-1}) 669, 770, 849, 928, 1018, 1122, 1423, 1526, 1603, 1965, 2400, 2854, 2927, 3019, 3272; ^1H NMR (400 MHz, $CDCl_3$): 2.70 (9H, s), 3.9 (3H, s), 6.60 (1H, s, BDP-β-Py), 6.86 (1H, s, BDP-β-Py), 6.99–7.02 (2H, m, BDP-β-Py), 7.07 (2H, d, J=8.7 Hz, BDP-Ar), 7.55–7.58 (8H, m), 8.03 (1H, s, α-Py), 8.05–8.11 (8H, m, Ar), 8.24 (2H, d, J=8.2 Hz), 8.94–9.00 (8H, m, β-py). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 21.69, 55.75, 65.73, 102.00, 113.97, 114.27, 118.89, 120.52, 120.70,121.85, 123.49, 126.55, 127.32, 127.60, 128.90, 129.60, 130.71, 130.90, 131.09, 131.25, 131.70, 132.21, 132.50, 132.64, 134.21, 134.34, 134.67, 134.86, 135.72, 136.20, 137.09, 137.56, 139.35, 139.42, 141.91, 143.89, 144.32, 145.20, 162.18. ^{19}F NMR (282.2 MHz, $CDCl_3$, δ in ppm): −145.92 (q, J_{B-F}=56.4 Hz). ^{11}B NMR (96.3 MHz, $CDCl_3$, δ in ppm): 0.69 (t, J_{B-F}=28.92 Hz). HR-MS calcd for ($C_{65}H_{46}BF_2N_6OZn$) m/z 1041.3164 observed 1040.3192.

4.4.6. BODIPY–21,23-dithiaporphyrin conjugate ***6***. Silica column (petroleum ether/dichloromethane 50:50) R_f (50% pet. ether/CH_2Cl_2) 0.30; 38% yield; IR (KBr, cm^{-1}) 669, 770, 849, 928, 1018, 1122, 1217, 1423, 1526, 1603, 1965, 2400, 2927, 3019, 3272; ^1H NMR (400 MHz, $CDCl_3$): 2.71 (9H, s), 3.93 (3H, s, OMe), 6.59 (1H, s, BDP-β-Py), 6.85 (1H, d, J=3.3 Hz, BDP-β-Py), 7.01 (2H, m, BDP-β-Py), 7.07 (2H, d, J=8.2 Hz, BDP-Ar), 7.57 (2H, d, J=8.5 Hz, BDP-Ar), 7.61–7.63 (8H, m), 8.04 (1H, s, α-py), 8.12–8.14 (6H, d, J=7.02 Hz, Ar), 8.27 (2H, d, J=8.2 Hz), 8.68–8.73 (4H, m, β-py), 9.66–9.73 (4H, m, β-Th). ^{19}F NMR (282.2 MHz, $CDCl_3$, δ in ppm): −146.07 (q, J_{B-F}=56.4 Hz). ^{11}B NMR (96.3 MHz, $CDCl_3$, δ in ppm):0.896 (t, J_{B-F}=27.4 Hz). HR-MS calcd for ($C_{65}H_{45}BF_2N_4OS_2$): calculated 1011.2994 found: 1011.3018.

4.4.7. BODIPY–thiasapphyrin conjugate ***7***. Alumina column (petroleum ether/dichloromethane 40:60) R_f (60% pet. ether/CH_2Cl_2) 0.60; 53% yield; IR (KBr, cm^{-1}) 710, 799, 856, 945, 1076, 1081, 1261, 1553, 2123, 2921, 2852, 3322; ^1H NMR (400 MHz, $CDCl_3$): −0.84 (2H, s, β-Th), 2.64 (6H, s, tol), 2.74 (3H, s, tol), 3.93 (3H, s, OMe), 6.62 (1H, s, BDP-β-Py), 6.87 (1H, d, J=4.27 Hz, BDP-β-Py), 7.02–7.18 (4H, m, BDP[β-Py+Ar]), 7.60 (10H, m, Ar[BDP+sap]), 8.06 (1H, s, BDP-α-Py), 8.12–8.21 (4H, m, Ar), 8.27 (2H, d, J=7.3 Hz, Ar), 8.35 (2H, d, J=8.2 Hz, Ar), 8.59–8.71 (4H, m, β-Py sap), 9.8 (2H, d, J=8.54 Hz, β-Th-bth), 10.25–10.28 (2H, m, β-Th-bth). ^{19}F NMR (282.2 MHz, $CDCl_3$, δ in ppm): −146.04 (q, J_{B-F}=56.0 Hz). ^{11}B NMR (96.3 MHz, $CDCl_3$, δ in ppm): 0.912 (t, J_{B-F}=28.9 Hz). HR-MS calcd for ($C_{69}H_{47}BF_2N_4OS_3$): 1093.3047 found: 1093.3051.

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Supplementary material

Complete characterization data of compounds, ^1H and ^{13}C NMR and ^{19}F spectra. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.05.089.

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