Dalton Transactions

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: I. -. GUPTA, P. E. Kesavan, S. Das, M. Y. Lone, P. C. Jha and S. Mori, *Dalton Trans.*, 2015, DOI: 10.1039/C5DT01925G.

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

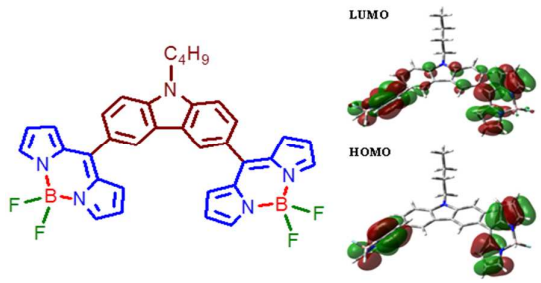
Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

View Article Online
DOI: 10.1039/C5DT01925G

TOC Graphic:



TOC Abstract:

The synthesis and studies of bridged bis-BODIPYs having spacers like thiophene, furan, N-butylcarbazole, phenylene and triphenylamine are reported.

Bridged Bis-BODIPYs: Synthesis, Structures and Properties

View Article Online
DOI: 10.1039/C5DT01925G

Praseetha E. Kesavan,[†] Sudipta Das,[†] Mohsin Y. Lone,[‡] Prakash C. Jha,[‡] Shigeki Mori[§] and Iti Gupta*[†]

[†]*Correspondence to: Dr. Iti Gupta, Indian Institute of Technology Gandhinagar, VGEC Campus, Chandkheda, Ahmedabad-382424, India. Phone: +91-9925479623, Fax: +91-23972324, E-mail: iti@iitgn.ac.in
[‡]School of Chemical Sciences, Central University of Gujarat, Gandhinagar382030, Gujarat, India
[§]Integrated Centre for Sciences, Ehime University, Matsuyama 790-8577, Japan

Abstract

A series of Bis-BODIPYs **1-6** bridged via thiophene, furan, N-alkylcarbazole, triphenyl-amine, *para*- and *meta*-phenylene groups have been synthesized and characterized by various spectroscopic techniques. The change in spectroscopic properties of Bis-BODIPYs upon varying the size of spacer was studied. X-ray crystal structures of three Bis-BODIPYs containing triphenylamine, *para*- and *meta*-phenylene bridges were solved. Intermolecular C(H)----π and π----π stacking interactions were observed in solid state structures of three Bis-BODIPYs. The dihedral angles between the spacer unit and two borondipyrrin units were lower in all three compounds as compared to their corresponding monomers. This suggests increased interactions between the two boron-dipyrrin units in molecules which in turn reflected in the anodic shifts in their reduction potentials. DFT studies indicated effective electronic interactions between spacers and two boron dipyrrins units in all the Bis-BODIPYs. The calculated HOMO-LUMO gap was found to be lower for Bis-BODIPY having bulky carbazole spacer and higher for Bis-BODIPY having smaller furan spacer. The change in spacer size clearly affected the spectroscopic properties of the Bis-BODIPYs and red shifted absorption and emission maxima were observed for Bis-BODIPYs with furan and thiophene spacers as compared to Bis-BODIPYs with phenylene or bulky aromatic spacers.

Key Words: Bis-BODIPYs, BODIPY Dimers, X-ray structures, DFT studies, Bridged BODIPYs

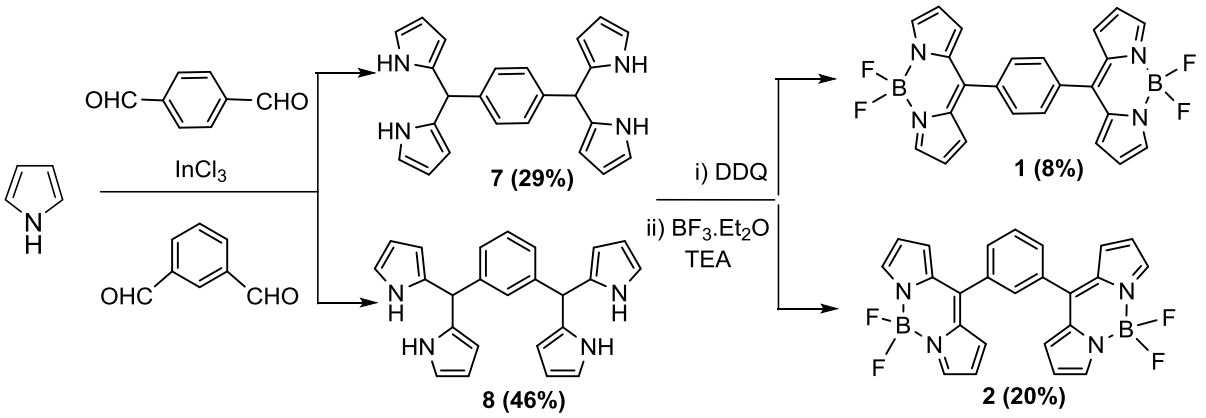
Introduction

Covalently linked pairs of chromophores have been a matter of interests for the scientific community from long time. Such chromophore dimers have been found in biology, such as photosynthetic bacterial proteins and natural light harvesting antenna systems.[1-3] Numerous artificial fluorescent dyes have been used in biosciences for cell imaging and investigation of in-vivo biological process. The boron dipyrromethenes (BODIPYs) are well known class of

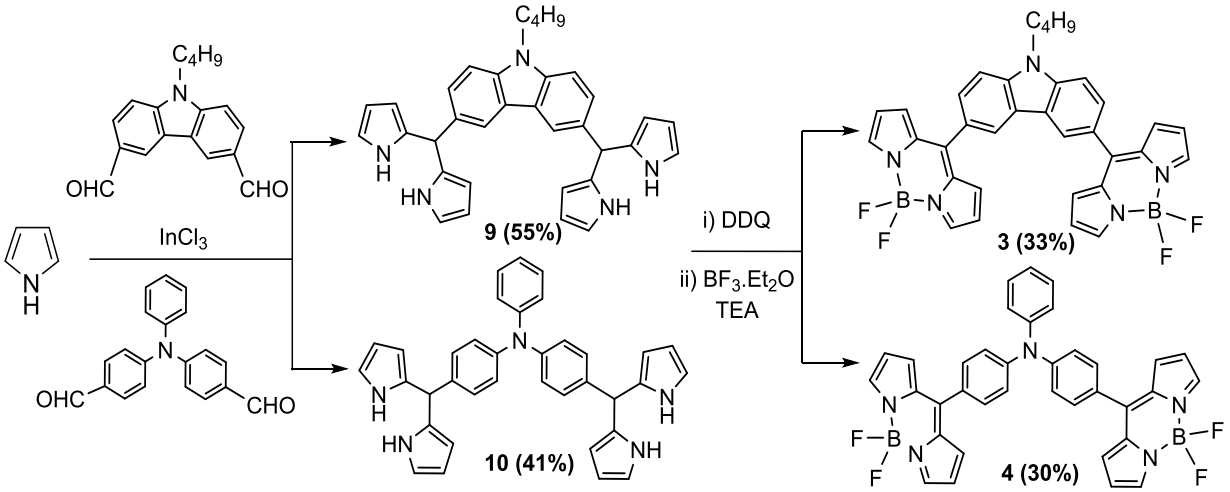
highly emissive molecules and they have been found extremely useful for biological applications, e.g. biochemical labelling,[4-6] photosensitizers for PDT (Photo Dynamic Therapy)[7] and fluorescent probes.[8-10] The electronic and photophysical properties of BODIPYs can be fine-tuned for different applications by structural modification of boron-dipyrrin core or by making their dimers and oligomers.[11] The substitution at *meso* positions of the boron dipyrrin core with bulky electron rich heterocycles could produce large Stokes Shifts of 100-120 nm.[12] The *β-β* linked dimers, *meso-meso* linked dimers and cofacial BODIPY dimers have been synthesised and studied.[13-15] Such artificial BODIPY dimers have increased Stokes Shifts, broad absorption and red shifted emission for efficient light harvesting ability for solar cells and biological applications. Recently Akkaya *et al.* have demonstrated that *meso-meso* and *meso-beta* linked BODIPY dimers can be used as singlet oxygen photosensitizer in nonpolar organic media.[16] Li and co-workers have synthesized *β–β* linked BODIPY dimers with triphenylsilylphenyl groups for increased solid state emission.[17] Bithiophene bridged BODIPY dimers have been prepared by Ziessel and co-workers with red shifted absorption and emission for future applications as NIR fluorescent probes.[18] The interesting symmetry breaking ICT (intramolecular charge transfer) properties have been observed for *p*-phenylene bridged *α*-alkylated BODIPY dimer.[19] Nishihara and co-workers have reported *p*-diethynylphenyl bridged BODIPY dimer and *meso*-alkynyl BODIPY with red shifted emission maxima.[20] Liu *et al*. have synthesized triphenylamine BODIPY monomer, bridged dimer and trimer in one pot reaction and their lasing properties in organic media were studied.[21] BODIPY dimers having bipyridine spacers with interesting ECL (electrogenerated chemiluminescence) properties have been reported by Bard and co-workers.[22] Benniston and co-workers have synthesized cofacial BODIPY dimers containing dibenzothiophene and dibenzofuran moieties; such dimers formed intramolecular excimer in emission studies.[23] Saki *et al.* have designed cofacial BODIPY dimers based on xanthene scaffold with efficient energy transfer between the two boron dipyrrins units.[24] The reports on covalently linked BODIPYs dimers are on rise but still there is a need to study the photophysical properties of *meso*-phenylene and heterocycle bridged BODIPY dimers. In this article we present the synthesis, crystal structures, photophysical and electrochemical properties of thiophene, furan, N-butyl carbazole, triphenylamine, *p*- and *m*-phenylene bridged Bis-BODIPYs. Also, DFT studies were carried out for all six Bis-BODIPYs and the HOMO-LUMO energy gap was calculated.

Results and Discussion

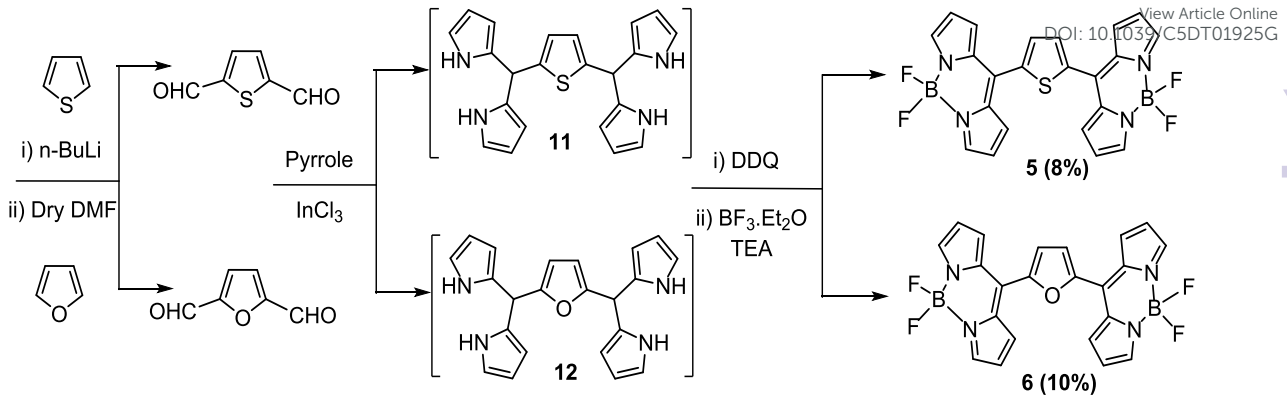
The stepwise synthesis of Bis-BODIPYs **1-6** is depicted in Schemes 1-3. The corresponding key precursors like bis-aromatic aldehydes were prepared by Vilsmeier Haack formylation reaction and bis-dipyrranes **7-12** were synthesized as per the reported procedure.[25] Terephthalaldehyde and isophthalaldehyde were condensed with pyrrole in the presence of catalytic amount indium chloride to form bis-dipyrranes **7** and **8** respectively (Scheme 1). Crude dipyrranes **7** and **8** were purified by silica gel column chromatography using 1:2:4 mixture of ethyl acetate/dichloromethane/petroleum ether in 29% and 46% yields respectively. The corresponding bis-aldehydes for bis-dipyrranes **9** and **10** were prepared by Vilsmeier Haack formylation reaction as per the reported procedure[25] (ESI). Bis-dipyrranes **9** and **10** were synthesized by indium chloride method[25] followed by silica gel column purification to yield 55% and 41% respectively (Scheme 2). The bis-dipyrranes **7-10** were oxidized by 2.4 equivalents of DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) and the resulting bis-dipyrrins were then complexed with $BF_3.OEt_2$ by doubling the equivalents of reagents required for the standard BODIPY synthetic method.[26]



Scheme 1. Synthetic route for Bis-BODIPYs **1** and **2**.



Scheme 2. Synthetic route for Bis-BODIPYs **3** and **4**.



Scheme 3. Synthetic route for Bis-BODIPYs **5** and **6**.

Silica gel column chromatographic purification afforded Bis-BODIPYs **1-4** as solid powders in 8% to 34% yields (Schemes 1, 2). In order to synthesize Bis-BODIPYs **5** and **6**, bis-formyl derivative of thiophene and furan were prepared (Scheme 3) by dilithiation of thiophene and furan followed by addition of dry DMF (N,N-dimethylformaldehyde). The bis-formylthiophene and furan were subjected to acid catalysed condensation with pyrrole to obtain the corresponding bis-dipyrranes **11** and **12**. The crude bis-dipyrrane **11** and **12** were directly used further for the next step without any purification due to their instability in column conditions. The bis-dipyrranes **11** and **12** were reacted with DDQ followed by the complexation with $BF_3.OEt_2$ in presence of TEA (triethylamine, Scheme 3). Silicagel column chromatographic purification of the crude reaction mixture in 60-70% dichloromethane/petroleum ether mixture yielded 8% of Bis-BODIPY **5** as dark orange powder and 10% of Bis-BODIPY **6** as dark brown powder.

The bis-dipyrranes **7-10** were characterized by HRMS and ^{1}H NMR spectroscopy. All Bis-BODIPYs **1-6** were characterized by HRMS, ^{1}H, ^{13}C, ^{19}F and ^{11}B spectroscopy (ESI). Molecular ion peaks in HRMS spectra of bis-dipyrranes **7-10** and bis-BODIPYs **1-6** confirmed the formation of these compounds (ESI). Also, single crystal X-ray structures were solved for Bis-BODIPYs **1**, **2** and **4**. Typically in the ^{1}H NMR of bis-dipyrranes **7** to **10** the four N-*H* protons appeared around 7.8-7.9 ppm as one singlet. The four α-pyrrole protons showed up between 6.65-6.83 ppm, whereas eight β-pyrrole protons gave two separate signals around 5.92-6.14 ppm. The two protons attached to sp^3 hybridized carbon (C-*H* protons) appeared around 5.45-5.29 ppm as one singlet (ESI). The appearance of characteristic signals for the aromatic protons present in bridging units also confirmed the

formation of bis-dipyrranes **7-10**. The formation of Bis-BODIPY **1-6** was evident in their ^{1}H NMR spectra. The representative ^{1}H, ^{19}F and ^{11}B NMR of Bis-BODIPY **6** is presented in

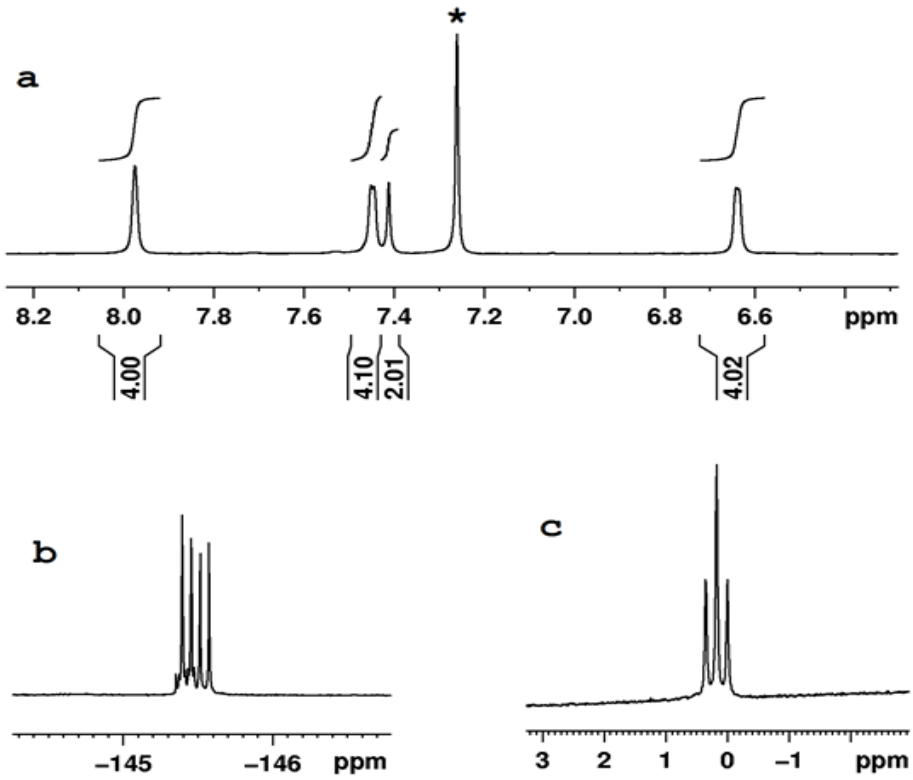


Figure 1. The NMR spectra (a) ^{1}H, (b) ^{19}F and (c) ^{11}B of Bis-BODIPY **6** in $CDCl_3$.

Figure 1. Compared to their corresponding dipyrranes proton NMRs, two protons (C-*H*) attached to sp^3 hybridized carbon and four N-*H* protons were missing in all the Bis-BODIPYs **1-6**. In the proton NMR of Bis-BODIPY **6** (Figure 1a) all the eight β-pyrrole protons appeared as two doublets at 6.64 and 7.68 ppm and the four α-pyrrole protons appeared as a singlet at 7.99 ppm. The two β-furan protons were showed up as a singlet at 7.32 ppm. As compared to the corresponding bis-dipyrranes **7-10**, the four α-pyrrole protons signal was downfield shifted and appeared around 7.93-8.01 ppm in the Bis-BODIPYs. In all Bis-BODIPYs the eight β-pyrrole protons showed up as two separate signals between at 6.61 - 7.02 ppm. In all the Bis-BODIPYs the aromatic protons of bridging spacers showed up in the range of 7.29 -7.59 ppm. The ^{19}F NMR of all Bis-BODIPYs **1-6** were recorded in $CDCl_3$ and fluorine resonance signals splitted into quartets due to the coupling with the adjacent boron atom (^{11}B, I= 3/2).[6] In ^{19}F NMR analysis of all Bis-BODIPYs **1-6**, the ^{19}F quartets appeared around -145 ppm and only one ^{19}F signal was observed due to symmetrical nature of the molecules (Figure 1b). ^{11}B NMR of all Bis-BODIPY **1-6** exhibited a triplet for ^{11}B between 0.18 and 0.36 ppm (Figure 1c).

Single crystal X-ray diffraction studies

The X-ray structures of Bis-BODIPYs **1**, **2** and **4** were determined. ORTEP views of Bis-BODIPY **1,** Bis-BODIPY **2** and Bis-BODIPY **4** are given in Figure 2. The single crystals of three Bis-BODIPYs were obtained by slow evaporation of the chloroform /n-heptane solution over a period of two weeks. The crystal structure and data refinement parameters for **1**, **2** and **4** are displayed in ESI (Table S38). Bis-BODIPY **1** (CCDC 1006185) gave red prism shaped crystals after solvent evaporation. Bis-BODIPY **1** was crystallised in monoclinic crystal system with $P2_1/c$ space group. The values of N-B-N and F-B-F angles were 106.03 ^{o}(12) and 109.12 ^{o}(13) respectively. Here two boron dipyrrin units were aligned in the same plane and the bridging phenylene ring was in a different plane. The dihedral angle between the boron dipyrrin units and the phenylene ring (C4-C5-C11-C12) was 54.00^o(18). The dihedral angle was comparatively lower than the *meso*-phenyl BODIPY[27] (reported value was 60.80^o). Bis-BODIPY **2** (CCDC 1006186) gave an orange rectangle shaped crystals on crystal growth. The crystals were monoclinic type with *I*2/a(#15) space group.

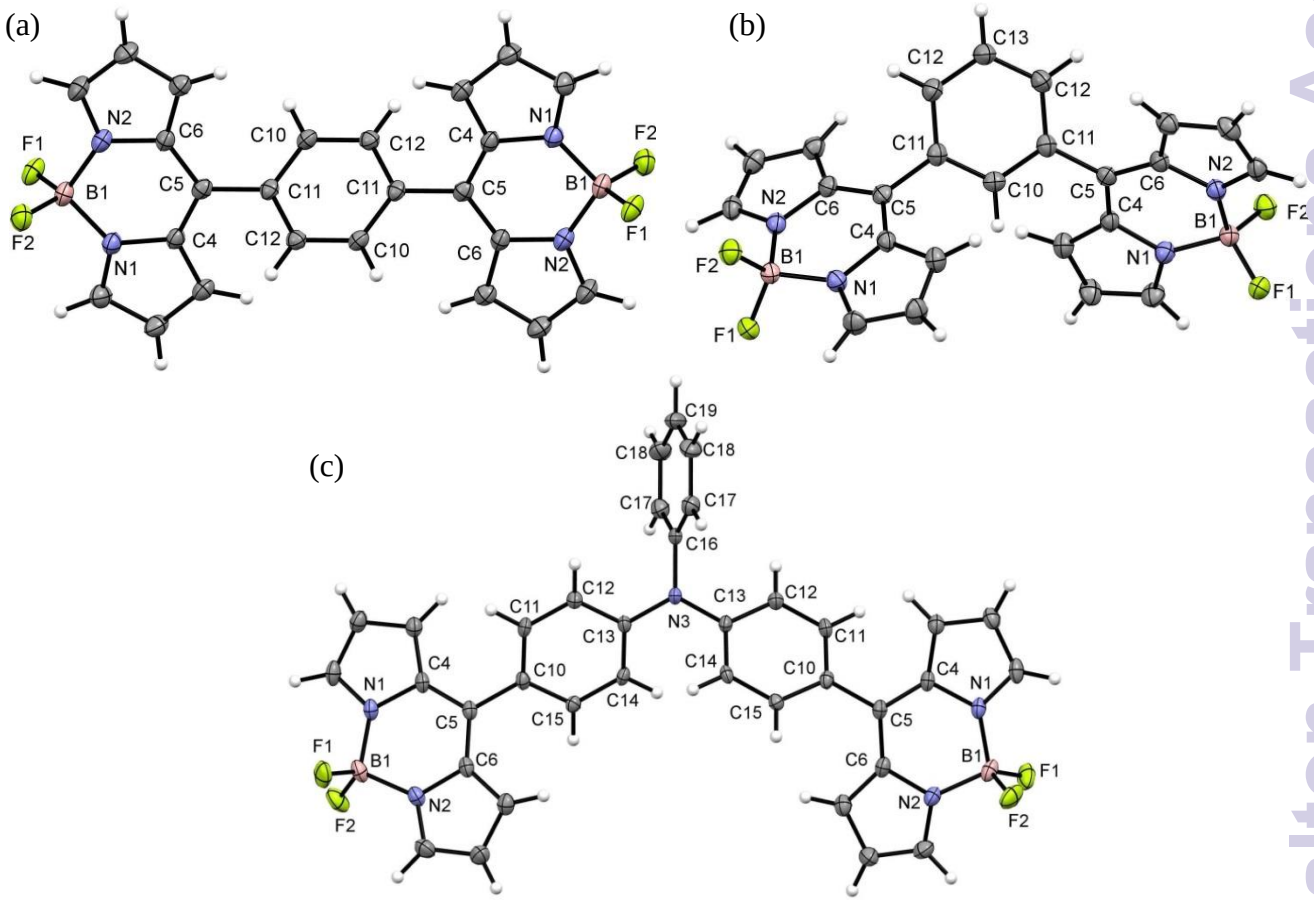


Figure 2. ORTEP views of (a) Bis-BODIPY **1**; (b) Bis-BODIPY **2** and (c) Bis-BODIPY **4.** Displacements are drawn at 50% probability level.

Table 1. Details of intermolecular interactions in the crystal structures of Bis-BODIPYs **1**, **2** and **4**.

	No.	Interaction	Distance (A^o)	Angle (^{o})
Bis-BODIPY **1**	1	C(1)-H(1)--- π (C(12) phenyl))	2.69	141.73
	2	C(2)-H(2)--- π (C(7) pyrrolic)	2.84	132.79
	3	C(3)-H(3)---B(1)	3.09	151.41
	4	C(3)-H(3)---F(1)	2.42	177.11
	5	C(7)-H(7)---F(1)	2.39	160.80
	6	C(10)-H(10)--- π (C(3) pyrrolic)	2.71	173.93
	7	(C(1) pyrrolic) π––– π (C(9) pyrrolic)	3.56(3)	_
	8	(C(2) pyrrolic) π––– π (C(7) pyrrolic)	3.55(3)	_
Bis-BODIPY **2**	1	C(1)-H(1)--- π(C(6) pyrrolic)	2.68	166.51
	2	C (1)-H(1)---N(2)	2.64	149.63
	3	C(3)-H(3)--- F(1)	2.30	164.40
	4	C(3)-H(3)---B(1)	3.06	138.83
	5	C(7)---F(1)	3.11(17)	_
	6	C(8)-H(8)---F(2)	2.58	117.53
	7	C(8)---F(2)	3.13(17)	_
	8	C(12)-H(12)---F(2)	2.64	143.28
	9	(C(1) pyrrolic) π––– π (C(8) pyrrolic)	3.54(3)	_
	10	(C(1) pyrrolic) π––– π (C(8) pyrrolic)	3.59(3)	_
	11	(C(2) pyrrolic) π––– π (C(13) phenyl)	3.48(18)	_
Bis-BODIPY **4**	1	(C(1)Pyrrolic) π––– π (C(11) phenyl)	3.26(4)	_
	2	C(8)-H(8)---F(2)	2.59	134.23
	3	C(11)-H(11)---F(1)	2.30	169.24
	4	C(12)-H(12)---F(2)	2.55	131.48
	5	(C(14)Phenyl) π––– π (C(15) phenyl)	3.31(3)	_
	6	(C(15)Phenyl) π––– π (C(15) phenyl)	3.33(3)	_
	7	C(19)-H(19)––– π (C(14) phenyl)	2.79	146.83

All three units in Bis-BODIPY **2** (two boron dipyrrin units and one phenylene unit) were aligned indifferent planes. The dihedral angle between C4-C5-C11-C10 was 52.01^o(17) and that between C6-C5-C11-C12 was 54.11^o (18). This suggested that the inward angle was lesser than the outward angle and thus the two boron-dipyrrin units are trying to come closer to each other. The values of N-B-N and F-B-F angles were 105.54^o(12) and 109.42^o(12) respectively. Bis-BODIPY **4** (CCDC 1028232) gave orange needle shaped crystals. The crystals were again monoclinic type with *C*2/c space group. The values of N-B-N and F-B-F angles were 106.21 ^{o}(15) and 109.53 ^{o}(17) respectively. The dihedral angles between the

boron dipyrrins units and the triphenylamine unit were 44.60°(3) for C4-C5-C10-C11 and 45.50°(3) for C6-C5-C10-C15. These values were much lower than that of the Bis-BODIPYs

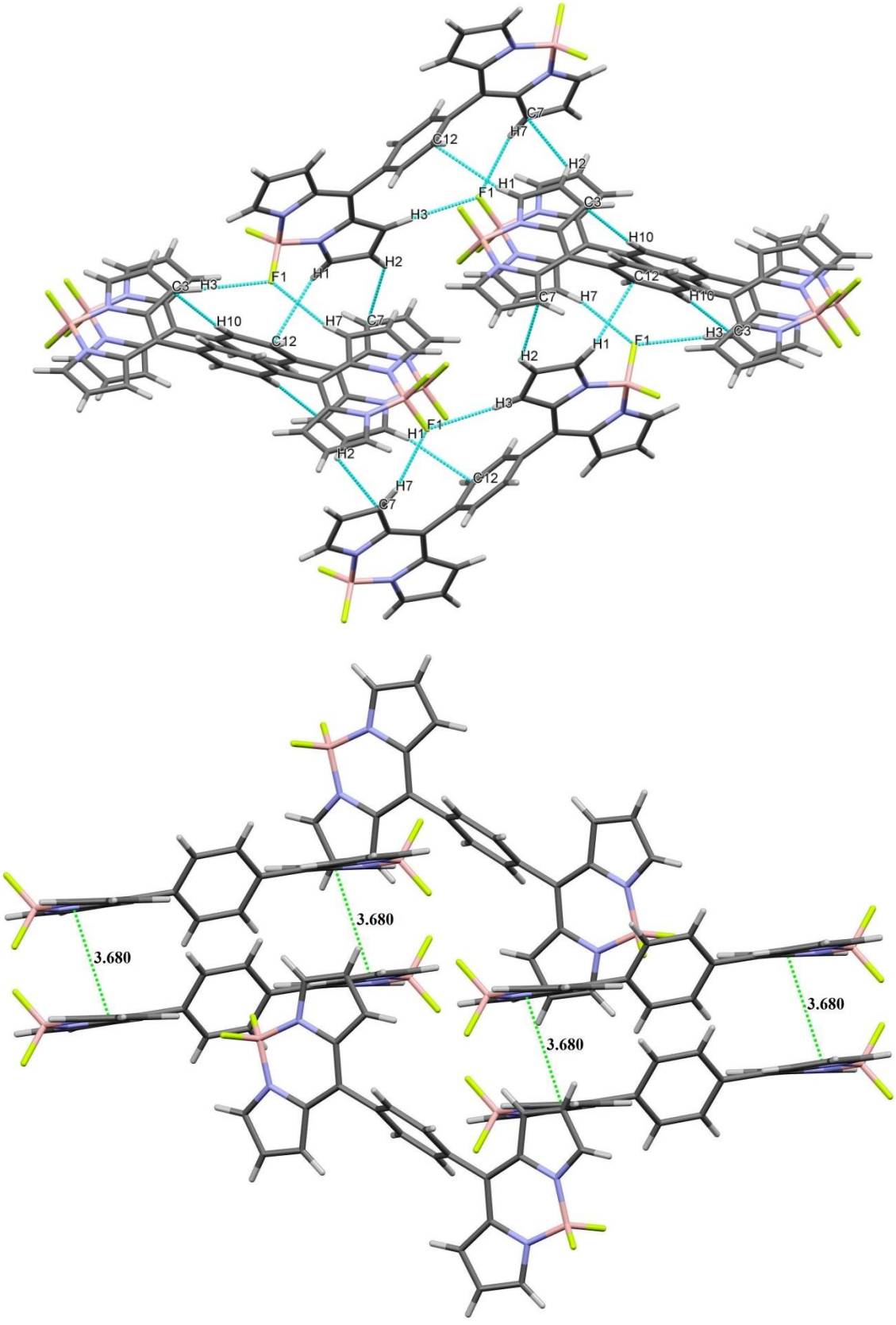


Figure 3. Packing diagram (above) and π–π stacking diagram (below) of Bis-BODIPY **1**.

View Article Online
DOI: 10.1039/C5DT01925G

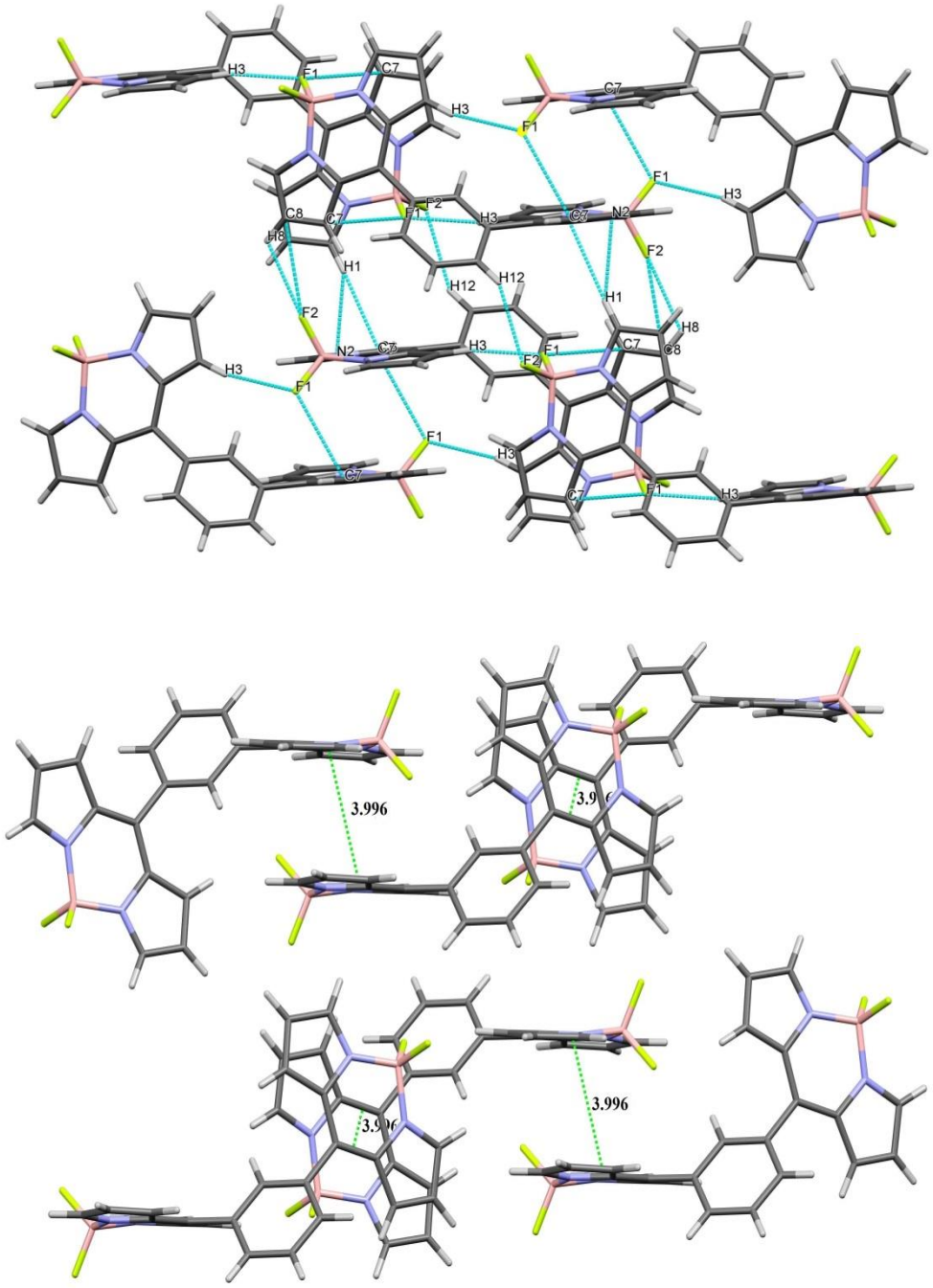


Figure 4. Packing diagram (above) and π–π stacking diagram (below) of Bis-BODIPY **2**.

1 and **2**. The N-B-N and F-B-F angles in all three Bis-BODIPYs were very similar to the reported *meso*-aryl BODIPY monomer. All three Bis-BODIPYs **1**, **2** and **4** exhibited supramolecular interactions in their packing diagrams and the distances and angles of the interactions in the packing mode are presented in Table 1. Bis-BODIPY **1** has formed layered structure in 3D framework through weak hydrogen bonding (C-H---F) and C-H---π interactions (Table 1). In crystal packing, one layer was connected to the other via a mutual

C(2)-H (2)---π (pyrrolic) and C(10)-H (10)---π (pyrrolic) interactions (Figure 3). In packing diagram of Bis-BODIPY **2**, molecules were connected through an antiparallel head to tail interaction via two mutual C(7)---F(1) interactions. Two boron dipyrrins units were connected to each other through C(3)-H(3)---F(1) and C(3)-H(3)---B(1) type weak intermolecular interactions to form stacked 3D network (Figure 3). One layer was also connected to other through C(1)-H(1)---π (pyrrolic), C(1)- H(1)---N(2) and C(8)-H(8)---F(2) interactions (Figure 4). The metric parameters for the interactions in Bis-BODIPY **1** and **2** were, C-H---π (pyrrolic) distances 2.69 to 2.84 Å and C-H---π (pyrrolic) angles 132.79^{o} and 173.93^{o} respectively (Table 1). In the crystal packing mode of Bis-BODIPY **4**, it formed a cluster of five molecules with the help of several intermolecular interactions (Figure S37, ESI). It included weak π---π interactions, hydrogen bonding and C-H---π interactions. These clusters were connected through C(11)-H(11)---F(1) to form the 3D structure of Bis-BODIPY **4**.

Photophysical properties

UV-vis absorption and fluorescence studies

The UV/vis absorption, fluorescence spectra and fluorescence lifetimes of Bis-BODIPY **1-6** were examined in five different solvents. The absorption spectra of compounds **1-6** are presented in Figure 5 and photophysical properties are summarized in Table 2. Bis-BODIPYs **1-4** showed slight polarity dependence and exhibited a strong absorption band around at 500 nm with a shoulder around at 480 nm. The strong absorption at 500 nm is attributed to a strong S_0-S_1 electronic transition and the shoulder band corresponds to S_0-S_1 vibrational

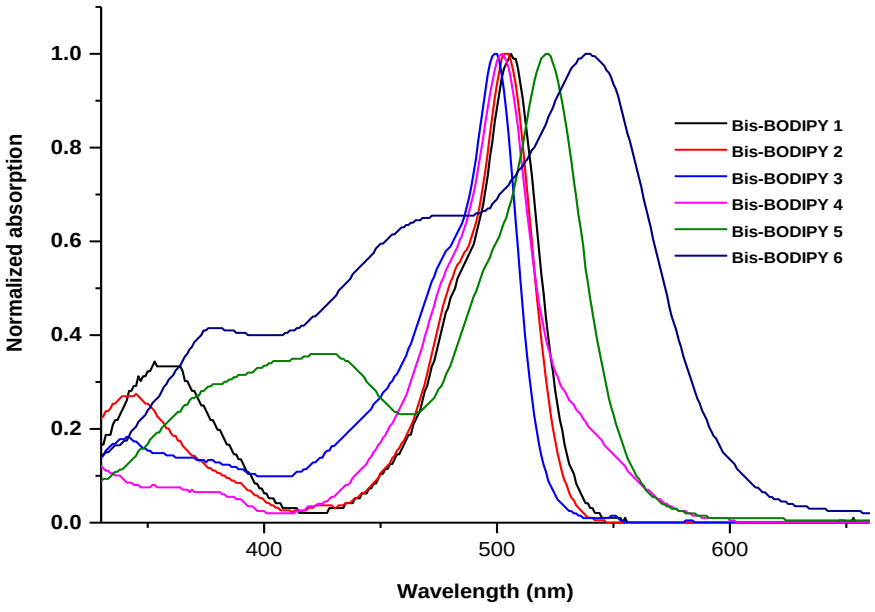


Figure 5. Comparison of normalized absorption spectra of compounds **1-6** in chloroform.

Table 2. Photophysical data of compounds**1-6** in different solvents. Concentration used was 2.4 x 10^{-6} M.

Compound	Solvent	λ_{abs} (nm)	$fwhm_{abs}$ (cm^{-1})	logε	λ_{emi} (cm^{-1})	$fwhm_{em}$ (cm^{-1})	$\Delta\nu_{st}$ (cm^{-1})	Φ_f	τ (ns)	k_r (10^9 s^{-1})	k_{nr} (10^9 s^{-1})
Bis-BODIPY	Toluene	506	1510	4.63	539	1675	1210	0.014	0.08	0.18	10.75
1	Dichloromethane	504	1485	4.46	531	1618	1009	0.012	0.07	0.17	14.11
	Chloroform	506	1516	4.59	534	1517	1036	0.015	0.08	0.19	12.31
	Tetrahydrofuran	503	1581	4.69	532	1731	1084	0.0085	0.06	0.14	16.53
	Acetonitrile	498	1610	4.75	526	1680	1069	0.0009	0.02	0.045	49.95
Bis-BODIPY	Toluene	503	1497	4.82	529	1502	977	0.051	0.27	0.19	3.51
2	Dichloromethane	502	1503	4.34	525	1335	873	0.042	0.26	0.16	3.68
	Chloroform	504	1534	4.89	527	1311	866	0.048	0.20	0.24	4.76
	Tetrahydrofuran	501	1638	4.52	525	1388	912	0.031	0.23	0.14	4.21
	Acetonitrile	496	1650	4.75	520	1428	931	0.009	0.04	0.23	24.78
Bis-BODIPY	Toluene	--	--	--	--	--	--	--	--	--	--
3	Dichloromethane	498	1630	4.66	581	3337	2869	0.173	2.90	0.06	0.29
	Chloroform	499	1724	4.74	517	2115	698	0.196	1.08	0.18	0.74
	Tetrahydrofuran	497	1637	4.91	569	3235	2546	0.18	0.07	0.07	0.30
	Acetonitrile	--	--	--	--	--	--	--	--	--	--
Bis-BODIPY	Toluene	503	1659	4.88	585	1953	2787	0.41	3.43	0.12	0.17
4	Dichloromethane	501	1724	4.69	680	2457	5254	0.018	2.18	0.008	0.38
	Chloroform	502	1666	4.80	633	2472	4123	0.135	4.12	0.033	0.21
	Tetrahydrofuran	500	1769	4.98	667	3981	5007	0.025	1.65	0.015	0.59
	Acetonitrile	495	1844	4.60	--	--	--	--	--	--	--
Bis-BODIPY	Toluene	523	1796	4.28	531	3423	288	0.012	--	--	--
5	Dichloromethane	520	1863	4.23	521	1977	37	0.009	0.03	0.3	33.03
	Chloroform	522	1772	4.30	529	2943	253	0.025	--	--	--
	Tetrahydrofuran	517	1895	4.42	524	2393	528	0.005	--	--	--
	Acetonitrile	513	1416	4.32	526	1993	482	0.0002	--	--	--
Bis-BODIPY	Toluene	542	5313	4.18	633	--	2652	0.0018	--	--	--
6	Dichloromethane	537	5235	4.15	627	--	2673	0.00087	0.06	0.0145	16.65
	Chloroform	539	5612	4.03	610	--	2159	0.0019	--	--	--
	Tetrahydrofuran	535	4983	4.33	576	--	1330	0.0016	--	--	--
	Acetonitrile	529	4831	4.05	577	--	1573	0.00038	--	--	--

$k_r = \Phi_f/\tau$ and $k_{nr} = (1-\Phi_f)/\tau$

transition. The broader and weaker band centred at 350 nm in Bis-BODIPYs **1-2** and around 380 nm in Bis-BODIPYs **3-4** was assigned to the higher energy S_0-S_2 electronic transition. The wavelength of major absorption band in Bis-BODIPYs **1-2** in toluene was comparable with that of the *meso*-phenyl BODIPY monomer.[28] Also, the absorption maxima varied slightly (2-8 nm) upon changing the solvent polarity from toluene to acetonitrile (ESI), reflecting the typical behavior of BODIPY chromophores.[11] The wavelength of major absorption band of Bis-BODIPYs **3** and **4** was similar to the corresponding *meso*-carbazole BODIPY (497 nm)[12] and *meso*-triphenylamine substituted BODIPY (500 nm).[29] Bis-BODIPY **5** and **6** exhibited 17 nm red shifted absorption band with reduced extinction coefficient as compared to the corresponding *meso*-thienyl- and *meso*-furyl-BODIPY monomers.[30,31] shifted by 18 nm in the former. The $fwhm_{abs}$ (full width at half maxima of major absorption band) of all the compounds **1-6** were calculated in different solvents (Table

2). Solvent polarity affected the broadening of the absorption band. Thus $fwhm_{abs}$ values of Bis-BODIPY **1-6** were appeared as lower in non-polar solvent (toluene) and higher in polar solvents (acetonitrile, tetrahydrofuran) for our compounds. This trend was in agreement with the *meso*-aryl BODIPYs. Compared to Bis-BODIPYs **1-4**, Bis-BODIPYs **5** and **6** showed more solvent polarity dependence. As polarity of the solvent is increased, the absorption maxima were shifted to blue region. Among all compounds, Bis-BODIPY **6** showed significantly large $fwhm_{abs}$ values, which suggests that significant changes occurred in bond lengths / bond angles upon excitation.[32]

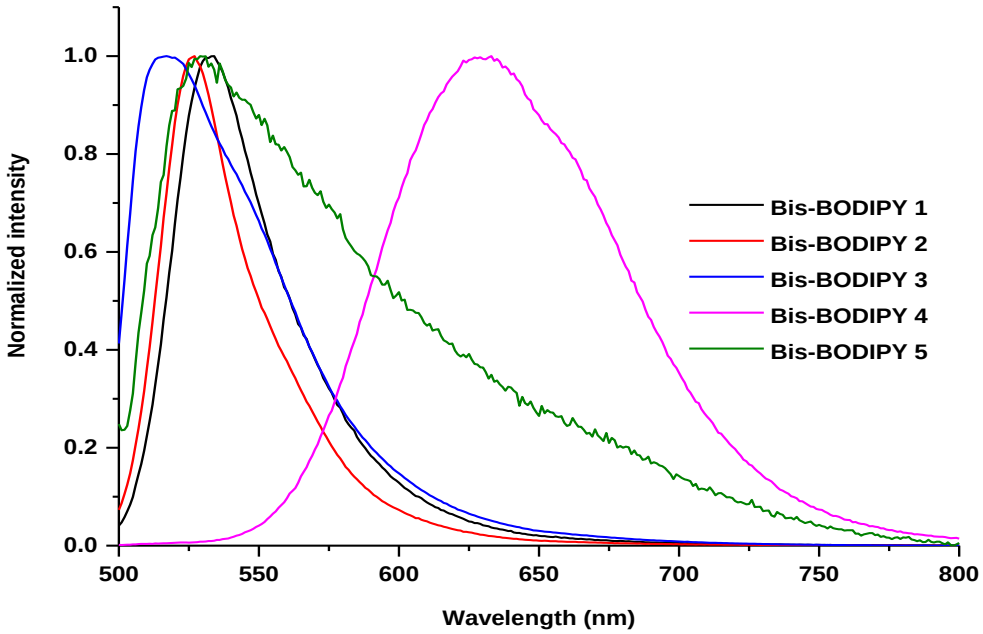


Figure 6. Comparison of normalized emission spectra of compounds **1-5** in chloroform (λ_{ex} = 488 nm).

A comparison of emission spectra of **1-5** is shown in Figure 6 and solvatochromism data is given in Table 2. The typical mirror-image relationship was observed for the lowest energy absorption band and emission spectra for Bis-BODIPYs **1-5**. The emission maxima for compounds **1** and **2** were blue shifted by 41 and 34 nm respectively as compared to that of *meso*-phenyl BODIPY (in chloroform). The $fwhm_{em}$ (full width at half maxima of emission band) and quantum yields of all the compounds **1-6** were calculated in different solvents (Table 2). Solvent polarity affected the broadening of the emission bands and typically $fwhm_{em}$ values were lower in non-polar solvent (toluene) and higher in polar solvents for our compounds. The fluorescence quantum yields for Bis-BODIPY **1-2** were lower than *meso*-phenyl BODIPY (0.06 in toluene).[28] Usually the *meso*-aryl BODIPYs showed 10-15 nm

Stokes shifts whereas these values were 26-33 nm for Bis-BODIPYs **1** and **2**. In polar media red shifted emission maxima reflects larger dipoles of the CT excited states, which was in agreement with the report by N. Boens et al.[32] The fluorescence quantum yields for Bis-BODIPY **3** and **4** were higher than the corresponding *meso*-carbazole- and meso-triphenylamine-BODIPY monomers.[12, 29] The Stokes shifts values were highest for compound **4** among all the Bis-BODIPYs **1-6**. The emission maxima were red shifted for Bis-BODIPY **5** and **6** as compared to the corresponding *meso*-thienyl- and *meso*-furyl-BODIPY monomer. However, the quantum yields were lower for both the Bis-BODIPYs **5** and **6** as compared to their corresponding BODIPY monomers.[30, 31]

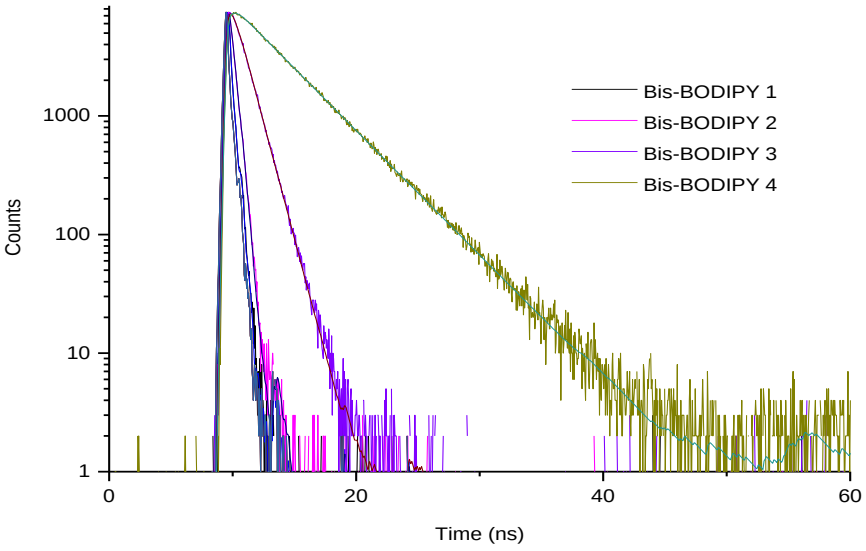


Figure 7. Fluorescence decay profiles of compounds **1-4** in chloroform. The excitation wavelength was 515 nm, collected at their respective emission maxima.

Among all the Bis-BODIPYs, compounds **3** and **4** showed higher quantum yields than **1-2** and **5-6**. Higher quantum yield indicates the possibility of restricted rotation of the two boron-dipyrrin units in Bis-BODIPYs **3** and **4** due to bulky spacer; it was supported by the fact that much lower rate constant values (k_{nr}, see Table 2) were observed for non-radiative decay processes in these two compounds. The lower quantum yields for compounds **1**, **2**, **5** and **6** suggests that other non-radiative decay processes (such as internal conversion or intersystem crossing from S_1 to T_1) might be more feasible in these compounds.[27] Also, the quantum yields of bis-BODIPYS **5** and **6** were much lower than other compounds could be associated with the electron donating ability of the heteroatom present in the bridging unit.[30] The quantum yields of Bis-BODIPYs **1-6** were higher in non-polar solvent (toluene) and lower in polar solvents (tetrahydrofuran); this is due to the large dipole moment difference

between CT excited state and ground state which in turn facilitate internal conversion in polar media.[32] The time-correlated single photon counting technique was used to measure the singlet state life times τ of Bis-BODIPYs **1-6**. The fluorescence decay of compounds **1-4** were fitted to a single exponential decay (Figure 7). However, in the case of Bis-BODIPYs **5** and **6** decay profiles fitted to three exponential decays (ESI). The bridging phenylene unit is more rigid in bis-BODIPY **2** as compared to bis-BODIPY **1** (Table 2), thus the non-radiative decay processes are less prominent in **2**. It has been reported that the *meso*-mesityl-BODIPY showed higher quantum yields and singlet state lifetimes than *meso*-phenyl BODIPY, because the hindered rotation of bulky mesityl group leads to drastic decrease in internal conversion process.[27] Therefore, the quantum yields and singlet state lifetimes of bis-BODIPY **2** are higher than the bis-BODIPY **1;** this was again supported by the lower value of non-radiative decay constant for **2** than **1** (Table 2). For Bis-BODIPYs **1-4** singlet state life times τ, were lower than their corresponding BODIPY monomers For example Bis-BODIPY **3** has life time of 1.9 ns in $CHCl_3$, whereas *meso*-carbazole BODIPY has 3.37 ns in same solvent.[12] The decrease in radiative decay constant k_r and the increase in non-radiative decay constant k_{nr} were in line with the quantum yield data.

Computational details

The ground state geometry optimization of the molecules **1-6** were performed with density functional theory (DFT) at B3LYP/6-31G (d) level,[33-35] using Gaussian 09 program package.[36] Frequency calculations were performed to guarantee the optimized geometriesare at energy minima on the potential energy surface. The vertical excitation energies were calculated employing time dependent density functional theory (TD-DFT) approach at the same functional and basis set.

Comparison of geometrical parameters

It is imperative to compare the vital structural parameters obtained as a result of geometry optimization of the molecules **1**, **2** and **4** with the X-ray crystallography results (ESI). To be more precise, the largest deviations in the bond lengths of the molecule **1**, **2** and **4** are 0.017 Å, 0.025 Å and 0.021 Å respectively. The deviations from the X-ray geometry is reflected from bond angles of the molecules (**1, 2** and **4**) and are found to be 2.59°, 2.29° and 1.43° respectively. Moreover, the maximum deviations of optimized dihedral angle in **1**, **2** and **4** are 6.14°, 12.54° and 8.87° respectively. The computed results compare well with the

experimental data, thereby providing reliable support for the use of selected level of theory for structural and spectroscopic studies of the rest of molecules.

Absorption studies

To get detailed insight into the roots of absorption bands the singlet-singlet transition of BODIPY molecules were simulated using TD-DFT/B3LYP level of theory at valence double-ζ6-31G(d) basis set.The gas phase determined electronic spectra exhibit number of absorption peaks and the peaks with maximum wavelength absorption (λ_{max}) were selected for the comparison.The effect of solvent polarities has not being taken into account as it is obvious from experimental results. Ineffectiveness of the solvent polarity on λ_{max} excludes any ground state intramolecular charge transfer (ICT) process of the molecules under consideration.[37] The lowest energy absorption maxima of molecules **1-6** are summarised in Table 3. The λ_{max} of **1**, **2**, **3** and **4** were observed at around 500 nm and for **5** and **6**, the red-shifted bands at 522 and 539 nm respectively indicate lower HOMO-LUMO gap, which is supported by DFT studies. The delocalization of frontier molecular orbitals (FMO's) of the compounds **1-6** indicated the significant electronic conjugation between the boron dipyrrin units and the spacers. Interestingly the HOMO-LUMO gap for **6** (2.513 eV) is less than that of **1** (2.877 eV), **2** (3.040 eV), **3** (3.050 eV), **4** (2.812 eV) and **5** (2.770 eV). Though DFT produced HOMO-LUMO gaps do not directly corroborate the experimentally observed (UV-Vis) energy gap values but, almost same trend of band gap increment (**3** > **2**> **1** > **4** > **5** >**6**) is reflected. For Bis-BODIPY **3**, in-spite of highest HOMO energy level, the most destabilized LUMO resulted in its highest HOMO-LUMO gap. On the other hand for Bis-BODIPY **6** the destabilization of the LUMO is considerably less because of approximately planar arrangement of the furan spacer increasing the level of effective conjugation, resulting in a HOMO-LUMO gap that was lower than rest of the molecules **1**, **2**, **3**, **4** and **5**.

Table 3. Absorption data of Bis-BODIPYs **1-6**

	Experimental λ_{max}(nm)	logϵ	Calculated λ_{max}(nm)	(F)
Bis-BODIPY **1**	506	4.59	472.02	0.0631
Bis-BODIPY **2**	504	4.89	466.98	0.0029
Bis-BODIPY **3**	499	4.74	445.05	0.2490
Bis-BODIPY **4**	502	4.80	520.17	0.0411
Bis-BODIPY **5**	522	4.30	493.65	0.0390
Bis-BODIPY **6**	539	4.03	541.08	0.0440

ϵ, is molar extinction coefficient and F, is oscillator strength.

View Article Online
DOI: 10.1039/C5DT01925G

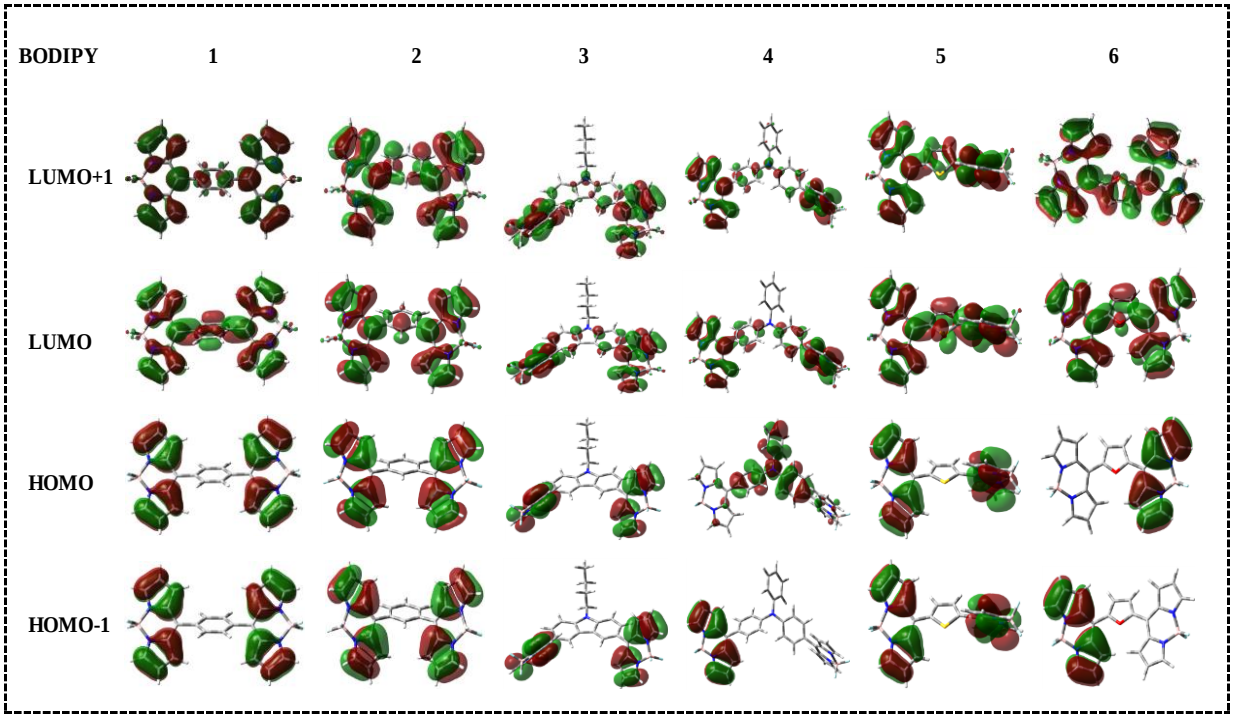


Figure 8. Frontier molecular orbitals of Bis-BODIPYs **1-6** at B3LYP/6-31G(d) level for all the atoms.

The frontier molecular orbitals of the molecules **1-6** are displayed in Figure 8. The distribution of HOMO and LUMO reflects the strong donor-acceptor interactions. In Bis-BODIPY **1, 2, 3** and **5**, the HOMO was localized on the BODIPY moiety and the LUMO was shifted to the corresponding spacer groups. On the other hand in **4** and **6**, the HOMO was localized on the spacer moieties whereas the LUMO was budged to the BODIPY moiety. The major absorption band in the electronic absorption spectra of molecule **1-6** is related to the BODIPY absorption which reflects that the origin of major absorption peaks is from HOMO energy levels. It can be seen that the TD-DFT calculations were in good agreement with the experimental results and unveil that the main transitions for **1**, **2**, **3**, **4**, **5** and **6** are from HOMO → LUMO, HOMO → LUMO+1, HOMO → LUMO+1, HOMO → LUMO, HOMO → LUMO and HOMO → LUMO+1 respectively.

Electrochemical Studies

The cyclic voltammetry measurements of Bis-BODIPYs **1-6** were carried out at the scan rate of 50 mV/s using tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The redox potential data and a comparison of reduction waves are summarised in the Table 4 and Figure 9 respectively. All the Bis-BODIPYs showed only reduction peaks. Bis-BODIPY **1**

showed two reduction peaks. The first reduction peak was chemically reversible at -0.49V and the other one was chemically irreversible around -1.75V. Bis-BODIPY **2** showed three reduction waves, two reversible and one irreversible.

Table 4. Electrochemical redox data (V) of compounds **1-6** in dichloromethane, containing 0.1 M TBAP as supporting electrolyte recorded at 50 mV/s scan speed.

	E_{red}(V *vs* SCE)		
	I	II	III
Bis-BODIPY **1**	-0.49	-1.75	-
Bis-BODIPY **2**	-0.55	-0.67	-1.67
Bis-BODIPY **3**	-0.66	-1.72	-
Bis-BODIPY **4**	-0.64	-1.36	-
Bis-BODIPY **5**	-0.17	-	-
Bis-BODIPY **6**	-0.17	-	-

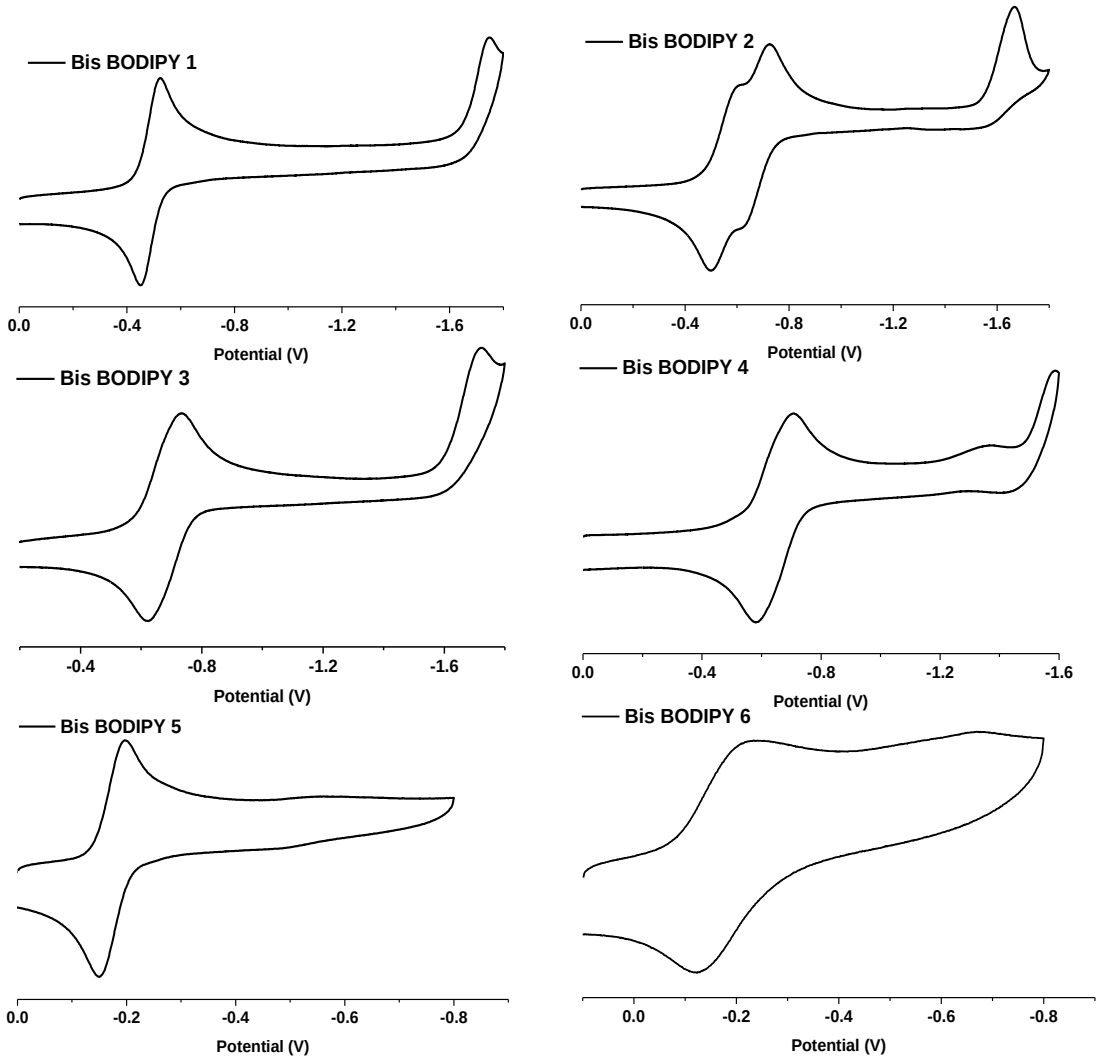


Figure 9. Comparison of cyclic voltammograms of compounds **1-6** in dichloromethane, containing 0.1 M TBAP as supporting electrolyte recorded at 50 mV/s scan speed (V vs. SCE).

View Article Online
DOI: 10.1039/C5DT01925G

The reported *meso*-tolyl BODIPY monomer, showed two reduction peaks at -0.788 and -1.81 V. As compared to the reduction potentials of *meso*-tolyl BODIPY,[31] the first reduction potential of both Bis-BODIPY **1** and **2** exhibited anodic shift; i.e. they were much easier to reduce compared to the monomer *meso*-tolyl BODIPY. Bis-BODIPY **3** also showed two reduction waves. The first reduction potential of Bis-BODIPY **3** was shifted towards the less negative side by 50 mV as compared to its corresponding monomer.[12] This reflects that the compound **3** was much easier to reduce compared to the monomer. Bis -BODIPY **4** also showed two reduction waves with a reduction potential at -0.64 V and -1.36 V. Bis-BODIPY **5** and **6** showed single reduction waves with a reduction potential around -0.17 V. The reported first reduction potential for monomeric *meso*-furyl BODIPY was -0.66 V.[31] The electrochemical study of compound **1-6** suggests that compared to their corresponding BODIPY monomers, the reduction potentials of **1-6** were low and they were very easy to reduce.

Conclusion

In conclusion, we have synthesized and characterized six boron-dipyrrins containing bridging arene or heterocyclic ring. Their absorption, emission, electrochemical and time resolved florescence studies were carried out. By changing the spacer size from bulky carbazole to phenylene to smaller thiophene and furan rings affected the spectroscopic properties of Bis-BODIPYs. The absorption and emission maxima were blue shifted for Bis-BODIPYs having bulky aromatic spacers and red shifted for Bis-BODIPYs having smaller thiophene/furan spacers. Also, the X-ray crystal structures of three Bis-BODIPYs were solved. The reduced dihedral angle between the bridging ring and dipyrrin core in all three crystal structures indicated better interactions between the two constituting boron dipyrrin units. Also, phenyl bridged Bis-BODIPYs showed C-H---π (pyrrolic) and π---π interactions in 3D structures. DFT calculations showed largest HOMO-LUMO gap for **3** and lowest for **6**. Also, gas phase absorption maxima calculated for **1-6** were closer to the experimental values. The observed anodic shifts in the reduction potentials of all six Bis-BODIPYs suggested increased electronic interactions between two boron dipyrrin units within the molecule. Also, as compared to their corresponding monomer BODIPYs all six Bis-BODIPYs were easier to reduce.

EXPERIMENTAL

View Article Online
DOI: 10.1039/C5DT01925G

General Methods and Reagents

Unless otherwise mentioned, all the reagents and solvents were purchased from Aldrich, Acros Organics or Merck and used without further purification. Pyrrole was distilled under vacuum prior to use. Silica gel (60-120 mesh size) used for column chromatography were procured from Merck. The solution NMR spectra of compounds were recorded with Bruker Avance III 500 MHz NMR spectrometer at IIT Gandhinagar. Absorption spectra were recorded with Shimadzu UV-1700 and Fluorescence emission studies were performed using Horiba-Jobin Yvon Fluolorog-3 Spectrometer at IIT Gandhinagar. The fluorescence quantum yields (Φ_f) were estimated from the emission and absorption spectra by a comparative method at the excitation wavelength of 488 nm using Rhodamine B (Φ_f = 0.49) in ethanol as the standard. The time-resolved fluorescence decay measurements were carried out at IIT Gandhinagar using a pico-second-diode-laser-based, time-correlated, single-photon counting (TCSPC) fluorescence spectrometer from Edinburgh Instruments Ltd., LifespecII, (Livingston, UK). Cyclic voltammetric (CV) studies were carried out with an electrochemical system utilizing the three electrode configuration consisting of a glassy carbon (working electrode), platinum wire (auxiliary electrode) and saturated calomel (reference electrode) electrodes. The experiments were done in dry dichloromethane using 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. All potentials were calibrated vs. saturated calomel electrode by the addition of ferrocene as an internal standard, taking E ½ (Fc/Fc^+) = 0.51 V vs. SCE.

Synthesis of bis-dipyrrane 7

To a stirred solution of terephthaldehyde (500 mg, 3.72 mmol) and pyrrole (38.79 mL, 559.14 mmol), acid catalyst ($InCl_3$, 82.49 mg, 0.37 mmol) was added at room temperature. The reaction mixture was allowed to stir for 2 h at room temperature under N_2 atmosphere. After stirring for 2 h, excess pyrrole was removed by distillation under reduced pressure. The crude residue was dissolved in small amount of dichloromethane and purified by column chromatography on silica gel (ethyl acetate/ dichloromethane/ hexane = 1:2:4) to give **7** as pale yellow powder. Yield: 29 % (400 mg). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.921 (bs, 4H), 7.170 (s, 4H), 6.695- 6.692 (d, *J* = 1.5 Hz, 4H), 6.160- 6.143 (m, 4H), 5.914 (s, 4H), 5.45 (s, 2H). HRMS [ESI]: calcd for $C_{24}H_{21}N_4$ [$(M-H)^+$]: *m/z* 365.1766 Obsvd: *m/z* 365.1769.

View Article Online
DOI: 10.1039/C5DT01925G

Synthesis of bis-dipyrrane 8

Isophthalaldehyde (600 mg, 4.47 mmol) and pyrrole (150 eq., 46.5 mL, 670 mmol) were taken in an 100 mL round bottom flask and stirred for 5 minutes under nitrogen at room temperature. After stirring for 5 min $InCl_3$ (0.1 eq., 98.91 mg, 0.44 mmol) was added and the reaction mixture was allowed to stir for another 2h. By vacuum distillation, the excess pyrrole was removed. The crude mixture was subjected to silica gel column chromatography (ethyl acetate/ dichloromethane/ hexane = 1:2:4) to isolate the desired compound **8** as a sticky yellow solid in 46% (750 mg). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.862 (bs, 4H), 7.263-7.233 (t, *J* = 6 Hz 1H), 7.121 (s, 1H), 7.089-7.074 (dd, 2H), 6.654-6.651 (d, *J* = 1.5 Hz, 4H) 6.140-6.123 (m, 4H), 5.864 (s, 4H), 5.367 (s, 2H). HRMS [ESI]: calcd for $C_{24}H_{21}N_4$ [(M-H)$^+$]: *m/z* 365.1766 Obsvd: *m/z* 365.1769.

Synthesis of bis-dipyrrane 9

N-butylcarbazolebis-aldehyde (500 mg, 1.78mmol) was dissolved in pyrrole (150 eq., 18.63 mL, 268.51 mmol) under a nitrogen atmosphere. After 5 min $InCl_3$ (0.1eq. 39.49 mg, 0.18 mmol) was added and the reaction mixture was allowed to be stirred for 2h. Excess pyrrole was removed by vacuum distillation The desired compound **9** was isolated via column chromatography (ethyl acetate/dichloromethane/hexane = 5:20:75) in 55%(550 mg). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.94 (s, 4H), 7.32 (s, 4H), 6.68 (s, 4H), 6.16 (d, *J*= 3 Hz, 4H), 5.96 (s, 4H), 5.62 (s, 2H), 4.26 (t, *J* = 7 Hz, 2H), 1.82 (m, 2H), 1.41 (m, 2H), 0.93 (m, 3H). HRMS [ESI]: calcd for $C_{34}H_{32}N_5$ [(M-H)$^+$]: *m/z* 510.2658 Obsvd: *m/z* 510.2657.

Synthesis of bis-dipyrrane 10

To a stirred solution of triphenylaminebis-aldehyde (700 mg, 2.32 mmol) and pyrrole (24.12 mL, 347.68 mmol), $InCl_3$ (51 mg, 0.23 mmol) was added. The reaction mixture was protected from light and kept for stirring under nitrogen for 8 h at room temperature. After verifying the formation of the compound by TLC, excess pyrrole was vacuum distilled and the crude compound was subjected to silica gel column chromatography. The desired compound **10** was eluted with 60% dichloromethane/hexane. Yield: 41 % (510 mg). ^{1}H NMR (500 MHz, $CDCl_3$,δ ppm): 7.93 (s, 4H), 7.07 (m, 7H), 7.00 (d, *J*= 8 Hz, 6H), 6.70 (s, 4H), 6.16 (d, *J* = 2.5 Hz, 4H), 5.93 (s, 4H), 5.41 (s, 2H). HRMS [ESI]: calcd for $C_{36}H_{32}N_5$ [(M+H)$^+$]: *m/z* 534.2658 Obsvd: *m/z* 534.2664.

View Article Online
DOI: 10.1039/C5DT01925G

Synthesis of Bis-BODIPY 1

Bis-dipyrrane **7** (200 mg 0.54 mmol) was dissolved in dichloromethane (75 mL) and oxidized with DDQ (297 mg, 1.3mmol 2.4 eq.) at RT under air. The reaction mixture was allowed to stir at room temperature for 1h. Triethylamine (6.1 mL, 80 eq.) followed by $BF_3{\cdot}Et_2O$ (6.80mL, 100 eq.) was added to the reaction mixture successively, without any time delay. The stirring was continued at room temperature for additional 30 min., the reaction mixture was evaporated and the crude product was purified by silica gel column chromatography and eluted with a ethyl acetate/dichloromethane/petroleum ether (5:15:80) mixture to afford Bis-BODIPY **1** as orange powder in 8% yield (20 mg). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 8.008 (s, 4H), 7.761 (s, 4H), 7.002-6.994 (d, *J* = 3.5 Hz, 4H), 6.615-6.609 (d, *J* = 3 Hz). ^{13}C NMR (125.7 MHz, $CDCl_3$, δ ppm): 145.44, 144.96, 136.15, 134.77, 131.47, 130.49, 119.03. ^{19}F NMR (470.4 MHz, $CDCl_3$, δ ppm): -145.03 (q, 4F). ^{11}B NMR (160 MHz, $CDCl_3$, δ ppm): 0.29 (t, 2B). HRMS [ESI]: calcd for $C_{24}H_{16}B_2F_3N_4$ $[(M\text{-}F)^+]$: *m/z* 439.1513 Obsvd: *m/z* 439.1520.

Synthesis of Bis-BODIPY 2

Bis-dipyrrane **8** (200 mg 0.54 mmol) was dissolved in dichloromethane (75 mL) and oxidized with DDQ (297 mg, 1.3mmol 2.4 eq.) at RT under air. The reaction mixture was allowed to stir at room temperature for 1h. Triethylamine (6.1 mL, 80 eq.) and $BF_3{\cdot}Et_2O$ (6.8mL, 100 eq.) were added to the reaction mixture without any time delay. The stirring was continued at room temperature for another 30 min, after this reaction mixture was evaporated and the crude product was purified by silica gel column chromatography. The column was eluted with ethyl acetate/dichloromethane/petroleum ether (5:15:80) mixture to afford Bis-BODIPY **2** as orange powder in 20% yield (50 mg). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.988 (s, 4H), 7.817-7.790 (t, *J* = 7.5Hz, 3H), 7.745-7.715 (d, *J* = 7.5 Hz, 1H), 6.944-6.938 (d, *J* = 3 Hz, 4H), 6.593-6.589 (d, *J* = 2 Hz 4H). ^{13}C NMR (125.7 MHz, $CDCl_3$, δ ppm): 145.22, 145.01, 134.84, 134.27, 132.42, 131.87, 131.31, 128.76, 119.11. ^{19}F NMR (470.4 MHz, $CDCl_3$, δ ppm): -145.01 (q, 4F). ^{11}B NMR (160 MHz, $CDCl_3$, δ ppm): 0.26 (t, 2B). HRMS [ESI]: calcd for $C_{24}H_{16}B_2F_3N_4$ $[(M\text{-}F)^+]$: *m/z* 439.1513 Obsvd: *m/z* 439.1520.

View Article Online
DOI: 10.1039/C5DT01925G

Synthesis of Bis-BODIPY 3

Bis-Dipyrrane **9** (200 mg 0.39 mmol) was dissolved in dichloromethane (54 mL) and oxidized with DDQ (213 mg, 0.94 mmol, 2.4 eq.) at RT under air. The reaction mixture was allowed to stir at room temperature for 1h. Triethylamine (4.3 mL, 80 eq.) followed by $BF_3{\cdot}Et_2O$ (4.91 mL, 100 eq.) was added to the reaction mixture without any time delay. The stirring was continued at room temperature for additional 30 min, the reaction mixture was evaporated and the crude product was purified by silica gel column chromatography and eluted with a dichloromethane/petroleum ether (80:20) mixture to afford Bis-BODIPY **3** as orange powder in 33% yield (80 mg). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 8.385 (s, 2H), 7.954 (s, 4H), 7.804-7.787 (d, *J* = 8.5 Hz 2H), 7.637-7.620 (d, *J* = 8.5Hz, 2H), 7.012-7.006 (d, *J* = 3 Hz, 4H), 6.579-6.575 (d, *J* = 2 Hz, 4H) 4.487-4.459 (t, *J* = 7 Hz, 2H), 2.016-1.987 (t, *J* = 7.5 Hz, 2H), 1.422-1.393 (t, *J* = 7 Hz, 2H), 1.067-1.038 (t, *J* = 7 Hz, 3H). ^{13}C NMR (125.7 MHz, $CDCl_3$, δ ppm): 143.40, 142.56, 135.19, 131.66, 129.53, 125.78, 123.63, 118.44, 109.29, 43.22, 31.21, 20.65, 13.89. ^{19}F NMR (470.4 MHz, $CDCl_3$, δ ppm): -145.10 (q, 4F). ^{11}B NMR (160 MHz, $CDCl_3$, δ ppm): 0.36 (t, 2B). HRMS [ESI]: calcd for $C_{34}H_{27}B_2F_4N_5$ $[(M-F)^+]$: *m/z* 584.2405 Obsvd: *m/z* 584.2444.

Synthesis of Bis-BODIPY 4

Bis-dipyrrane **10** (500 mg, 0.94 mmol) was dissolved in 75 mL of dichloromthane and oxidised with DDQ (511 mg, 2.27 mmol, 2.4 eq.) at room temperature under air. The reaction mixture was allowed to stir at RT for 1h. After 1h triethylamine (10.4 mL, 75 mmol, 80 eq.), followed by $BF_3{\cdot}Et_2O$ (8.13 mL, 94 mmol, 100 eq.) was added to the reaction mixture one by one without much time lag. The reaction mixture was allowed to stir at room temperature for 30 min, after this solvent was evaporated and the crude product was purified by silica gel column chromatography. Desired compound Bis-BODIPY **4** was eluted with ethyl acetate/ hexane (15:85) mixture in 30% yield (176 mg, reddish powder).^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.937 (s, 4H), 7.557-7.540 (d, *J* = 8.5 Hz, 4H), 7.467-7.436 (t, *J* = 8.5 Hz, 2H), 7.306-7.275 (m, 7H), 7.063-7.057 (d, *J* = 3 Hz, 4H), 6.577-6.573 (d, *J* = 2 Hz, 4H). ^{13}C NMR (125.7 MHz, $CDCl_3$, δ ppm): 149.65, 146.89, 145.88, 143.51, 134.71, 132.30, 131.19, 130.19, 128.32, 126.94, 125.96, 122.55, 118.32. ^{19}F NMR (470.4 MHz, $CDCl_3$, δ ppm): -145.13 (q, 4F). ^{11}B NMR (160 MHz, $CDCl_3$, δ ppm): 0.29 (t, 2B). HRMS [ESI]: calcd for $C_{36}H_{25}B_2F_3N_5$ $[(M-F)^+]$: *m/z* 606.2248 Obsvd: *m/z* 606.2269.

View Article Online
DOI: 10.1039/C5DT01925G

Synthesis of Bis-BODIPY 5

Bis-dipyrrane **11** (400 mg, 0.28 mmol) and pyrrole (30 mL, 428 mmol) were stirred under nitrogen for 5 min. Added $InCl_3$ (6 mg, 0.03 mmol) and allowed to stir for further 2 h. after 2h excess pyrrole was vacuum distilled and the crude reaction mixture dissolved in 50 mL of dichloromethane and oxidised with DDQ (292 mg) and allowed to stir for 1h at RT. After 1h triethylamine (10.4 mL, 75 mmol, 80 eq.) and $BF_3{\cdot}Et_2O$ (8.13 mL, 94 mmol, 100 eq.) were added to the reaction mixture. The stirring was continued at room temperature for further 30 min, then reaction mixture was evaporated and crude product was subjected to silica gel column chromatography. Desired compound was eluted in dichloromethane/hexane (70:30) mixture in 8% yield (25 mg, dark orange powder). ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.999 (s, 4H), 7.689 (s, 4H), 7.331-7.323 (d, *J* = 4 Hz, 4H), 6.652-6.645 (d, *J* = 3.5 Hz, 4H). ^{13}C NMR (125.7 MHz, $CDCl_3$, δ ppm): 145.16, 139.38, 137.26, 134.21, 132.86, 131.43, 119.22. ^{19}F NMR (470.4 MHz, $CDCl_3$, δ ppm): -145.13 (q, 4F). ^{11}B NMR (160 MHz, $CDCl_3$, δ ppm): 0.20 (t, 2B). HRMS [ESI]: calcd for $C_{22}H_{14}B_2F_3N_4S$ $[(M\text{-}F)^+]$: *m/z* 445.1077 Obsvd: *m/z* 445.1107

Synthesis of Bis-BODIPY 6

The synthesis of Bis-BODIPY **6** was performed by following similar procedure used for Bis-BODIPY **5**. Yield: 10% (25 mg) ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm):7.976 (s, 4H), 7.452-7.445 (d, *J* = 3.5 Hz, 4H), 7.413 (s, 2H), 6.642-6.637 (d, *J* = 2.5 Hz, 4H). ^{13}C NMR (125.7 MHz, $CDCl_3$, δ ppm): 151.75, 144.70, 130.84, 121.23, 119.37. ^{19}F NMR (470.4 MHz, $CDCl_3$, δ ppm): -145.49 (q, 4F). ^{11}B NMR (160 MHz, $CDCl_3$, δ ppm): 0.18 (t, 2B). HRMS [ESI]: calcd for $C_{22}H_{14}B_2F_3N_4O$ $[(M\text{-}F)^+]$: *m/z* 429.1306 Obsvd: *m/z* 429.1277

Acknowledgements

IG gratefully acknowledges DST (New Delhi), CSIR, (New Delhi) and IIT Gandhinagar for financial support. IG thanks IIT Bombay, Chemistry Department for CV studies and Prof. H. Furuta, Kyushu University for X-ray measurements. PEK and SD thank IIT Gandhinagar for their fellowship. PCJ acknowledges CUG for providing basic computational facilities and UGC, New Delhi for start-up grants. MYL thanks UGC for fiscal assistance.

View Article Online
DOI: 10.1039/C5DT01925G

Supporting Information

The synthetic procedures of some starting materials, characterization data like HRMS, ^{1}H, ^{13}C, ^{19}F, ^{11}B NMR spectra, fluorescence decay profiles, DFT calculation and X-ray structure details of reported compounds are available as supporting information.

References

1. L. L. Shipman, T. M. Cotton, J. R. Norris and J. J. Katz, *Proc. Natl. Acad. Sci. U.S.A.* 1976, **73**, 1791.
2. J. Deisenhofer, O. Epp, R. Miki, R. Huber and H. Michel, *J. Mol. Biol*. 1984, **180**, 385.
3. J. Deisenhofer, O. Epp, R. Miki, R. Huber and H. Michel, *Nature* 1985, **318**, 618.
4. M.-C. Yee, S. C Fas,. M. M. Stohlmeyer, T. J. Wandless and K. A. Cimprich, *J. Biol. Chem.* 2005, **280**, 29053.
5. M. Fa, F. Bergstrom, P. Hagglof, M. Wilczynska, L. B. A. Johansson and T. Ny, *Structure* 2000, **8**, 397.
6. J. Karolin, L. B. A. Johansson, L. Strandberg, and T. Ny, *J. Am. Chem. Soc*. 1994, **116**, 7801.
7. A. Kamkaew, S. H. Lim, H. B. Lee, L. V. Kiew, L. Y. Chung and K. Burgess, *Chem. Soc. Rev.* 2013, **42**, 77.
8. Y. Wu, X. Peng, B. Guo, J. Fan, Z. Zhang, J. Wang, A. Cui and Y. Gao, *Org. Biomol. Chem.* 2005, **3**, 1387.
9. Z. N. Sun, H. L. Wang, F. Q. Liu, Y. Chen, P. Kwong, H. Tam and D. Yang, *Org. Lett*. 2009, **11**, 1887.
10. R. J. Middleton, S. J. Briddon, Y. Cordeaux, A. S. Yates, C. L. Cale, M. W. George, J. G. Baker, S. J. Hill and B. Kellam, *J. Med. Chem.* 2007, **50**, 782.
11. K. Loudet and K. Burgess, *Chem. Rev.* 2007, **107**, 4891.
12. P. E. Kesavan and I. Gupta, *Dalton. Trans.* 2104, **43**, 12405.
13. R. Ziessel and A. Harriman, *Chem. Commun.* 2011, **47**, 611.
14. Y. Hayashi, S. Yamaguchi, W. Y. Cha, D. Kim and H. Shinokubo, *Org. Lett.* 2011, **13**, 2992.
15. W. Pang, X. F. Zhang, J. Y. C. Zhou, A. Haoa and L. Jiao, *Chem. Commun*. 2012, **48**, 5437.

16. Y. Cakmak, S. Kolemen, S. Duman, Y. Dede, Y. Dolen, B. Kilic, Z. Kostereli, L.T. Yildirim, A. L. Dogan, D. Guc and E. U. Akkaya, *Angew. Chem. Int. Ed.* 2011, **50**, 11937.
17. L. Gai, B. Lu, B. Zou, G. Lai, Z. Shen and Z. Li, *Rsc. Adv.* 2012, **2**, 8840.
18. A. Poirel, A. D. Nicola, P. Retailleau and R. Ziessel, *J. Org. Chem.* 2012, **11**, 7512.
19. M. T. Whited, N. M. Patel, S. T. Roberts, K. Allen, P. I. Djurovich, S. E. Bradforth and M. E. Thompson, *Chem. Commun.* 2012, **48**, 284.
20. S. Kusaka, R. Sakamoto, Y. Kitagawa, M. Okumura and H. Nishihara. *Chem. Asian. J.* 2013, **8**, 723.
21. V. Yang, L. Li. B. Zhang. L. Zhanga and X. Liu, *Rsc. Adv.* 2013, **3**, 16933.
22. H. Qi, J. J. Teesdale, R. C. Pupillo, J. Rosenthal and A. J. Bard, *J. Am. Chem. Soc.* 2013, **135**, 13558.
23. A.V. Benniston, G. Copley, A. Harriman, D. Howgego, R. S. Harrington and W. Clegg, *J. Org. Chem.* 2010, **75**, 2018.
24. N. Saki, T. Dinc and E. U. Akkaya, *Tetrahedron* 2006, **62**, 2721.
25. H. Zhao, J. Liao, D. Yang, Y. Xie, Y. Xu, H. Wang and B. Wang, *Aust. J. Chem.* 2013, **66**, 972.
26. R. W. Wagner and J. S. Lindsey, *Pure. Appl. Chem.* 1996, **68**, 1373.
27. H. L. Kee, C. Kirmaier, L. Yu, P. Thamyongkit, W. J. Younblood, M. E. Calder, L. Ramos, B. C. Noll, D. B. Bocian, R. Scheidt, R. R. Brige, J. S. Lindsey and D. Holten, *J. Phys. Chem. B.* 2005, **109**, 20433.
28. C. Yu, L. Jiao, H. Yin, J. Zhou, W. Pang, Y. Wu, Z. Wang, G. Yang and E. Hao, *Eur. J. Org. Chem.* 2011, **28**, 5460.
29. E. Lager, J. Liu, A. Aguilar-Aguilar, B. Z. Tang and P. E. Cabrera, *J. Org. Chem.* 2009, **74**, 2053.
30. K. Kim, C. Jo, S. Eswaramoorthi, J. Sung, D. H. Kim and D. G. Churchill, *Inorg. Chem.* 2010, **49**, 4881.
31. T. K. Khan, S. K. Jana, M. R. Rao, M. S. Shaikh and M. Ravikanth, *Inorg. Chim. Acta* 2012, **383**, 257.
32. W. Qin, M. Baruah, M. V. D. Auweraer, F. C. D. Schryver and N. Boens, *J. Phys. Chem. A.* 2005, **109**, 7371.
33. A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648.
34. A. D. Becke, *Phys. Rev. A.*1998, **38**, 3098.
35. A. D. Becke, *J. Chem. Phys.* 1986, **84**, 4524.

36. M. J. Frisch, G. W. Trucos, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci and G. A. Petersson et al. Gaussian 09 Revision A 02 Gaussian Inc. Wallingford CT, 2009.
37. A. S. P. Chinna, M. Sunoj and T. Pakkirisamy, *Inorg. Chem.* 2014, **53**, 4813.