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Hexa Boron-Dipyrromethene Cyclotriphosphazenes: Synthesis, Crystal Structure, and Photophysical Properties

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We have synthesized four examples of a cyclotriphosphazene ring appended with six boron-dipyrromethene dyes $N_3P_3(BODIPY)_6$ by adopting two different methods. In method I, 1 equiv of $N_3P_3Cl_6$ was treated with 6 equiv of *meso*-(*o*- or *m*- or *p*-hydroxyphenyl)boron-dipyrromethene in tetrahydrofuran (THF) in the presence of cesium carbonate. This afforded $N_3P_3(BODIPY)_6$ in yields ranging from 80 to 90%. In method II, we first prepared hexakis(*p*-formylphenoxy)cyclotriphosphazene $N_3P_3(CHO)_6$ by treating 1 equiv of $N_3P_3Cl_6$ with 6 equiv of 4-hydroxybenzaldehyde in the presence of cesium carbonate in THF. In the second step, $N_3P_3(CHO)_6$ was condensed with excess of pyrrole in the presence of catalytic amount of trifluoroacetic acid (TFA) in CH_2Cl_2 at room temperature and afforded hexakis(*p*-phenoxy dipyrromethane)cyclotriphosphazene. In the last step, the hexakis(*p*-phenoxy dipyrromethane)cyclotriphosphazene was first oxidized with 6 equiv of DDQ in CH_2Cl_2 at room temperature for 1 h followed by neutralization with triethylamine and further reaction with excess $BF_3 \cdot Et_2O$ afforded the target $N_3P_3(BODIPY)_6$ in 16% yield. The route II was used only for the synthesis of one target compound whereas the route I was used for the synthesis of all four target compounds. The four compounds were characterized by mass, NMR, absorption, electrochemical, and fluorescence techniques. The crystal structure solved for one of the compounds revealed that the P_3N_3 ring is slightly puckered and the six substituents were not interacting with each other and attained pseudo-axial and pseudo-equatorial positions. The photophysical studies in five different solvents indicated that the compounds exhibit large Stokes' shifts unlike reference monomeric BODIPYs indicating that the compounds are promising for fluorescence bioassays. The quantum yields and lifetimes of compounds **1**−**4** depends on the type of BODIPY unit attached to the cyclotriphosphazene ring.

Introduction

Among the fluorescent dyes available, the boron-dipyrromethene (BODIPY) dyes are becoming increasingly popular because the BODIPY dyes have remarkable characteristics such as high absorption coefficients, high fluorescence yields, long excited state lifetimes, and good solubility in organic solvents with excellent photostability and amenability toward chromatography on silica and alumina.[1] BODIPY dyes have been used extensively as labeling reagents, fluorescent switches, chemosensors, and as laser dyes.[1] Multi-BODIPY dyes containing more than one BF_2-dipyrrin complex have recently attracted considerable attention owing to their novel features and also their potential use as functional dyes in biomedical and material applications.[2] Porphyrins,[2a] anthracenes,[2b] pyrenes,[2c] truxene,[2d] and so forth have been used as scaffolds to build multi-BODIPY systems. However, most BODIPY dyes have the fatal disadvantage that their Stokes' shifts are less than 20 nm. A small Stokes' shift can cause self-quenching and measurement error by excitation light and scattered light. Both of these can decrease the detection sensitivity to a great extent. Therefore, the BODIPY dyes with a larger Stokes' shift are very promising for fluorescence bioassays. Hexachlorocyclotriphosphazene is a robust inorganic ring containing six labile groups that can be substituted with the desired groups. This feature has been exploited by several researchers and used to prepare a variety of hexa-substituted cyclotriphosphazenes.[3] Specially, the cyclotriphosphazenes

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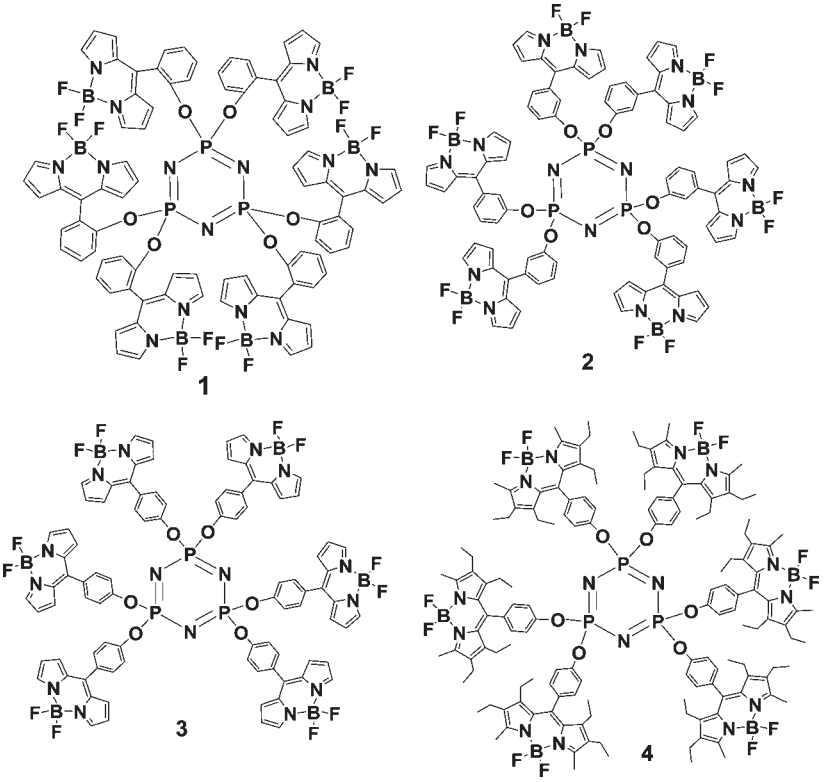
Chart 1



containing coordinating groups such as pyrazoles,[4] hydrazones,[5] hydrazine motifs,[6] pyridines,[7] and so forth have been synthesized and studied extensively for their metal complexing properties. The redox active groups such as ferrocenes have also been substituted on cyclotriphosphazene and explored for their redox properties.[8] Interestingly, the reports on cyclotriphosphazene containing fluorescent groups are very few. Majoral and co-workers[9] synthesized a series of phosphorus dendrimers containing fluorophores using cyclotriphosphazene as platform, and their photophysical studies indicated that this kind of compound would find applications in devices such as organic light emitting diodes and organic nanodots and also for the elucidation of biological mechanisms and for medical imaging. We recently prepared cyclotriphosphazene appended with six porphyrins in high yield under simple reaction conditions.[10] Porphyrins are tetrapyrrolic aromatic macrocycles present at the active site of several biomolecules and well-known for their metal coordination properties. However, porphyrins are moderately fluorescent, and their fluorescence yields are much lower than many other commercially available aromatic fluorescent compounds such as pyrene, anthracene, fluorenene, rhodamine, and so forth. In this paper, we used BODIPY dye as fluorophore and synthesized four novel hexa BODIPY appended cyclotriphosphazenes, hexa(boron-dipyrromethene)cyclotriphosphazenes $N_3P_3(BODIPY)_6$ **1**−**4** (Chart 1) under mild reaction conditions. The spectral, electrochemical, and photophysical

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Scheme 1. Synthesis of BODIPY **5**

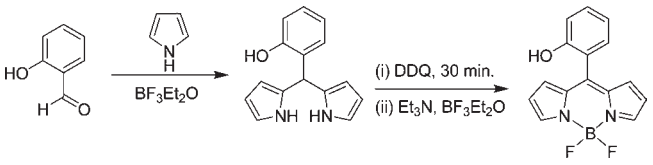
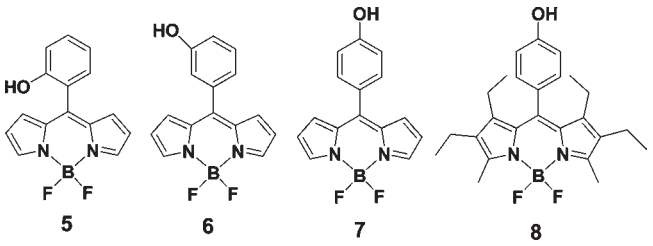


Chart 2



properties were investigated and in one case the single crystal structure was determined. The photophysical studies of compounds **1**−**4** studied in different solvents indicated that the compounds exhibit large Stokes' shifts compared to their corresponding reference monomers and thus may find applications as fluorescent labels in biological experiments.

Results and Discussion

Synthesis and Characterization. The required boron-dipyrromethene precursors containing hydroxyphenyl functional group **5**−**8** were synthesized by following the standard protocol[11] as shown for the BODIPY dye **5** in Scheme 1. In the first step, the corresponding dipyrromethanes were prepared by condensing 1 equiv of appropriate aldehyde with 25 equiv of pyrrole in the presence of 0.1 equiv of $BF_3 \cdot OEt_2$ for 10 min at room temperature.[12] The crude compounds were purified by flash column chromatography and yielded the corresponding dipyrromethanes as white solids. The dipyrromethanes were then subjected to a two step one pot reaction by oxidizing the dipyrromethanes in the first step with DDQ and reacted in second step with $BF_3 \cdot OEt_2$ at room temperature. Column chromatographic purification on silica yielded the functionalized BODIPY dyes **5**−**8** (Chart 2) as bright fluorescent green powders in 33−42% yields. The BODIPYs **5**−**8** were confirmed by the molecular ion peak in mass spectra and characterized by various spectroscopic techniques. The ^{1}H NMR spectra of BODIPYs **5**−**8** were slightly different from each other because of the presence of hydroxyl group at different position on *meso*-phenyl group. However, there are some major differences were noted in their ^{19}F and ^{11}B NMR spectra of **5**−**8**. In ^{19}F NMR, the compounds **6**−**8** exhibited a typical quartet at −145 ppm but compound **5** showed a complicated two sets of doublet of quartets in the −144 to −146 ppm region (Supporting Information). This is due to the ortho-substitution causing inequivalence in the chemical environment for two fluoride ions. The fluoride ion first couples with boron (I = 3/2) and gives a quartet which then couples with the second fluoride ion to give a doublet of a quartet. In ^{11}B NMR, a typical triplet was observed at 0.5 ppm for compounds **5**−**7** and at 1.0 ppm for compound **8**. The more downfield shift of compound **8** in ^{11}B NMR is due to the presence of electron donating alkyl groups at β-pyrrole carbons.

To prepare the target compounds **1**−**4**, we first attempted to prepare hexa(BODIPY)cyclotriphosphazene **3** by two different routes. Initially, we synthesized the compound **3** by following the method[10] which we used earlier for the synthesis of hexaporphyrinyl substituted cyclotriphosphazene (Route I) (Scheme 2). The compound **3** was prepared by reacting 1 equiv of $N_3P_3Cl_6$ with 6 equiv of *N*,*N*′-difluoroboryl-5-(*p*-hydroxyphenyl) dipyrrin[13] **7** in the presence of 12 equiv of cesium carbonate in tetrahydrofuran (THF) at 0 °C and continued stirring at 50 °C for 6 h. The progress of the reaction was monitored by thin layer chromatography (TLC) analysis which initially showed the spots corresponding to partially substituted products which disappeared as the reaction progressed and showed one single spot corresponding to the compound **3**. The crude reaction mixture was subjected to column chromatography and afforded pure compound **3** as red powder in 88% yield. Alternately, the compound **3** was also prepared by following route II in three steps (Scheme 3). In the first step, hexakis(*p*-formylphenoxy)cyclotriphosphazene $N_3P_3(CHO)_6$ **9** was synthesized[14] by treating 1 equiv of $N_3P_3Cl_6$ with 6 equiv of *p*-hydroxybenzaldehyde in the presence of cesium carbonate in THF at 0 °C and stirred additionally for 48 h at 50 °C. The crude compound was purified by column chromatography and afforded desired aldehyde **9** as a white solid in 92% yield. The molecular ion peak at 861.9 in the matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrum confirmed the identity of the compound **9**. The compound **9** was further confirmed by ^{31}P and ^{1}H spectroscopy. In ^{31}P NMR, the compound **9** showed only one signal at 5.31 ppm supporting the hexasubstitution on the cyclotriphosphazene ring. In ^{1}H NMR, a singlet at 9.94 ppm corresponding to an aldehyde proton was present. In the second step, 1 equiv of compound **9** was condensed with 240 equiv of pyrrole in the presence of 0.6 equiv of trifluoroacetic acid (TFA) in CH_2Cl_2[12] at room temperature for 30 min followed by standard workup, and quick flash column chromatographic purification afforded hexakis-(*p*-phenoxydipyrromethane)cyclotriphosphazene **10** as a brownish solid in 62% yield. The compound **10** was characterized by ^{31}P and ^{1}H spectroscopic techniques. In ^{31}P NMR, compound **10** showed a singlet at 7.04 ppm which was upfield shifted by 2.2 ppm compared with compound **9**. In ^{1}H NMR, the 36 pyrrole protons of six *meso*-aryl dipyrromethane units appeared as sets of three signals at 5.81, 6.09, and 6.82 ppm and 12 pyrrole -NH protons appeared as one broad singlet at 7.79 ppm. The six *meso* protons appeared as a singlet at 5.30 ppm (Supporting Information). In the last step, the compound **10** was first oxidized with 6 equiv of DDQ in CH_2Cl_2 at room temperature for 1 h followed by neutralization with triethylamine, and further reaction with excess $BF_3 \cdot Et_2O$ afforded the crude product. The crude product was

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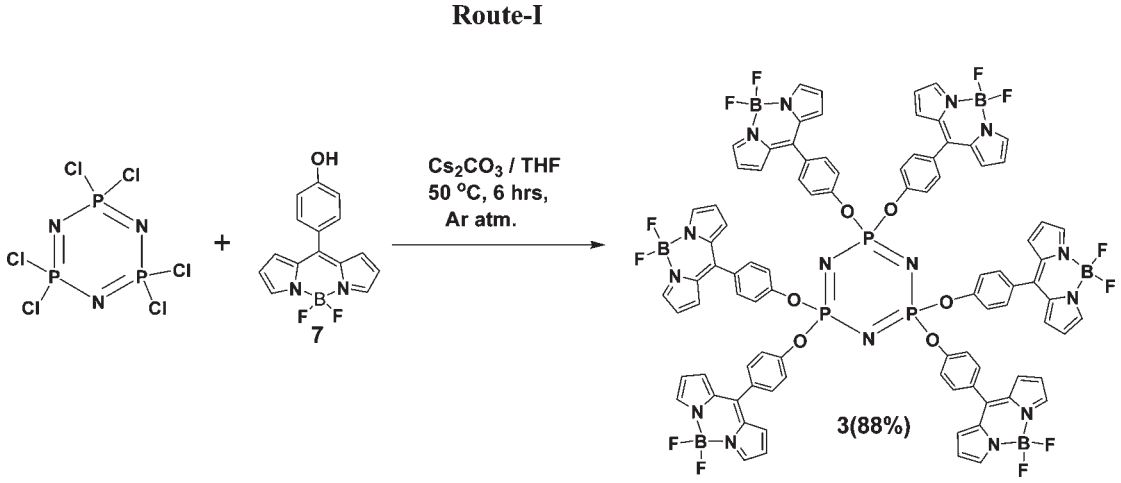
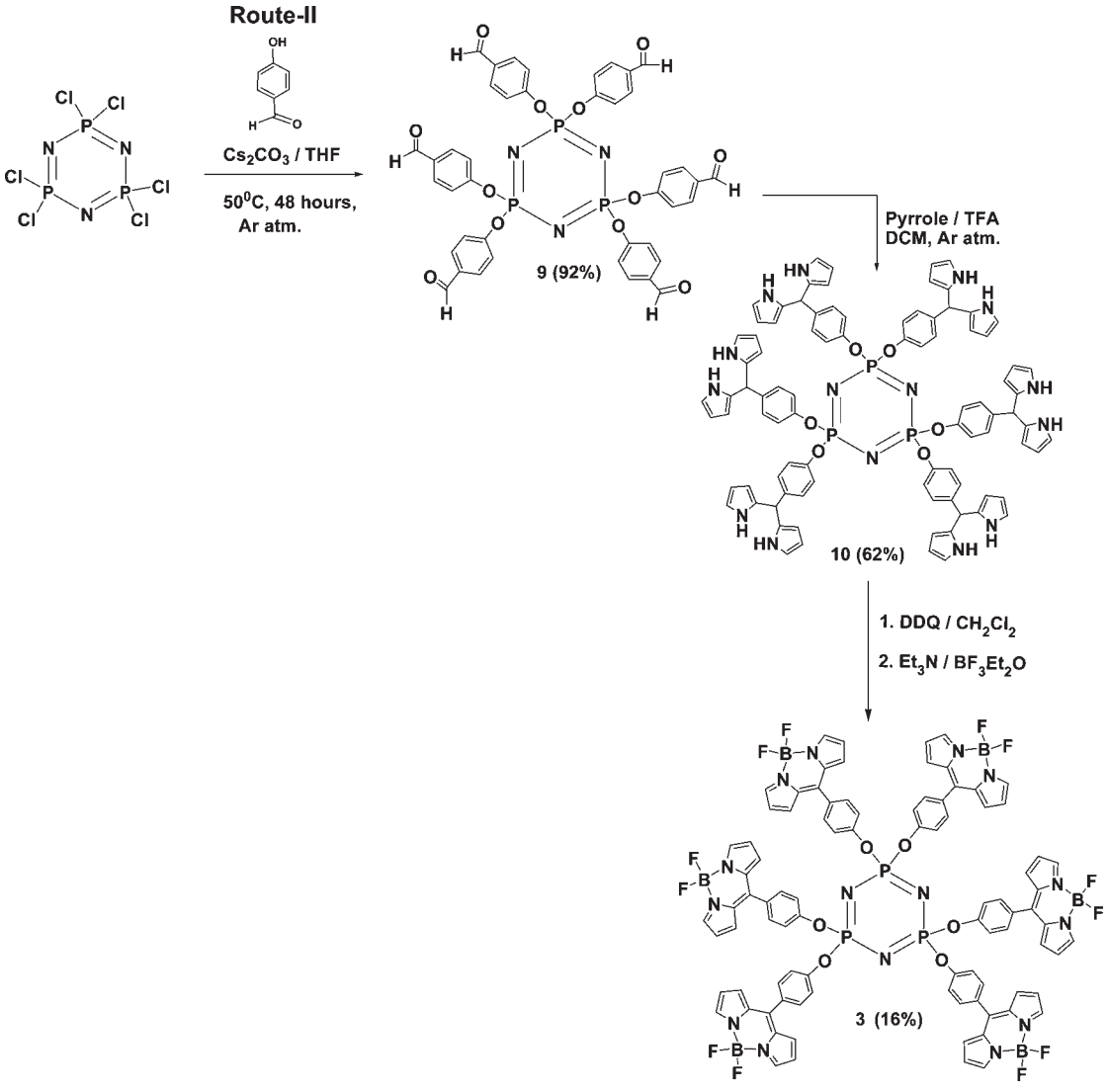
Scheme 2. Synthesis of Compound **3** by Route I



Scheme 3. Synthesis of Compound **3** by Route II



subjected to column chromatographic purification and afforded the desired pure compound **3** as orange solid in 16% yield. Since the route I is more convenient and involves less steps, the other hexa BODIPY appended cyclotriphosphazenes **1**, **2**, and **4** were prepared by following route I. Coupling of $N_3P_3Cl_6$ with 6 equiv of corresponding *meso*-hydroxyphenyl BODIPY **5**, **6**, and **8** in the presence of Cs_2CO_3 in THF for 6 h at room temperature

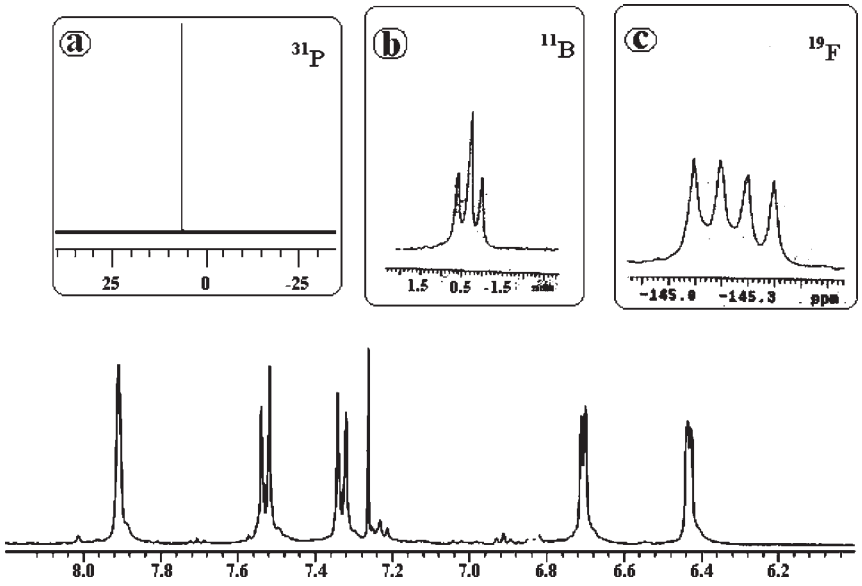


Figure 1. ^{1}H NMR spectrum of compound **3** recorded in $CDCl_3$. The ^{31}P, ^{11}B, and ^{19}F NMR spectra of compound **3** recorded in $CDCl_3$ were shown as inset (a), (b), and (c), respectively.

followed by alumina column chromatography yielded red solids of hexa BODIPY appended cyclotriphosphgazenes **1**, **2**, and **4** respectively in 80−90% yields. In all these reactions, initially we noticed the formation of partially substituted products which slowly converted to hexa BODIPY substituted cyclotriphosphazenes as the reaction progressed. It is noted that the compounds **1** and **2** were formed only at room temperature conditions, and any heating of the reaction mixture even to 50 °C resulted in decomposition. The compounds **1**−**4** were freely soluble in common organic solvents. The compounds **1**−**4** were confirmed by the appropriate molecular ion peak in ES-MS mass spectra (Supporting Information). The compounds **1**−**4** were characterized by ^{31}P, ^{11}B, ^{19}F and ^{1}H NMR spectroscopy as shown for compound **3** in Figure 1. We also recorded $^{1}H-^{1}H$ COSY spectrum for compound **1** to arrive at the structures of these compounds (Supporting Information). The compounds **1**−**4** showed one singlet in 5.1−6.8 ppm region in ^{31}P NMR (Figure 1a) supporting the hexa substitution of the cyclotriphosphazene ring. In ^{11}B NMR, the compounds **1**−**3** showed a triplet at ∼0.5 ppm (Figure 1b) and compound **4** at 1.0 ppm. These chemical shifts in ^{11}B NMR spectra of compounds **1**−**4** are almost identical with their corresponding monomeric BODIPYs supporting the magnetically equivalent environment for all six boron atoms in compounds **1**−**4**. Similarly, in ^{19}F NMR, a quartet signal at −145 ppm (Figure 1c) was observed for compounds **2**−**4** which is in agreement with their corresponding monomeric BODIPYs. However, like monomeric BODIPY **5**, the corresponding hexa BODIPY substituted cyclotriphosphazene **1** also showed two sets of doublet of quartets in the −145 ppm region in ^{19}F NMR. The most interesting observations were made in the ^{1}H NMR spectra of compounds **1**−**4**. Compounds **3** and **4** exhibited a simple ^{1}H NMR (Figure 1) spectra which closely matched with their corresponding monomeric BODIPYs **7** and **8** respectively. This indicated that the BODIPY units are not influencing each others in compounds **3** and **4**. However, compounds **1** and **2** exhibited quite different ^{1}H NMR compared with their corresponding monomeric BODIPYs **5** and **6** respectively (Supporting Information). In compounds **1** and **2**, the number of signals were more and appeared at upfield compared with their corresponding monomeric BODIPYs. This supports an interaction among BODIPY units in compounds **1** and **2**. Thus, the NMR studies supported that the six BODIPY units in compounds **1** and **2** interact with each other whereas in compounds **3** and **4**, the BODIPY units behave independently and do not interact with each other.

Crystallographic Studies. The single crystal of compound **1** was obtained from deuterated chloroform in an NMR tube on slow evaporation over a period of two weeks, and the complex crystallized with four molecule of $CDCl_3$ in the unit cell (not shown). The compound **1** crystallized in monoclinic with a $P\bar{1}$ space group. Figure 2a shows the X-ray structure of **1** (CCDC-786046) and the selected parameters, bond lengths, and bond angles are summarized in Table 1. For clarity, simplified structures of **1** are also shown in Figures 2b and 2c. As clear from the structure, the six BODIPY pendant groups are arranged in a symmetric manner about the cyclotriphosphazene ring, and each side of the ring contains three BODIPY pendant groups (Figure 2c). The P_3N_3 ring is slightly puckered in a chair conformation. The mean deviation of the ring atoms from their mean plane (rms) is 0.088 Å. Because of puckering of P_3N_3 ring, the six substituents can be considered as pseudo-equatorial and pseudo-axial which can be clearly seen in the deviation of the oxygen atoms from the P_3N_3 ring. Thus O1a (+1.01°), O2b (−0.84°), and O2c (+0.97°) are pseudo-equatorial and O2a (−1.41°), O1b (+1.50°), and O1c (−1.40°) are pseudo-axial. The P−N distance, P−N−P angles, and N−P−N angles are very close to previously observed hexasubstituted cyclotriphosphazenes. The average P−N bond length in P_3N_3 ring is 1.58 Å while the average N−P−N and P−N−P bond angles are 117.5° and 121.2° respectively. The average P−O bond length is 1.58 Å while the average O−P−O bond angle is 99.2°. Each BODIPY framework consisting two pyrrole rings and

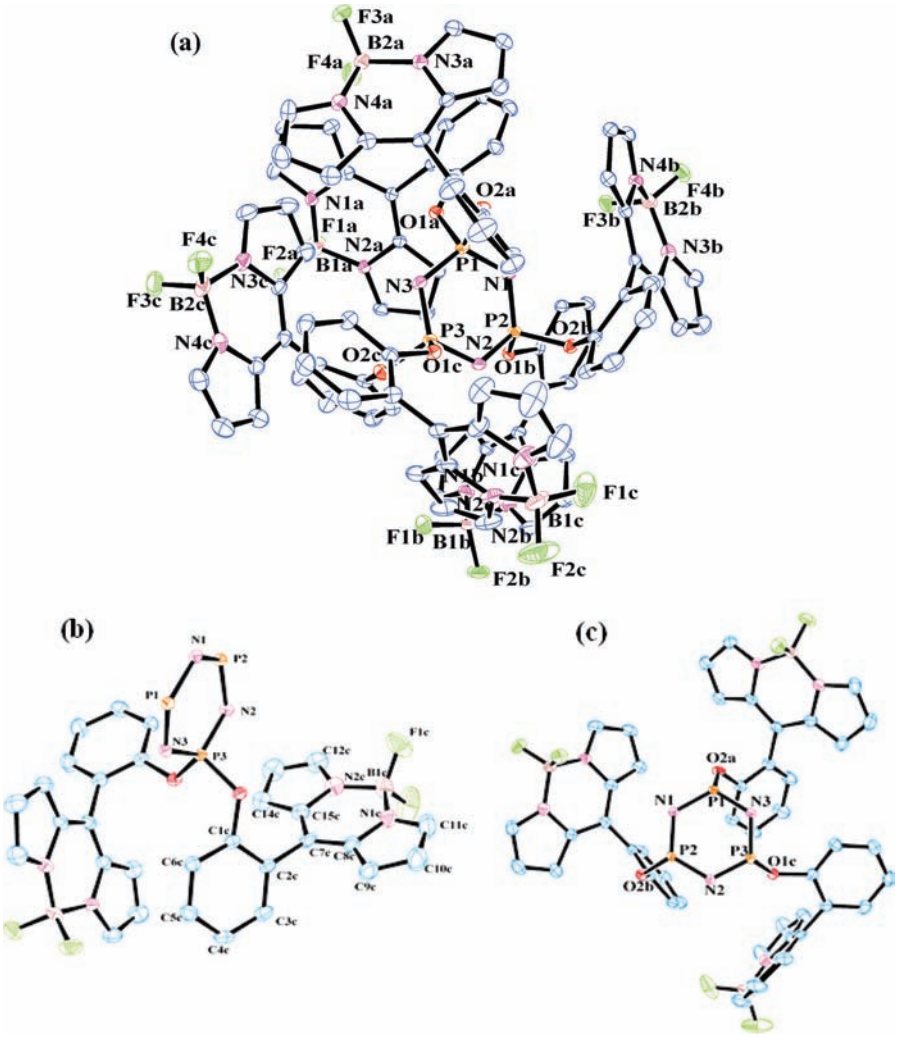


Figure 2. (a) Crystal structure of compound **1.** Hydrogen atoms and solvent molecules have been omitted for clarity. Simplified crystal structure of compound **1** showing only (b) two BODIPYs on one "P" and (c) one BODIPY on each "P" of P_3N_3 ring.

Table 1. Selected Bond Lengths [Å] and Bond Angles [deg] for compound **1**

bond length (deg)		bond angle (Å)	
P1−N1	1.583(4)	O1A−P1−O2A	100.6(2)
P1−N3	1.574(4)	O1B−P2−O2B	98.7(2)
P2−N1	1.586(4)	O1C−P3−O2C	98.3(2)
P2−N2	1.580(4)	N1−P2−N2	117.1(2)
P3−N2	1.578(4)	N1−P1−N3	118.0(2)
P3−N3	1.585(4)	N2−P3−N3	117.5(2)
P1−O1A	1.579(3)	P1−N1−P2	121.2(2)
P1−O2A	1.597(3)	P1−N3−P3	120.6(2)
P2−O1B	1.577(3)	P2−N2−P3	121.8(2)
P2−O2B	1.589(3)	N1−B−N2	105.8(4)−106.4(5)
P3−O1C	1.581(3)	N1−B−F1	109.8(5)−110.1(5)
P3−O2C	1.590(3)	N1−B−F2	109.5(5)−111.0(5)
B−F1	1.383(7)−1.390(6)	N2−B−F1	110.1(5)−111.5(5)
B−F2	1.376(7)−1.392(7)	N2−B−F2	109.5(5)−110.1(5)
B−N1	1.542(7)−1.552(8)	F1−B−F2	109.4(4)−109.9(4)
B−N2	1.531(7)−1.557(6)		
N1−C8	1.386(6)−1.398(6)		
N1−C11	1.338(8)−1.345(6)		
C7−C8	1.380(6)−1.400(6)		
C2−C7	1.491(6)−1.495(6)		

the central six membered ring containing boron atom is essentially planar like its monomeric BODIPY.[15] The two fluorine atoms are equidistant above and below the plane of the pyrrole moieties. The six dihedral angles between the *meso*-aryl ring and the plane defining various dipyrrin atoms in compound **1** is in the range 60−81° which is almost similar to the reported monomeric BODIPYs.[15]

Absorption and Electrochemical Studies. The absorption properties of compounds **1**−**4** were studied in five different solvents, and the data are presented in Table 2. The comparison of absorption spectra of compounds **1**−**4** recorded in chloroform is shown in Figure 3 and the comparison of compound **3** with its monomer **7** recorded in chloroform at the same concentration is presented as an inset in Figure 3. The inspection of data in Table 2 and the Figure 3 reveal the following: (1) compounds **1**−**4** showed typical BODIPY absorption features[15] with a strong band at the 500−530 nm region corresponding to $S_0 \rightarrow S_1$ transition with a vibronic transition on the higher energy side as a shoulder and an ill-defined, weak band corresponding to the $S_0 \rightarrow S_2$ transition at about 420 nm in all solvents. The absorption spectra exhibited 8−10 nm blue shift when solvent is

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Table 2. Photophysical Properties of BODIPYs **1**−**4** in Different Solvents

compound	solvent	λ_{abs}(nm)	λ_{em}(nm)	FWHMabs (cm^{-1})	$\Delta\nu_{st}$(cm^{-1})	ε	ϕ	τ(ns)	k_r 10^8 s^{-1}	k_{nr} 10^9 s^{-1}
	C_6H_6	516	536	2371	723	4.41	0.100	1.16	0.86	0.77
	$CHCl_3$	514	534	2575	728	4.48	0.103	1.28	0.80	0.70
1	THF	517	534	2308	615	4.49	0.056	1.33	0.42	0.70
	MeOH	513	532	2683	696	4.45	0.009	0.53	0.17	1.86
	MeCN	506	531	2500	930	4.43	0.005	0.20	0.25	4.97
	C_6H_6	510	540	1901	1089	4.56	0.057	0.77	0.74	1 22
	$CHCl_3$	509	534	1925	919	4.61	0.062	0.72	0.86	1.30
2	THF	506	535	1929	1071	4.57	0.040	0.83	0.48	1.15
	MeOH	504	530	1984	973	4.45	0.003	0.30	0.10	3.32
	MeCN	503	528	1888	941	4.51	0.003	0.28	0.10	3.56
	C_6H_6	508	564	1683	1954	4.49	0.042	0.60	0.70	1.59
	$CHCl_3$	505	530,553	1764	930,1718	4.55	0.039	0.49	0.79	1.96
3	THF	503	528,557	1865	941,1927	4.53	0.027	0.43	0.62	2.26
	MeOH	501	523	2034	839	4.28	0.003	0.14	0.21	7.12
	MeCN	499	522	1844	882	4.48	0.003	0.14	0.21	7.12
	C_6H_6	530	546	1191	552	4.43	0.518	4.51	1.14	0.10
	$CHCl_3$	531	546	1512	517	4.48	0.627	5.48	1.14	0.07
4	THF	526	542	1191	561	4.39	0.534	5.16	1.03	0.09
	MeOH	525	540	1230	529	4.36	0.270	3.04	0.88	0.24
	MeCN	524	539	1289	531	4.39	0.228	2.34	0.97	0.33

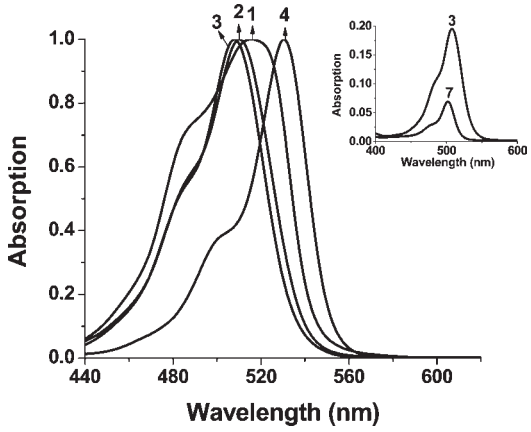

Figure 3. Comparison of normalized absorption spectra of compounds **1**−**4** recorded in chloroform. Inset shows the comparison of absorption spectra of compound **3** along with its monomer **7** recorded in chloroform using concentration of 8×10^{-6} M.

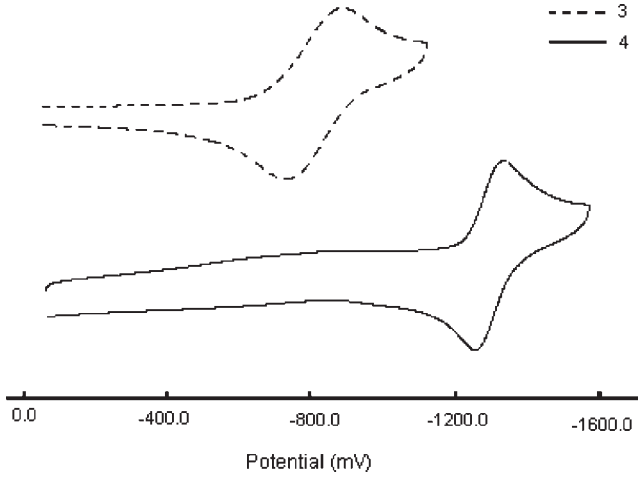

Figure 4. Comparison of reduction waves of cyclic voltammograms of compounds **3** and **4** recorded in CH_2Cl_2 containing 0.1 M TBAP as supporting electrolyte recorded at 50 mV s^{-1} scan speed.

changed from benzene or chloroform to acetonitrile, which is consistent with the general behavior of monomeric BODIPY chromophores;[16] (2) The compounds **1**−**4** exhibited slight red shifts (up to 10 nm) with approximately three times intensity enhancement compared with their respective monomers. (3) The $S_0 \rightarrow S_1$ transition in compounds **1**−**4** is generally broad with fwhm ~1500−2500 cm^{-1} compared with their corresponding monomeric BODIPYs **5**−**8**. However, among compounds **1**−**4**, the $S_0 \rightarrow S_1$ transition in compounds **2**−**4** is relatively sharp with fwhm ~1500−1900 cm^{-1} whereas it is quite broad in **1** with fwhm ~2500 cm^{-1}. This may be related to the type of linking of BODIPY units to the cyclotriphosphazene ring. In compound **1**, the BODIPY units are linked through its *ortho* position of *meso*-phenyl group causing steric crowding resulting in broadening of the absorption band. The solvent effect on absorption properties studied for compounds **1**−**4** indicated that the effects are similar to those of corresponding monomers[16] and no unusual effects were observed in any solvent. The electrochemical properties of compounds **1**−**4** were determined by cyclic voltammetry at a scan rate of 50 mV/s using tetrabutylammonium perchlorate as supporting electrolyte. A comparison of reduction waves of compounds **3** and **4** is shown in Figure 4, and the redox potential data is presented in Table 3. All four compounds showed one reversible reduction and one ill-defined oxidation except for compound **4** which showed one reversible oxidation. The compound **4** exhibited easier oxidation and difficult reduction compared with compounds **1**−**3** which is due to the electron rich BODIPY core.

Fluorescence Studies. The steady state fluorescence studies were carried out on compounds **1**−**4** in different solvents, and the comparison of normalized steady state fluorescence spectra of compounds **1**−**4** recorded in chloroform using excitation wavelength of 488 nm is presented in Figure 5. The fluorescence studies of compounds

(16) (a) Costela, A.; García-Moreno, I.; Gomez, C.; Sastre, R.; Amat-Guerri, F.; Liras, M.; López Arbeloa, F.; Bañuelos Prieto, J.; López Arbeloa, I. *J. Phys. Chem. A* **2002**, *106*, 7736–7742. (b) Bañuelos Prieto, J.; López Arbeloa, F.; Martínez Martínez, V.; Arbeloa López, T.; Amat-Guerri, F.; Liras, M.; López Arbeloa, I. *Chem. Phys. Lett.* **2004**, *385*, 29–35. (c) López Arbeloa, F.; Bañuelos Prieto, J.; Martínez Martínez, V.; Arbeloa Lopez, T.; López Arbeloa, I. *ChemPhysChem* **2004**, *5*, 1762–1771.

Table 3. Electrochemical Redox Data [V] of **1**−**4** in CH_2Cl_2 Containing 0.1 M TBAP as the Supporting Electrolyte

compound	E_{ox}(V)	E_{red}(V)
1	1.59[a]	−0.79
2	1.61[a]	−0.71
3	1.87[a]	−0.72
4	1.12	−1.25

[a] Irreversible oxidation waves.

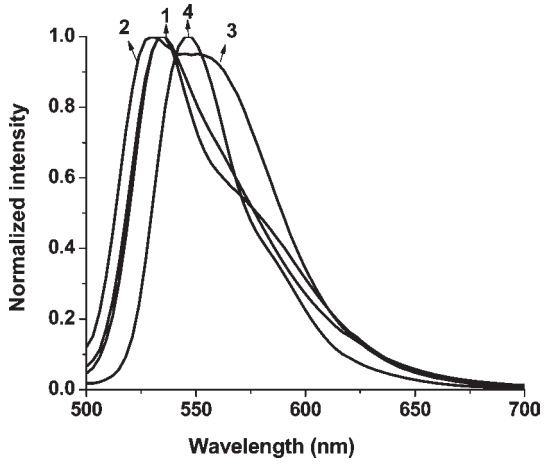

Figure 5. Comparison of normalized emission spectra of compounds **1**−**4** recorded in chloroform.

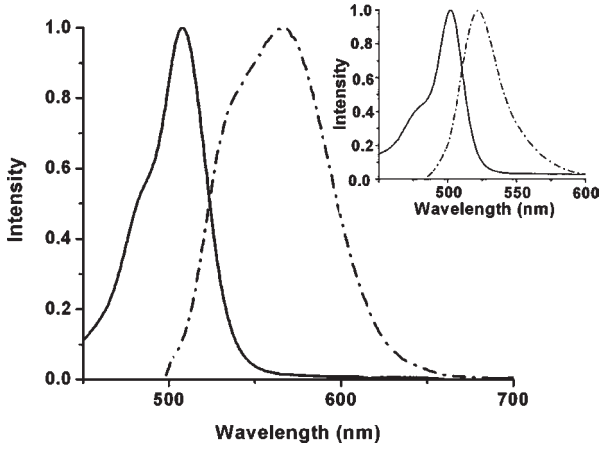

Figure 6. Normalized absorption (solid line) and emission spectra (dashed line) of **3** recorded in benzene. The inset shows absorption (solid line) and emission spectra (dashed line) of corresponding monomer **7** recorded in benzene. The concentrations used were 8×10^{-6} M.

1−**4** reveal the following: (1) the compounds **1**, **2**, and **4** showed one single fluorescence band in all solvents whereas the compound **3** showed either two banded fluorescence spectrum or a broad fluorescence band with a shoulder in all solvents; (2) the fluorescence band was blue-shifted on increasing solvent polarity for compounds **1**−**4**; (3) the bandwidth of the fluorescence depended on the type of BODIPY connected to the cyclotriphosphazene ring; compound **4** showed sharp emission and compound **3** showed very broad emission; (4) the fluorescence band of compound **4** was maximum red-shifted compared with compounds **1**−**3** because of the presence of electron donating substituents on BODIPY

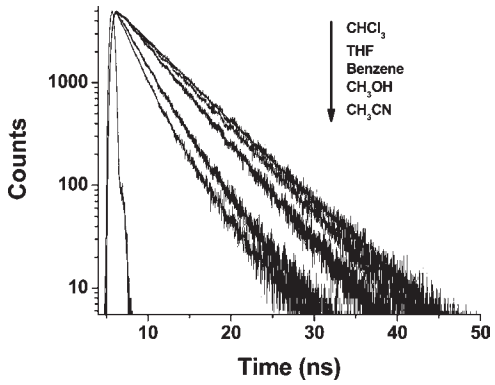

Figure 7. Fluorescence decay profile and weighted, residual, distribution fit of **4** in five different solvents. The excitation wavelength used was 406 nm.

core; (5) Stokes' shift which is the difference between the maximum of the lowest-energy absorption band and the maximum of the emission band was found to be larger for compounds **1**−**4** compared with their respective monomers **5**−**8**. The overlay of absorption and emission spectra of compound **3** is shown in Figure 6, and its inset shows it for the corresponding reference monomer **7**. It is clear from Figure 6 that the compound **3** exhibits 1718 cm^{-1} nm Stokes' shift compared with 618 cm^{-1} Stokes' shift[16] observed for compound **7**. This supports a geometric displacement of the excited state of compounds **1**−**4** and the maximum for **3** with respect to the ground state; Thus, the larger Stokes' shifts observed for compounds **1**−**4** are advantageous for their potential applications in direct multicolor labeling experiments. (6) the quantum yields of compounds **1**−**4** in a solvent like chloroform are in the range of 0.04−0.6, and compound **4** is the most fluorescent compound among all; the quantum yield decreases in solvents of increasing polarity, and compound **4** exhibited decent quantum yields in all solvents compared to compounds **1**−**3**. Furthermore, the quantum yields of compounds **1**−**4** are in the range of their respective reference monomers indicating that the fluorophores in compounds **1**−**4** behave independently. Similar observations were made by Ainscough and coworkers[7e] in their recent report on cyclotriphosphazene appended with Ru(II) and Re(I) bipyridyl complexes.

To explore the fluorescence dynamics of compounds **1**−**4**, the fluorescence decay profiles in different solvents were collected. The fluorescence decays of compounds **1**−**4** were fitted to a single exponential in all solvents, and the fluorescence decay traces of compound **4** collected at respective emission maxima in different solvents are presented in Figure 7. The singlet state lifetimes τ depended on the type of BODIPY dye connected to cyclotriphosphazene, and the lifetimes are in the range of 0.5 to 5 ns. The compound **4** which showed maximum quantum yields exhibited the highest singlet state lifetime. The singlet state lifetime is also solvent dependent like the quantum yield and lower in solvents with high polarity. Using quantum yield and singlet state lifetime, we calculated radiative (k_r) and nonradiative (k_{nr}) rate constants (Table 2). The k_r and k_{nr} data are in agreement with the quantum yield and lifetime data, and maximum k_r and minimum k_{nr} were observed for compound **4**, the most fluorescent compound among the compounds studied

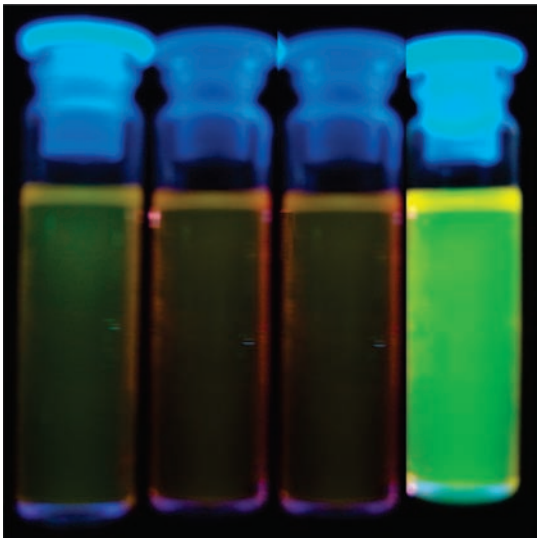

Figure 8. Color response of compounds **1**−**4** under a UV lamp.

here. Furthermore, we also observed clear changes in color under a UV lamp as well as the naked eye (Supporting Information). The chloroform solutions of compounds **1**−**4** under a UV lamp is shown in Figure 8. As clearly noted from Figure 8 compound **4** is bright green fluorescent compared with others.

Conclusions

In conclusion, we have described the synthesis of four cyclophosphazene appended with six boron-dipyrromethenes $N_3P_3(BODIPY)_6$ **1**−**4** by following two different routes. Although route I was straightforward to synthesize the desired compound, the route II gives an idea about the robustness of the cyclotriphosphazene ring toward various reaction and purification conditions used here. The NMR studies indicated that the BODIPY units are interacting with each other in solution although the crystal structure solved for one of the compounds showed no interaction between the BODIPY units in the solid state. The absorption and fluorescence properties studied in different solvents indicated that the properties are sensitive to the type of BODIPY units connected to the cyclophosphazene ring. The compounds exhibited large Stokes' shifts with comparable quantum yields compared to their respective reference boron-dipyrromethene monomers. This kind of cyclophosphazene appended with fluorophores may have potential applications as organic light emitting diodes.

Experimental Section

General Information. Chemicals. THF and benzene were dried with sodium benzophenone ketyl, and $CHCl_3$, CH_3OH, and MeCN were dried with calcium hydride and distilled prior to use. $BF_3 \cdot OEt_2$ and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were obtained from Spectrochem (India) and 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).

Instrumentation. ^{1}H NMR spectra (δ values, ppm) were recorded using Varian VXR 300 and 400 MHz spectrometers. ^{13}C NMR spectra were recorded with a Varian spectrometer operating at 100.6 MHz. ^{19}F NMR spectra were recorded with a Varian spectrometer operating at 282.2 MHz. ^{11}B NMR spectra were recorded with a Varian spectrometer operating at 96.3 MHz. Tetramethylsilane (TMS) was used as an external reference for recording ^{1}H (of residual proton; δ = 7.26 ppm) and ^{13}C (δ = 77.0 ppm) spectra in $CDCl_3$. Absorption and steady-state fluorescence spectra were obtained with a Perkin−Elmer Lambda-35 spectrometer and a PC1 Photon Counting Spectrofluorimeter (ISS, U.S.A.). Fluorescence spectra were recorded at 25 °C in a 1 cm quartz fluorescence cuvette. The fluorescence quantum yields (Φf) were estimated from the emission and absorption spectra by the comparative method at the excitation wavelength of 488 nm using Rhodamine 6G (Φf = 0.88)[17] as the standard. The time-resolved fluorescence decay measurements were carried out at the magic angle using a picosecond- diode-laser-based, time-correlated, single-photon-counting (TCSPC) fluorescence spectrometer from IBH, U.K. All the decays were fitted to a single exponential. Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) studies were carried out with an electrochemical system utilizing a three-electrode configuration consisting of a glassy carbon (working) electrode, platinum wire (auxiliary) electrode, and a saturated calomel (reference) electrode. The experiments were performed in dry CH_2Cl_2 using 0.1 M TBAP as the supporting electrolyte. Half-wave potentials were measured using DPV and also calculated manually by taking the average of the cathodic and anodic peak potentials. MALDI-TOF spectra were obtained with an Axima- CFR spectrometer, manufactured by Kratos Analyticals. The ES-MS spectra were recorded with a Q-Tof micro mass spectrometer.

The single crystals of compound **1** (CCDC-786046) was obtained from deuterated chloroform in NMR tube on slow evaporation over a period of two weeks. Crystal data for compound **1** was measured at 100(2) K on a Bruker SMART APEX CCD area detector system [λ(Mo−Kα) = 0.71073 Å], graphite monochromator, 2400 frames were recorded with an ω scan width of 0.3°, each for 8 s, crystal-detector distance 60 mm, collimator 0.5 mm. Data reduction by SAINTPLUS (Software for the CCD Detector System, Bruker Analytical X-ray Systems Inc., Madison, WI, 1998). Structure solution for the compound **3** was obtained using direct methods (SHELXS-97)[18] and refined using full-matrix least-squares methods on F^2 using SHELXL-97.[19]

General Procedure for the Preparation of *meso*-(hydroxyphenyl)-dipyrromethane. Pyrrole (25 equiv) and the hydroxy aldehyde (1.0 equiv) were added to a dry round-bottomed flask and degassed with a stream of nitrogen for 5 min. TFA (0.10 equiv) was then added, and the solution was stirred under nitrogen at room temperature for 10 min and then quenched with 0.1 M NaOH. Ethyl acetate was then added. The organic phase was washed with water and dried (Na_2SO_4), and the solvent removed under vacuum to afford orange oil. The resulting crude product was purified by silica gel column chromatography to give pure *meso*-(hydroxyphenyl)dipyrromethane as a crystalline white solid.

General Procedure for the Synthesis of *meso*-(hydroxyphenyl)-BODIPYs 5−8. A sample of *meso*-(*o*/*m*/*p*-hydroxyphenyl)-dipyrromethane (0.84 mmol) is dissolved in dichloromethane and oxidized with DDQ (1 mmol) at room temperature under stirring for 1 h. Triethylamine (33 mmol) was added, and the solution stirred for an additional 10 min. $BF_3 \cdot Et_2O$ (42 mmol) was then added, and continued stirring at room temperature for additional 1 h. TLC analysis indicated the formation of expected

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(18) Sheldrick, G. M. *SHELXS-97: Program for crystal structure solution*; University of Göttingen: Göttingen, Germany, 1997.

(19) Sheldrick, G. M. *SHELXL-97: Program for crystal structure refinement*; University of Göttingen: Göttingen, Germany, 1997.

compound as an orange-red spot. The reaction mixture was then diluted with CH_2Cl_2 and washed thoroughly with 0.1 M NaOH solution and water. The organic layers were combined, dried over Na_2SO_4, filtered, and solvent was removed on a rotary evaporator under vacuum. The resulting crude product was purified by column chromatography on silica gel, using petroleum ether/ethyl acetate (85:15) to afford the expected *meso*-(hydroxyphenyl)BODIPYs **5**−**8** as orange solids.

4,4-Difluoro-8-(*o*-hydroxyphenyl)-4-bora-3a,4a-diaza-*s*-indacene (5). 33% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 6.53 (d, ^3J = 3.6 Hz, 2H; py), 6.93 (d, ^3J = 3.9 Hz, 2H; py), 7.03−7.07 (m, 2H; Ar), 7.28 (d, ^3J = 7.3 Hz, 1H; Ar), 7.44 (t, ^3J = 7.2 Hz, 1H; Ar), 7.94 (s, 2H, py); ^{19}F NMR (282.2 MHz, $CDCl_3$, δ in ppm): −144.6 [dq, J(B, F), J(F, F)], −145.6 [dq, J(B, F), J(F, F)]; ^{11}B NMR (96.3 MHz, $CDCl_3$, δ in ppm): 0.53 [t, J(B,F)]; ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 117.0, 119.0, 120.1, 120.4, 131.6, 135.2, 143.0, 144.8, 153.6; ES-MS: ($C_{15}H_{11}BF_2N_2O$) 265 [M^+ − F].

4,4-Difluoro-8-(*m*-hydroxyphenyl)-4-bora-3a,4a-diaza-*s*-indacene (6). 37% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 6.52−6.53 (m, 2H; py), 6.95 (d, ^3J = 4.0 Hz, 2H; py), 6.99 (s, 1H; Ar), 7.04−7.06 (m, 1H; Ar), 7.09 (d, ^3J = 7.6 Hz, 1H; Ar), 7.37 (t, ^3J = 7.9 Hz, 1H; Ar), 7.93 (s, 2H, py); ^{19}F NMR (282.2 MHz, $CDCl_3$, δ in ppm): −144.6 [q, J(B, F)]; ^{11}B NMR (96.3 MHz, $CDCl_3$, δ in ppm): 0.54 [t, J(B,F)]; ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm):117.5, 118.0, 118.7, 123.2, 129.9, 131.8, 135.0, 135.2, 144.3, 147.0, 155.7; ES-MS: ($C_{15}H_{11}BF_2N_2O$) 265 [M+1]$^+$.

1,2,6,7-Tetraethyl-4,4-difluoro-8-(*p*-hydroxyphenyl)-3,5-dimethyl-4-bora-3a,4a-diaza-*s*-indacene (8). 42% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 0.67−0.70 (t, ^3J = 7.3 Hz, 6H; $-CH_3$), 1.01−1.05 (t, ^3J = 7.3 Hz, 6H; $-CH_3$), 1.60−1.66 (q, ^3J = 7.3 Hz, 4H; $-CH_2$), 2.27−2.33 (q, ^3J = 7.3 Hz, 4H; $-CH_2$), 2.53 (s, 6H; $-CH_3$), 6.89 (d, ^3J = 8.2 Hz, 2H; Ar); 7.25 (d, ^3J = 8.2 Hz, 2H; Ar); ^{19}F NMR (282.2 MHz, $CDCl_3$, δ in ppm): −145.5 [q, J(B, F)]; ^{11}B NMR (96.3 MHz, $CDCl_3$, δ in ppm): 1.08 [t, J(B, F)]; ES-MS: ($C_{25}H_{31}BF_2N_2O$) 405.2 [M^+ − F].

Hexakis[4,4-difluoro-8-(*p*-phenoxy)-4-bora-3a,4a-diaza-*s*-indacene]cyclotriphosphazene (3). Route-I. A sample of **7** (18.6 mg, 0.06 mmol) and cesium carbonate (42 mg, 0.13 mmol) was added to a hexachlorocyclotriphosphazene (4 mg, 0.01 mmol) in THF at 0 °C. The reaction was brought to room temperature and stirred for 6 h at 50 °C. The progress of the reaction was monitored with TLC analysis at regular intervals. The reaction was stopped after complete disappearance of **7** and appearance of a new spot corresponding to the required compound **3** as judged by TLC analysis. The reaction mixture was concentrated on a rotary evaporator under reduced pressure, and the resulting crude compound was subjected to silica gel column chromatography. The desired compound was collected as the first band using dichloromethane. The solvent was removed under reduced pressure and afforded **3** as a red solid in 88% yield (18.5 mg); mp 180−181 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 6.43 (m, 12H), 6.71 (m, 12H), 7.31 (d, ^3J (H, H) = 8.5 Hz, 12H; Ar), 7.51 (d, ^3J (H, H) = 8.5 Hz, 12H; Ar), 7.90 (s, 12H); ^{31}P{^{1}H} NMR (161.8 MHz, $CDCl_3$, δ in ppm): 6.36 (s); ^{19}F NMR (282.2 MHz, $CDCl_3$, δ in ppm): −145.1 [q, J(B, F)]; ^{11}B NMR (96.3 MHz, $CDCl_3$, δ in ppm): 0.36 [t, J(B,F)]; ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 118.9, 121.0, 130.9, 131.0, 131.5, 132.1, 134.6, 144.9; ES-MS: ($C_{90}H_{60}B_6N_{15}O_6P_3$): 1815.17 [$M^+$ − F].

Route-II. Hexakis(4-formylphenoxy)cyclotriphosphazene (9). A sample of 4-hydroxybenzaldehyde (22.1 g, 180.5 mmol) was added to a mixture of $P_3N_3Cl_6$ (10.3 g, 29.74 mmol) and K_2CO_3 (50.0 g, 361.76 mmol) in THF (250 mL) at 0 °C. The reaction mixture was then stirred at 50 °C for 48 h. The solvent was removed under vacuum. The residue was extracted with CH_2Cl_2, and the solvent was removed on a rotary evaporator to afford the crude compound. The crude compound was subjected to silica gel column chromatography using dichloromethane and afforded pure **9** as a white solid in 92% yield (23.5 g). mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) 7.16 (d, ^3J (H, H) = 8.5 Hz, 12H; Ar), 7.75 (d, ^3J (H, H) = 8.5 Hz, 12H; Ar), 9.94 (s, 6H; −CH0); ^{31}P{^{1}H} NMR (161.8 MHz, $CDCl_3$, δ in ppm): 5.34 (s); ES-MS: ($C_{42}H_{30}N_3O_{12}P_3$) m/z (%): 862.9 [M^+].

Hexakis(*meso*-phenyldipyrromethane)cyclotriphosphazene (10). A mixture of **9** (0.5 g, 0.58 mmol) and pyrrole (6.0 mL, 86 mmol) in a 100 mL flask was degassed by bubbling argon for 10 min. Trifluoroacetic acid (0.026 mL, 0.34 mmol) was added to initiate the reaction, and the mixture was stirred at room temperature for 20 min. The reaction mixture was then diluted with ethyl acetate (50 mL) and washed with 0.1 M NaOH (2 × 100 mL). The organic layer was dried over anhydrous Na_2SO_4. The solvent and excess pyrrole was removed on a rotary evaporator under reduced pressure. The resulting crude viscous liquid was purified by column chromatography, and the desired compound **10** was collected as a brown solid using dichloromethane/methanol (98:2) in 62% yield (0.55 g). mp 120−121 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 5.30 (s, 6H, −CH), 5.81 (s, 12H, Py), 6.10 (m, 12H), 6.60 (m, 12H), 6.82 (d, ^3J (H, H) = 8.5 Hz, 12H; Ar), 6.94 (d, ^3J (H, H) = 8.5 Hz, 12H; Ar), 7.79 (s, 12H); ^{31}P{^{1}H} NMR (161.8 MHz, $CDCl_3$, δ in ppm): 7.04 (s).

Hexakis[4,4-difluoro-8-(*p*-phenoxy)-4-bora-3a,4a-diaza indacene]cyclotriphosphazene (3). In the final step, compound **10** (500 mg, 0.32 mmol) was taken in CH_2Cl_2 (30 mL) and oxidized with a solution of DDQ (437 mg, 1.9 mmol) in CH_2Cl_2 (30 mL) at room temperature for 1 h. Triethylamine (10.71 mL, 76 mmol) was added to the solution, and the mixture was stirred for 10 min. BF_3 Et_2O (12.01 mL, 96 mmol) was then added to the reaction mixture, and stirring was continued at room temperature for additional 1 h. The reaction mixture was diluted with CH_2Cl_2 and washed thoroughly with 0.1 M NaOH (2 × 100 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and solvent was removed to afford crude product. The crude product was purified by silica gel column chromatography using CH_2Cl_2 and afforded pure compound **3** as red solid in 16% yield (93 mg).

Hexakis[4,4-difluoro-8-(*o*-phenoxy)-4-bora-3a,4a-diaza indacene]cyclotriphosphazene (1). The compound **1** was prepared by following **route I**

80% Yield; ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 6.30 (s, 12H; py), 6.47 (d, ^3J = 3.0 Hz, 12H; py), 6.55 (d, ^3J = 8.2 Hz, 6H; Ar), 6.77 (t, ^3J = 8.2 Hz, 6H; Ar), 6.98 (t, ^3J = 7.3 Hz, 6H; Ar), 7.15 (d, ^3J = 7.3 Hz, 6H; Ar), 7.82 (s, 12H, py); ^{31}P{^{1}H} NMR (161.8 MHz, $CDCl_3$, δ in ppm): 5.17 (s); ^{19}F NMR (282.2 MHz, $CDCl_3$, δ in ppm): −144.4 [dq, J(B, F), J(F, F)], −145.0 [dq, J(B, F), J(F, F)]; ^{11}B NMR (96.3 MHz, $CDCl_3$, δ in ppm): 0.40 [t, J(B,F)]; ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 118.6, 122.9, 123.2, 131.1, 131.6, 132.0, 133.3, 135.2, 144.5, 150.4; ES-MS: ($C_{90}H_{60}B_6F_{12}N_{15}O_6P_3$) 1855.2 [M+Na]$^+$

Hexakis[4,4-difluoro-8-(*m*-phenoxy)-4-bora-3a,4a-diaza indacene]cyclotriphosphazene (2). The compound **2** was prepared by following **route I**

85% Yield; ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 6.33−6.34 (m, 12H; py), 6.63 (d, ^3J = 3.7 Hz, 12H; py), 7.12 (d, ^3J = 8.0 Hz, 12H; Ar), 7.18 (s, 6H; Ar), 7.23 (m, 6H; Ar), 7.87 (s, 12H, py); ^{31}P{^{1}H} NMR (161.8 MHz, $CDCl_3$, δ in ppm): 6.80 (s); ^{19}F NMR (282.2 MHz, $CDCl_3$, δ in ppm): −144.5 [q, J(B, F)]; ^{11}B NMR (96.3 MHz, $CDCl_3$, δ in ppm): 0.40 [t, J(B,F)]; ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 118.8, 122.7, 122.9, 127.9, 130.0, 131.2, 134.4, 135.3, 144.8, 149.9; ES-MS: ($C_{90}H_{60}B_6F_{12}$-$N_{15}O_6P_3$) 1814.6 [M^+-F]

Hexakis[1,2,6,7-tetraethyl-4,4-difluoro-8-(*p*-phenoxy)-3,5-dimethyl-4-bora-3a,4a-diaza-*s*-indacene]cyclotriphosphazene (4). The compound **4** was prepared by following **route I**

83% Yield; ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 0.67−0.70 (t, ^3J = 7.3 Hz, 6H; $-CH_3$), 1.01−1.05 (t, ^3J = 7.3 Hz, 6H;

$-CH_3$), 1.60−1.66 (q, ^3J = 7.3 Hz, 4H; $-CH_2$), 2.27−2.33 (q, ^3J = 7.3 Hz, 4H; $-CH_2$), 2.53 (s, 6H; $-CH_3$), 6.89 (d, ^3J = 8.2 Hz, 2H; Ar); 7.25 (d, ^3J = 8.2 Hz, 2H; Ar); $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$, δ in ppm): 5.61 (s); ^{19}F NMR (282.2 MHz, $CDCl_3$, δ in ppm): −146.1 [q, J(B, F)]; ^{11}B NMR (96.3 MHz, $CDCl_3$, δ in ppm): 1.07 [t, J(B,F)]; ES-MS: ($C_{150}H_{180}B_6F_{12}N_{15}O_6P_3$) 2697.4 $[M+Na]^+$

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Supporting Information Available: Crystallographic data in CIF format. Further details are given in Figures 1−47. This material is available free of charge via the Internet at http://pubs.acs.org.