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Highly Luminescent Heavier Main Group Analogues of Boron-Dipyrromethene

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Supporting Information

ABSTRACT: The preparation and photophysical properties of two heavier main group element analogues of boron-dipyrromethene (BODIPY) chromophores are described. Specifically, we have prepared dipyrrin complexes of dichlorogallate (GADIPY) or phenylphosphenium (PHODIPY) units. Whereas cationic PHODIPY is labile, decomposing to a phosphine over time, GADIPY is readily prepared in good yield as a crystalline solid having moderate air- and water-stability. Crystallographically characterized GADIPY displays intense green photoluminescence (λ_{em} = 505 nm, Φ_{em} = 0.91 in toluene). These inaugural heavier main group element analogues of BODIPY offer a glimpse into the potential for elaboration to a panoply of chromophores with diverse photophysical properties.

The boron-dipyrromethene (BODIPY) chromophores (Chart 1) have attracted broad multidisciplinary interest owing to their advantageous and tunable combination of photophysical features. Although many fluorescent dipyrrinato complexes have been reported,[2] including Zn(II),[3−6] Mg(II),[7,8] Ir(III),[9] Cu(II),[10] Al(III),[11] PO_2,[12,13] and Sn(II)[14,15] complexes, it is striking that direct BODIPY analogues composed of dipyrromethane adducts of other heavier main group elements have not been elucidated. Substitution of second row elements by heavier main group elements can have dramatic impacts on a molecule's optical and electronic properties,[16−20] so pursuing heavier main group dipyrrin complexes has attracted some attention. Although some mono(diiminato)gallium complexes[21−24] and bis- or tris-(dipyrrin) complexes (Chart 1)[25,26] have been characterized, the mono(dipyrrin)gallium complexes (direct analogues of BODIPY) have not been observed. Whereas BODIPY chromophores generally have a photoluminescent quantum efficiency (Φ) >60%, making them outstanding fluorescent probes, the oligo(*N*-chelating ligand) gallium complexes exhibit very poor Φ (<3%, Table 1).

Chart 1. Selected Structure of BODIPY and Coordination Complexes of Gallium(III) with *N*,*N*′-Bidentate Ligands

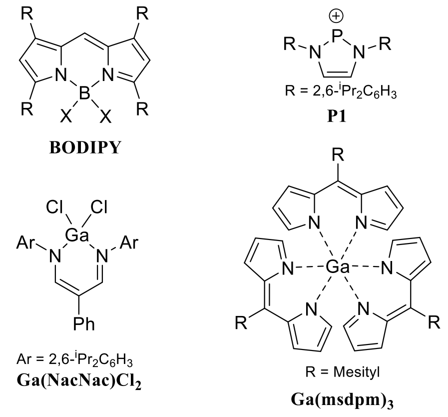

Table 1. Select Photophysical Properties

	Φ (%)	λ_{max} (nm)	λ_{em} (nm)	E_g (eV)[e]
BODIPY	80[a]	505[a]	516[a]	2.9
Ga(NacNac)Cl_2	<1[b]	382[b]	ND	ND
Ga(msdpm)$_3$	2.4[c]	496[c]	528[c]	ND
GADIPY (CH_2Cl_2)	82	494	501	3.0
GADIPY (Toluene)	91	497	505	3.0
PHODIPY[d]	80	467	510	3.1

[a]BODPY data are as reported in CH_2Cl_2.[1] [b]In THF. [c]In hexane. [d]Data are for the equilibrium mixture in CH_2Cl_2 that produced the ^{31}P NMR shown in Figure S3 of the SI. [e]From DFT calculations in vacuo.

The established preparation of BODIPY is very low yielding, and so requires column chromatographic purification.[27] The instability of heavier main group element-halogen bonds to chromatographic purification on silica/alumina precludes the isolation of direct BODIPY analogues via this route, possibly explaining their absence from the literature. Recent insightful improvements to the traditional BODIPY synthesis by Thompson's group[27] have inspired the current effort to explore heavier main group analogues of BODIPY. In the improved procedure, Thompson reported that isolation of the dipyrrinato lithium salt (**1**, Scheme 1) prior to installation of the boron center leads to near quantitative yields of BODIPY chromophores, foregoing the need for chromatographic purification. We hypothesized that the high yield and attendant purification by crystallization using this protocol would facilitate ready access to the desired heavier main group

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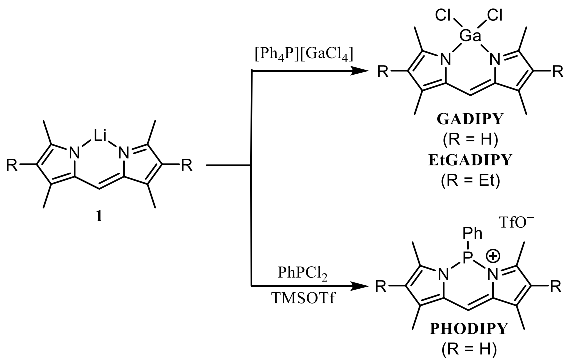
Scheme 1. PHODIPY and GADIPY Are Readily Prepared from the Lithium Dipyrrin Salt



analogues. Several fragments that are pseudoisolobal to borane were considered for this initial study. Dichlorogallate (GADIPY) (Scheme 1) was the most obvious target because gallium is a heavier congener of boron that will yield analogous bonding geometry and should exhibit photophysical properties similar to the BODIPY analogues. Furthermore, GADIPY could have an advantage over BODIPY for biomedical applications because gallium compounds are useful for biomedical radiolabeling.[28−35]

Our initial effort to prepare GADIPY involved reaction of **1** with GaCl$_3$, analogous to how the boron analogue is prepared. This reaction gave a mixture of products, likely due to the high reactivity of GaCl$_3$. Reaction of [PPh$_4$][GaCl$_4$][36] with **1**, however, gave GADIPY in 42% yield as an analytically pure crystalline solid. Crystals of GADIPY are stable at room temperature in the air, and were suitable for single crystal X-ray diffraction. The X-ray structure of GADIPY (Figure 1 and Table 2) reveals the tetrahedral, BODIPY-like geometry about Ga (full structural details are provided in the SI). The bond lengths and angles about Ga in GADIPY are quite comparable to those observed in Ga(NacNac)Cl$_2$ (Chart 1).[21] Other GADIPY complexes such as EtGADIPY (Scheme 1, R = C$_2$H$_5$, X-ray structure provided in Figure S7 in the SI) can be similarly generated. Cyclic voltammetry (Figure S8 in the SI) for GADIPY reveals a reversible oxidation at 1.30 V and a partially reversible reduction at −1.10 V. These features are analogous to those observed in BODIPY at +1.22 and −1.24 V, respectively.[37]

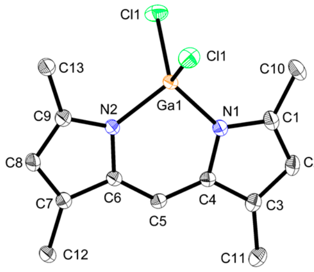


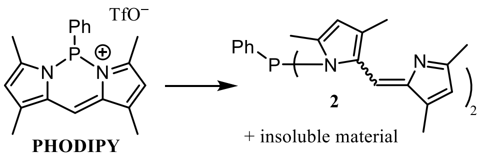
Figure 1. Single-crystal X-ray diffraction structure of GADIPY. The image is an ORTEP rendering of 50% probability ellipsoids. H atoms are omitted for clarity.

Table 2. Select Bond Distances (Å) and Angles (deg) for GADIPY

Ga1−N1	1.898(2)	Ga1−N2	1.8949(19)
Ga1−Cl1	2.1694(5)	Ga1−Cl2	2.1694(5)
N2−Ga1−N1	98.77(8)	N2−Ga1−Cl1	111.10(3)
N1−Ga1−Cl1	113.46(3)	N2−Ga1−Cl2	111.10(3)
N1−Ga1−Cl2	113.46(3)	Cl1−Ga1−Cl2	108.70(3)

Whereas successful preparation of GADIPY demonstrates the success of the proposed strategy for preparing heavier main group analogues of BODIPY, the ability to install other main group fragments should also allow access to dipyrrin complexes having properties inaccessible to their borane analogues. Given the significant differences in biolocalization for neutral versus charged probes, a readily prepared, inherently cationic BODIPY analogue could be a valuable cellular imaging agent, specifically as a mitochondria-targeting therapeutic.[38−40] An inherently cationic dipyrrin-phosphenium complex was therefore a tantalizing target. Although phosphenium fragments are unstable, there are several approaches[41−43] for their generation *in situ* that allow them to be trapped by *N*,*N*-chelating ligands (i.e., **P1**, Chart 1).[44−50] In the current case, phenylphosphenium was generated by reaction of PhPCl$_2$ and TMSOTf. Reaction of the [PhPOTf]$^+$ fragment so generated with **1** produced phenylphosphenium (PHODIPY) having a ^{31}P NMR spectroscopic shift (65.5 ppm) consistent with previously reported *N*,*N*-chelate phosphenium triflate complexes (70.9 ppm).[51] Unlike GADIPY, however, PHODIPY is labile even under an inert atmosphere. When the solvent is removed from the reaction mixture and the crude material is immediately analyzed, 81% of the phosphorus-bearing species is present as PHODIPY. The decomposition products are tentatively assigned as phosphine **2** (HRMS, M + 1 calcd for C$_{32}$H$_{36}$N$_4$P, 507.2678; found, 507.2690) and insoluble material (Scheme 2). The ^{31}P NMR chemical shift of **2** (48.8 ppm) is consistent with that of other bis(*N*-aryl)phenylphosphines such as bis(*N*-indolyl)phenylphosphine (48.6 ppm).[52] Extensive efforts to isolate PHODIPY from the mixture were unfortunately unsuccessful, and photophysical properties reported in Table 1 are for the mixture under nitrogen.

Scheme 2. Decomposition of PHODIPY



The photophysical properties (Table 1 and Figure 2) of GADIPY in CH$_2$Cl$_2$ are quite similar to those of the direct BODIPY analogue (Chart 1, X = Cl, R = H). Compared to BODIPY, GADIPY exhibits only slight blue shifts of 11 nm in λ_{max} and 15 nm in λ_{em}, while the Φ values for the two are identical within error (both ~80%). Depending on the solvent, the Φ of GADIPY is as high as 91% (in toluene).

The mixture of PHODIPY and **2** (Scheme 2) produces the absorption and emission spectra represented by the black traces in Figure 2. The absorption spectrum of PHODIPY exhibits a small band at 511 nm of intensity consistent with ~20% contribution of **2**, and a peak at 467 nm attributable to PHODIPY. Independently prepared dipyrrin phosphines[53] such as **2** exhibit very low Φ (<1%), consistent with other chromophore-derivatized phosphines,[54−56] so photoluminescence from the mixture is attributable exclusively to PHODIPY. This is further confirmed by noting only very

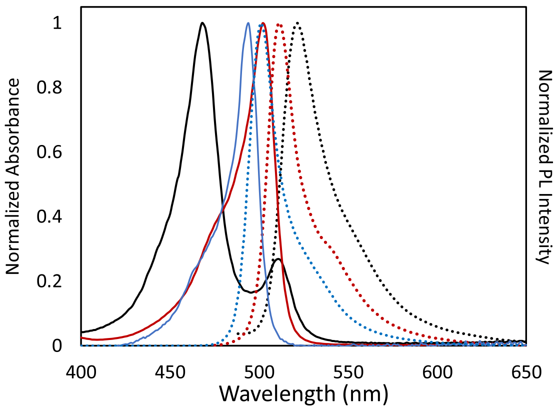


Figure 2. UV−vis absorbance (solid lines) and photoluminescence (PL, dotted lines) spectra for BODIPY (red), GADIPY (blue), and PHODIPY (black) in dichloromethane.

weak photoluminescence upon excitation into the band at 511 nm. The PHODIPY λ_{max} is blue-shifted, whereas the λ_{em} of PHODIPY is red-shifted relative to the values for GADIPY and BODIPY.

Density functional theory (DFT) calculations were employed to gain a better understanding of the observed photophysical properties of the three chromophores. The calculated highest occupied molecular orbitals (HOMOs) and lowest occupied molecular orbitals (LUMOs) and their energies are provided for the three chromophores in Figure 3. Calculations reveal that both GADIPY and PHODIPY have electron distributions in their HOMOs and LUMOs that are very similar to those of BODIPY, despite the positive charge on PHODIPY. The trigonal pyramidal geometry about P in PHODIPY suggests that phosphorus P orbitals are not involved in the π-conjugation or aromaticity of the system. While the calculated bandgaps in vacuo for the three chromophores are also quite similar at $\sim$3 eV (Table 1), the energies of the HOMO and LUMO for GADIPY lie slightly lower than those in BODIPY. HOMO and LUMO energies for cationic PHODIPY of course lie significantly lower in energy than those of the other two chromophores, suggesting the accessibility of different redox potentials for this heaver main group BODIPY analogue. The calculations would suggest that PHODIPY should have nearly identical λ_{max} as the other two chromophores shown in Figure 3. Stabilization of the ground state by solvation (not reflected in these calculations) will be more pronounced in cationic PHODIPY versus its neutral analogues, accounting for both its higher Stokes shift and the blue-shifted λ_{max}.

In conclusion, the current work has demonstrated a protocol to access the first direct analogues of the widely explored BODIPY chromophores in which heavier main group elements are substituted for the borane. The strategy employed herein is effective for generating neutral and cationic dipyrrin complexes of group 3 and 5 elements, and should be readily extended to a wide range of other heavier main group elements. Given the wide range of *N*,*N*-chelating ligands and boron-containing chromophores that have been reported,[57−63] the facile method reported herein should be applicable to a broad spectrum of new chromophores beyond dipyrrin complexes as well. Efforts are underway in our laboratory to prepare gallium complexes of variously substituted dipyrrins to unveil their structure−property relationships and to prepare isolable, kinetically stabilized PHODIPY analogues.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b03235.

Synthetic procedures, analytical data, NMR spectra, and additional photophysical data (PDF)

X-ray crystallographic data for GADIPY and EtGADIPY (CIF)

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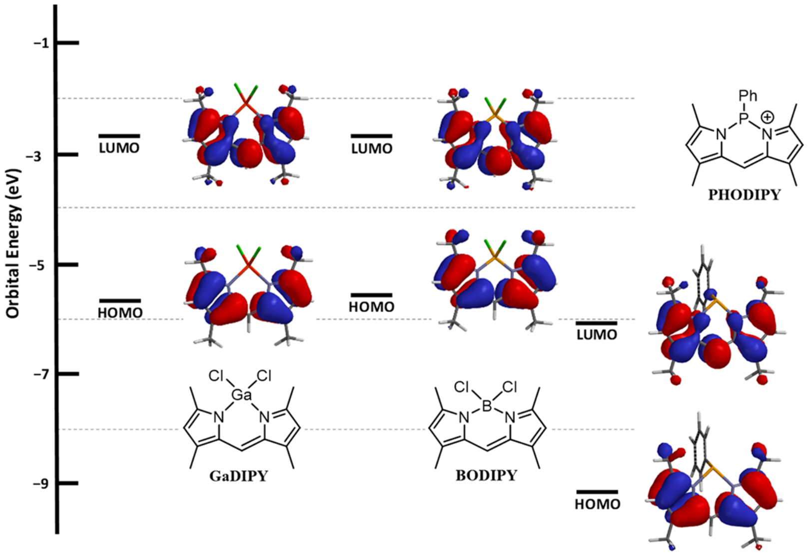

Figure 3. Ground state HOMO and LUMO distributions for GADIPY, BODIPY, and PHODIPY calculated by density functional theory at the B3LYP-6-31G* level.

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Notes

The authors declare no competing financial interest.

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