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Ambient-Temperature Metal-to-Ligand Charge-Transfer Phosphorescence Facilitated by Triarylboron: Bnpa and Its Metal Complexes

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A Cu(I) complex, **1**, and a Pt(II) complex, **2a**, of a triarylboron ligand, Bnpa, with bright ambient-temperature phosphorescence have been obtained. The phosphorescence of these complexes is highly sensitive toward molecular oxygen and has a distinct response to fluoride ions. For **1**, the fluoride ion causes phosphorescent quenching and Bnpa dissociation, and for **2a**, it switches phosphorescent color from yellow to green. The Cu(I) complex has an exceptionally high emission quantum yield (0.88) in the solid state.

Luminescent triarylborons have versatile applications in materials sciences. For example, they can function as effective and highly selective sensors toward anions such as fluoride or cyanide ions,[1] as emitters or electron transport materials in organic light-emitting devices (OLEDs),[2] or as nonlinear optical materials in photonic devices.[3] Although many examples (small molecules, oligomers, and polymers) of luminescent three-coordinate organoboron compounds are known previously, their emissions are all dominated by fluorescence at ambient temperature.[1,2] Phosphorescent materials have several key features distinguishing them from fluorescent materials, including high device efficiency of OLEDs if used as emitters,[4,5] high sensitivity to triplet-state quenchers such as oxygen thus enabling them as potential oxygen sensors,[6] and high color tunability via metal ions. Phosphorescent triarylboron-containing metal complexes are especially attractive because we and others have demonstrated recently that metal chelation/binding to a conjugate triarylboron ligand can greatly enhance the electron-accepting ability of the boron center,[7] which, when combined with phosphorescence, enables their potential use as bifunctional electron transport—phosphorescent emitters in OLEDs.[9c] Furthermore, phosphorescent triarylboron metal complexes offer the possibility for direct probing of the impact of anion binding at the boron site and ancillary ligands on photophysical properties of the metal complexes, which can, in turn, lead to the development of better phosphorescent emitters, more sensitive and versatile sensing systems. Despite the great potentials and the increasing number of

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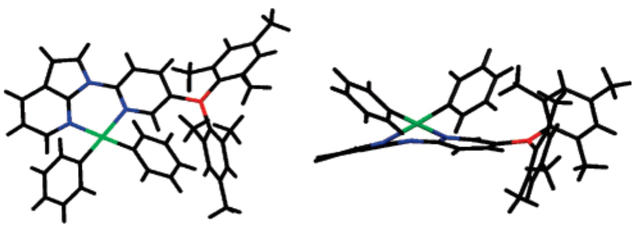
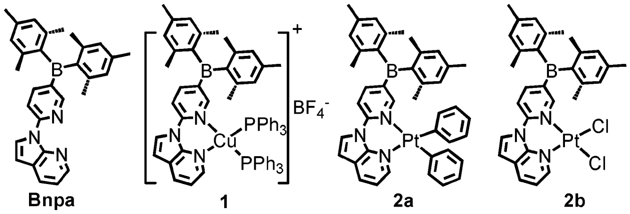


Figure 1. Crystal structure of **2a**: top view (left) and side view (right).

Scheme 1. Structures of Bnpa and Complexes **1**, **2a**, and **2b**



examples of boron-containing metal complexes in recent literature,[1j,7−9] ambient-temperature phosphorescent metal complexes that contain a triarylboron group remain elusive.[9] In search of bright phosphorescent emitters with a triarylboron functional group, we have developed a new ligand system, Bnpa (Scheme 1). We have found that Cu(I) and Pt(II) complexes of Bnpa with appropriate ancillary ligands display bright room-temperature phosphorescence in the solution and solid state that is very sensitive toward oxygen and anions such as fluoride ions. The preliminary results are reported herein.

The synthesis of Bnpa was achieved by Ullmann condensation of 7-azaindole with 2,5-dibromopyridine to produce *N*-(2-Brpy)-7-azaindole (Brnpa), followed by the substitution of the bromo group with $BMes_2$. A Cu(I) complex, $[Cu(Bnpa)(PPh_3)_2][BF_4]$ (**1**), and two Pt(II) complexes, $Pt(Bnpa)Ph_2$ (**2a**) and $Pt(Bnpa)Cl_2$ (**2b**), were obtained by the reaction of Bnpa with $[Cu(MeCN)_2(PPh_3)_2][BF_4]$, $[PtPh_2(\mu\text{-}SMe_2)]_n$ (n = 2 and 3), and K_2PtCl_4, respectively. The crystal structures of Bnpa and complexes **2a** and **2b** were determined by single-crystal X-ray diffraction analyses, and the structure of **2a** is shown in Figure 1. The Pt(II) center in **2a** and **2b** has a typical square-planar geometry. Compared to the free Bnpa ligand, where the py and azaindolyl rings are nearly coplanar, the Bnpa ligand in both complexes has considerable distortion due to the formation of the six-membered chelate ring, as evidenced by a large torsion angle between the py and azaindolyl rings (25.01° for **2a** and 36.65° for **2b**). Although the structure of **1** was not determined because of the lack of suitable crystals, the coordination environment around the Cu center is believed to be similar to that in $[Cu(npa)(PPh_3)_2][BF_4]$ [**3**; npa = *N*-(2-py)-7-azaindolyl], synthesized by us, where the Cu(I) center has a distorted tetrahedral geometry [N−Cu−N = 92.17(15)°] and the py and azaindolyl rings have a very large torsion angle of 38.67° (see Figure S12 of the Supporting Information).

Bnpa displays a reversible reduction peak at $E_{1/2}^{\mathrm{red}} = -2.22$ V vs $FeCp_2^{0/+}$ in the cyclic voltammetry (CV) diagram recorded in *N*,*N*-dimethylformamide, corresponding to the reduction of the boron center. Consistent with the previously reported B2bipy complexes,[7a] the binding of metal ions to the Bnpa ligand shifts the first reduction potential to more positive (0.16 V for **2a** and 0.32 V for **2b**) relative to the free ligand, albeit much less dramatically than B2bipy complexes. The fact that **2b** has a more positive reduction potential than **2a** supports the presence of electronic communication between the metal and the boron center and is consistent with the chloride ligand being a weaker electron donor relative to phenyl. The metal-to-ligand charge-transfer (MLCT) absorption band of **2a** appears at a lower energy than that of **2b**, further supporting such electronic communication.

When irradiated by UV light, Bnpa is fluorescent in the violet-blue region, with the emission energy shifting toward a longer wavelength with increasing solvent polarity (see Figure S4.1 of the Supporting Information), consistent with charge-transfer emission between the boron center and the npa portion. In contrast, the emission of complexes **1** and **2a** is dominated by a yellow and highly visible phosphorescence (see Figure S4.2 of the Supporting Information) at ambient temperature with $\lambda_{\max} = 540$ nm, $\tau = 8.0$ μs, and $\Phi = 0.04$ for **1** and $\lambda_{\max} = 543$ nm, $\tau = 25.0$ μs, and $\Phi = 0.004$ for **2a** in CH_2Cl_2. The phosphorescent nature of the emission spectra of **1** and **2a** is confirmed by their high sensitivity toward oxygen, which quenches the emission of the complexes. The Pt complex **2a** is much more sensitive toward oxygen than the Cu complex **1** because ~2% O_2 causes >90% quenching of the phosphorescent peak of **2a** (at 4.0×10^{-5} M) while more than 20% O_2 is needed to achieve the same effect for **1** (see Figure S8 of the Supporting Information). This difference is most likely caused by the much longer phosphorescent decay lifetime of the Pt complex, compared to the Cu complex. Complexes **1** and **2a** are stable in solution under air, and their phosphorescent response toward oxygen is fully reversible by using nitrogen or argon, thus making them potentially useful as oxygen-sensing reagents.

Both **1** and **2a** also display bright-yellow-green phosphorescence in the solid state at ambient temperature with emission wavelengths at 527 nm ($\tau = 7.5$ μs) and 519 nm ($\tau = 10.9$ μs), respectively. Most impressive is compound **1**, which has an unusually high emission quantum efficiency of 0.88 in the solid state (see Figure S4 of the Supporting Information; $\Phi = 0.10$ for **2a**), determined by using an integration sphere fluorimeter. Although a number of phosphorescent Cu(I) complexes with coordination environments similar to that of **1** and N,N-chelate ligands such as 1,10-phenanthroline[10a] (e.g., $[Cu(9,10\text{-phenanthroline})(PPh_3)_2][BF_4]$) and 2-(2-pyridyl)benzimidazole[10b,c] have been demonstrated successfully for use as triplet emitters in OLEDs, their emission quantum efficiencies are all much lower than that of **1**. The highest solid-state emission quantum efficiency at ambient temperature for previously known Cu(I) complexes is 0.69 for $[Cu(dnbp)(DPEphos)][BF_4]$ (dnbp = 2,9-di-*n*-butyl-1,10-phenanthroline; DPEphos = bis[2-(diphenylphosphino)phenyl] ether) in a poly(methyl methacrylate) matrix, reported by Wang and co-workers, which was shown to be an excellent emitter in OLEDs.[10a] The exceptionally

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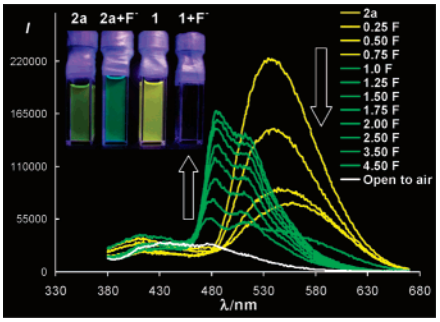

Figure 2. Phosphorescent spectral change of **2a** ($\lambda_{ex} = 360$ nm) with the addition of Bu_4NF (TBAF; [**2a**] = 4.0×10^{-5} M in CH_2Cl_2). Inset: photograph of the solutions of **1** and **2a** (4.0×10^{-5} M in CH_2Cl_2) with and without the addition of excess TBAF under UV light. The solutions in this experiment were prepared in a drybox under nitrogen.

high emission quantum efficiency and the incorporation of an electron-transporting boron functionality make **1** a very promising candidate as an efficient bifunctional phosphorescent emitter for OLEDs, which is being investigated in our laboratory. **2b**, a chloride analogue of **2a**, does not show any phosphorescence at ambient temperature in solution or in the solid state. The significant impact by ancillary ligands on the reduction potential, the MLCT absorption energy, and phosphorescence leads us to suggest that the phosphorescence in **2a** is most likely from a MLCT state.

To establish the role of the boron center in the phosphorescence of **1** and **2a**, we examined the photophysical properties of their non-boron-containing analogues [Cu(npa)-$(PPh_3)_2$][BF_4] (**3**) and Pt(npa)Ph_2 (**4**). **3** has no detectable phosphorescence, and **4** only displays very weak and hardly visible greenish phosphorescence ($\lambda_{max} = 487$ nm; $\tau = 18.5$ μs) at ambient temperature (see Figure S4.2 of the Supporting Information). The contrasting properties of **1** and **2a** versus **3** and **4** illustrate that the $BMes_2$ group in complexes **1** and **2a** is critical for achieving the bright ambient-temperature phosphorescence in solution. The role of the $BMes_2$ group is most likely to lower the energy level of the MLCT state below that of the ligand-centered excited state, because of its electron-accepting nature, thus facilitating the MLCT emission.

The impact of anion binding at the boron center on phosphorescence was investigated by examining the phosphorescent spectral change of **1** and **2a** in the presence of various amounts of fluoride ions. In contrast to the free ligand Bnpa, which experiences a typical fluorescent quenching upon the addition of fluoride ions (see Figure S6 of the Supporting Information), the addition of fluoride ions to the solution of **2a** causes a phosphorescent color switch from yellow to green, as shown by Figure 2 (see also Figure S10 of the Supporting Information). The yellow phosphorescent band at 543 nm diminishes, while a new oxygen-sensitive green phosphorescent emission band at $\lambda_{max} = 497$ nm ($\tau =$ 10.9 μs, determined in the presence of excess fluoride ions) appears and increases in intensity with the amount of fluoride ions, which can be attributed to the adduct **2a·F**$^-$. Fluoride ion binding to the boron in **2a** was also confirmed by ^{19}F NMR and UV−vis titration experiments (see Figures S5 and S11 of the Supporting Information). The green emission band of **2a·F**$^-$ has the distinct vibrational structure of npa and resembles the weak phosphorescent spectrum of Pt(npa)Ph_2 (**4**). The phosphorescent color switch of **2a** can therefore be explained as fluoride-induced color switching from MLCT to ligand-centered emission due to the impact of fluoride ion binding on the energy level of the MLCT state. The much brighter emission intensity of **2a·F**$^-$, compared to that of **4**, may be attributed to the bulky $BMes_2$ group that can effectively reduce intermolecular interactions, hence triplet−triplet annihilation of **2a·F**$^-$. Although the green emission of **2a·F**$^-$ is readily quenched by air, this adduct is stable toward air.

The behavior of the complex **1** toward fluoride ions is quite different. The addition of <0.8 equiv of fluoride ions under nitrogen results in quenching of the phosphorescent peak and a rise in the Bnpa fluorescent peak, which is subsequently quenched with additional fluoride ions in the same manner as the free Bnpa does, resulting in a nonemissive solution, as shown by the photograph in Figure 2. The instability of **1** toward fluoride ions was further confirmed by UV−vis and NMR spectral data (see Figure S11 of the Supporting Information), which can be attributed to the known poor N,N-chelating ability of the npa moiety[11] and the steric congestion caused by the two PPh_3 ligands. This is further supported by the NMR titration experiment of **3**, which was found to undergo decomposition upon the addition of fluoride ions. The consequence of the instability of **1** toward fluoride ions is that it has the potential to serve as a turn-on sensor for fluoride ions at $[F^-]/[\mathbf{1}] < 0.8$ ($[\mathbf{1}] = \sim 10^{-5}$ M) under air because the phosphorescent emission of **1** is mostly suppressed by oxygen and the fluorescence of Bnpa is switched on in this concentration regime, as confirmed by the fluorescent titration experiment performed under air.

In summary, we have demonstrated the first examples of bright ambient-temperature phosphorescent transition-metal complexes with a triarylboron group. We have shown that the boron group in these complexes plays a key role in achieving the bright phosphorescence. We have also illustrated that the Pt(II) and Cu(I) complexes have a distinct phosphorescent response toward fluoride ions at ambient temperature due to a fluoride-triggered energy level change in **2a** and ligand dissociation in **1**. Last we have shown that the Cu(I) complex **1** is an exceptionally bright phosphorescent emitter in the solid state and thus a very promising candidate for use as a phosphorescent emitter or a bifunctional electron-transport phosphorescent emitter in OLEDs.

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Supporting Information Available: Experimental section, CV diagrams, UV−vis spectra, emission spectra, UV−vis titration spectra, fluorescent titration spectra, phosphorescent titration spectra, NMR titration, and crystal structural data. This material is available free of charge via the Internet at http://pubs.acs.org.

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