# Gram Scale Synthesis of Benzophenanthroline and Its Blue Phosphorescent Platinum Complex

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Ⓢ *Supporting Information*

ABSTRACT: The design, synthesis, and characterization of 12-phenyl-benzo[*f*][1,7]phenanthroline, Bzp, is reported. Its use as a fluorine-free ligand for sky blue phosphorescence is demonstrated in a cyclometalated platinum complex, BzpPtDpm. BzpPtDpm phosphoresces at the same wavelength as its analogous 4,6-difluorophenylpyridine complex at both room temperature (466 nm) and 77 K (458 nm). Finally, production of a conformationally restricted derivative of BzpPtDpm with greatly increased quantum yield (46%) validates the versatility of the synthetic route.
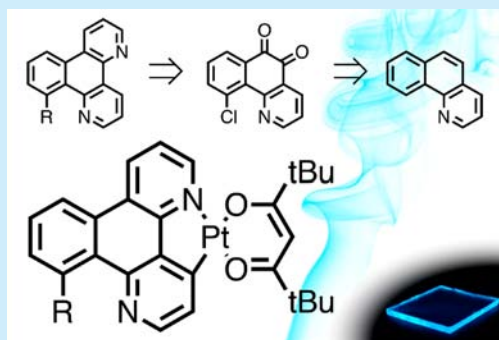
Triphenylene derivatives have found widespread use in materials science applications. The π-stacking interactions of the tetracyclic aromatic system that lead to discotic liquid crystalline behavior[1] also lead to high charge carrier mobilities,[2] making triphenylenes well suited for applications in organic electronics. Furthermore, triphenylene has a high triplet state energy (E_T = 2.9 eV),[3] making it a good candidate for inclusion in blue phosphorescent organometallic complexes, which are comprised of a central heavy atom, such as Ir or Pt, and coordinated organic ligands. These phosphors are desirable as organic light emitting diode (OLED) materials,[4] as well as photoredox catalysts,[5,6] and optogenetic[7] probes. Our interest in phosphorescent OLED materials led us to consider how to modify the D_{3h} symmetric triphenylene framework for use as a cyclometallating ligand. Depending principally on the structures of the organic ligands (most commonly phenylpyridine derivatives), the emission wavelengths of these transition metal complexes can span the visible spectrum,[8] but the design of blue emitting ligand systems has proven to be more challenging than that of their green to red emitting counterparts. Due at least in part to their relative synthetic inaccessibility with respect to phenylpyridines, triphenylenes are an underexplored ligand framework for blue phosphors. The title compound, benzophenanthroline (Bzp), is a low symmetry substituted diazatriphenylene designed with specific regiochemical features that facilitate blue phosphorescence.

Efficient organometallic phosphors commonly contain the phenylpyridine-like cyclometalation motif shown in Scheme 1. A carbon γ to nitrogen is deprotonated and bound to a metal ion to form a five-membered metallacycle. Table 1 lists calculated triplet, HOMO, and LUMO energies for triphenylene (**1**) and three aza-triphenylenes (**2**–**4**) that inform the rational design of Bzp. The triplet excited state energies of **2**–**4** do not differ markedly from **1**. However, the frontier orbitals of

Scheme 1. Phenylpyridine-like Cyclometallation and Representative Triphenylenes
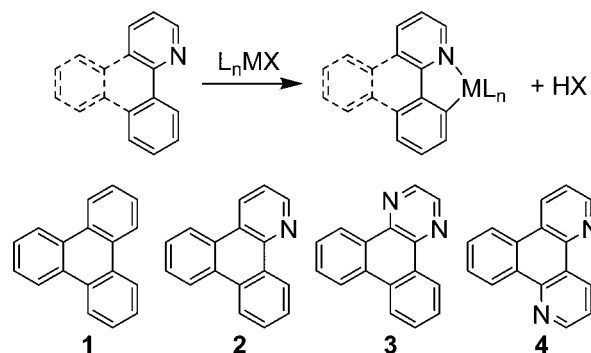

Table 1. Calculated[a] Frontier Orbital and Triplet State Energies of Candidate Triphenylenes

	1	2	3	4
Triplet (eV)	3.12	3.10	3.12	3.13
LUMO (eV)	−1.34	−1.63	−2.19	−1.79
HOMO (eV)	−5.70	−5.83	−5.94	−5.98

[a]Calculated at the B3LYP/631G** level.

2–**4** are stabilized relative to **1** due to the greater electronegativity of nitrogen. In particular, the extent to which the LUMO energies of **3** and **4** are stabilized depends on the nitrogen substitution pattern. The pyrazine moiety in **3** strongly stabilizes its LUMO. In contrast, the two pyridines in **4** are harder to reduce than pyrazine, which is reflected in its

comparatively less stabilized LUMO. The emission wavelengths of efficient organometallic phosphors depend on the energy of the lowest triplet excited state, which consists of an admixture of $\pi \rightarrow \pi^*$ ligand centered triplet (^{3}LC) and triplet metal to ligand charge transfer (d $\rightarrow \pi^*$, ^{3}MLCT) transitions.[9] Given that **2**–**4** have near isoenergetic ^{3}LC states, the emission wavelength of complexes using these compounds as cyclometalated ligands is governed by the energy of the ^{3}MLCT state. For example, a bis-cyclometalated iridium complex using **2**, (**2**)$_2$Ir(acac), phosphoresces green (λ_{em} = 540 nm)[10] whereas the analogous derivative using **3** emits red (λ_{em} = 640 nm).[11] In the case of **3**, stabilizing the LUMO relative to **2** lowers the energy of the ^{3}MLCT state. On the other hand, the nitrogen in **4** that is para to the carbon–metal bond should stabilize the metal d orbitals, thus stabilizing the HOMO and making the complex harder to oxidize. Since the nitrogen in this position has a minimal stabilizing effect on the LUMO, the net result is an increase in the HOMO–LUMO gap and destabilization of the ^{3}MLCT state. This effect has been demonstrated in Ir complexes cyclometalated with 2,3′-bipyridine ligands.[12] Lastly, because **4** has two inequivalent sites for cyclometalation, the coordination regiochemistry of **4** must be controlled with a substituent that blocks the nitrogen that is not intended to participate in cyclometalation. The target structure, Bzp, is therefore a derivative of **4** with an R group in the 12 position (see Figure 1). Unfortunately, only the unsubstituted **4** is
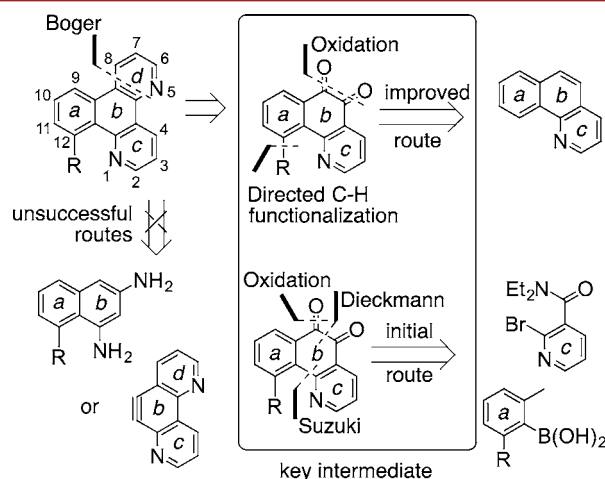

Figure 1. Retrosynthetic analysis of Bzp.

known, synthesized from diaminonaphthalene by a double Skraup quinoline synthesis.[13] Attempts to analogously synthesize substituted derivatives were unsuccessful in our hands, and subsequent attempts to benzannulate 1,7-phenanthroline by cycloaddition of its corresponding aryne to substituted furans[14] were not productive.

A Boger pyridine synthesis[15] of the d-ring via a 1,2,4-triazine became appealing due to the versatility of the orthoquinone precursor to the triazine. This key intermediate can be converted into a variety of heterocycles including the desired pyridine, thereby providing synthetic access to a broad tetracyclic chemical space of potentially useful materials, which we are also exploring. Our initial retrosynthetic analysis of the key intermediate involved disconnection of the B ring by a Dieckmann condensation,[16,17] which symmetrizes the A ring in the case of R = Me. Milligram quantities of the R = Me derivative were produced in this manner, preliminary
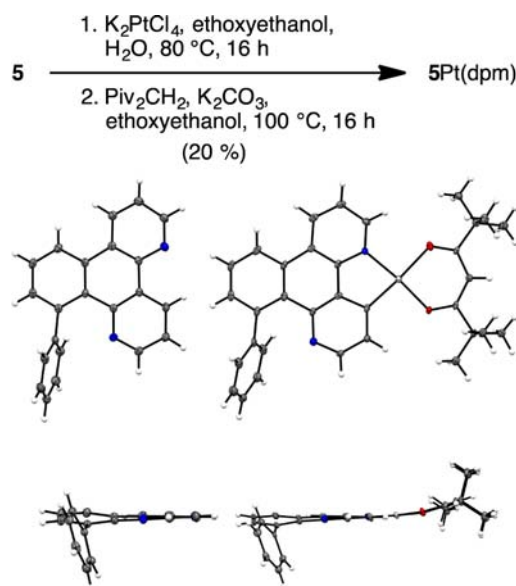
exploration of which indicated the need for other R groups and a gram scale preparative method. Here we report an improved synthetic route that employs the directing effect of the benzoquinoline nitrogen to install the R group. Palladium,[18,19] ruthenium,[20,21] and cobalt[22] catalyzed methods are known for 10 position functionalization of benzo[*h*]-quinoline. The improved route is demonstrated in the synthesis of **5** (Scheme 2), the R = Ph derivative.

Scheme 2. Synthesis of 5
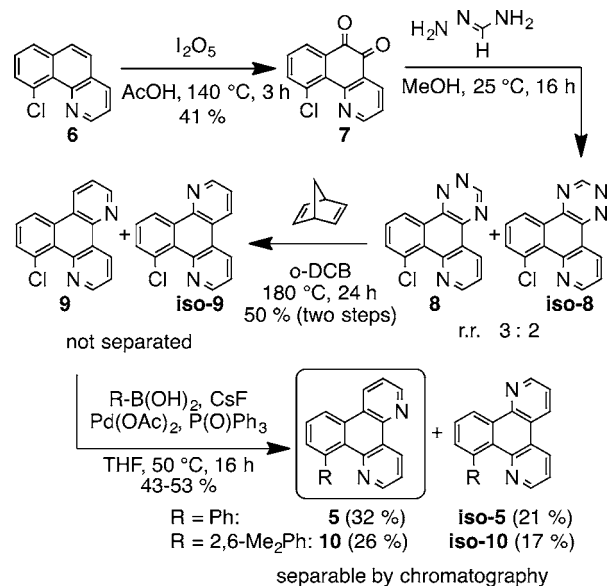
In order to maximize the versatility of the key intermediate, we elected to install a halogen as a placeholder for the R group, allowing it to be defined late in the synthetic route. The starting material, **6**, is readily obtained by functionalizing the 10 position of commercially available benzo[*h*]quinoline by Sanford's palladium catalyzed oxidative halogenation conditions.[23] The 5,6-orthoquinone **7** can be accessed directly with iodic anhydride as oxidant in refluxing acetic acid.[24] These transformations are easily carried out on multigram scale to generate the key intermediate **7**. Treatment of **7** with freshly prepared formamidhydrazone[25] yields a mixture of triazines **8** and **iso-8**, which are recovered by simple filtration. The isomeric mixture is subjected to 10 equiv of norbornadiene at 180 °C in dichlorobenzene[26] to yield a mixture of **9** and **iso-9**. While standard Suzuki–Miyaura conditions fail to catalyze coupling of **9** with phenylboronic acid, a modified procedure[27] completes the functional group transformation to phenylbenzophenanthrolines **5** and **iso-5** in a regiomeric ratio of 3:2 as judged by NMR. Fortunately, **5** is readily separable from its structural isomer **iso-5** by chromatography, though **iso-5** could not be separated from traces of **4** which form as the result of hydrodehalogenation of **9** during the cross-coupling. In order to assess its use as a ligand, **5** was then platinated similarly to the previously reported[28] **2** to form its analogous platinum dipivaloylmethane complex, **5**Pt(dpm) (Scheme 3).

The X-ray crystal structure of **5** reveals a 69° dihedral angle between the phenyl group and the a-ring to which it is bound. This angle is 65° in **5**Pt(dpm). Furthermore, the triphenylene core of **5** is slightly twisted, with a 10° angle between the mean plane of the a-ring and that of the c- and d-rings [9° in **5**Pt(dpm)]. The photoluminescence spectrum of **5** at 77 K

Scheme 3. Synthesis of 5Pt(dpm) and Crystal Structures[a] of 5 and 5Pt(dpm)

1. K$_2$PtCl$_4$, ethoxyethanol,
   H$_2$O, 80 °C, 16 h

5 ⟶ 5Pt(dpm)

2. Piv$_2$CH$_2$, K$_2$CO$_3$,
   ethoxyethanol, 100 °C, 16 h

(20 %)

[a]ORTEP structures shown at 50% probability level.

(Figure 2a) shows both fluorescence (E_{00} = 340 nm) as well as phosphorescence (E_{00} = 425 nm), the latter corresponding to a
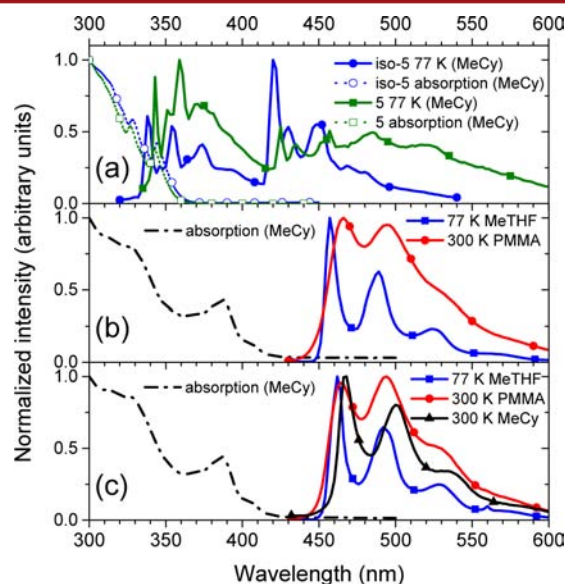
Figure 2. Absorption and emission spectra of (a) **5** and **iso-5**; (b) **5PtDpm**; (c) **10PtDpm**. All absorption spectra were collected in methylcyclohexane at 298 K. MeCy = methylcyclohexane; MeTHF = 2-methyltetrahydrofuran; PMMA = poly(methyl methacrylate).

triplet energy of 2.9 eV. As expected from our earlier analysis, **iso-5** has a similar triplet energy to **5** but lacks the specific nitrogen substitution pattern leading to sky-blue phosphorescence. Triplet energies for **5**Pt(dpm) and **iso-5**Pt(dpm) are predicted to be 2.75 and 2.48 eV, respectively (see Supporting Information), so **iso-5**Pt(dpm) was not pursued. At 77 K in frozen MeTHF, **5**Pt(dpm) exhibits sky blue phosphorescence (E_{00} = 458 nm, 2.71 eV, τ = 12.1 μs), 70 meV higher in energy than its isoelecronic parent, **2**PtDpm (E_{00} = 470 nm, 2.64 eV). Unfortunately, **5**Pt(dpm) is nonemissive in fluid solution at

room temperature, likely due to structural distortions in the luminescent excited state leading to other, nonemissive states.[29] Indeed, the complex becomes emissive when dispersed (0.5 wt %) in the rigid poly(methyl methacrylate) (PMMA) matrix (Φ = 0.11). By inspection of the crystal structures of **5** and **5**Pt(dpm), we hypothesized that partial rotation of the phenyl group may constitute a mode of deactivation which is not completely restricted in PMMA. Therefore, we expected an increased quantum yield from a rotationally restricted 2,6-dimethylphenyl substituted derivative, **10**Pt(dpm). Synthesis of the ligand, **10**, required only a trivial variation of the last step in the production of **5**, illustrating the versatility of our synthetic approach. Gratifyingly, this simple modification resulted in a 4-fold increase in quantum yield in PMMA (Φ = 0.46). Furthermore, luminescence from **10**Pt(dpm) can be observed in fluid solution (Φ = 0.01, τ = 118 ns). It is notable that **10**Pt(dpm) shares the same triplet energy as the analogous difluorophenylpyridine complex, (F$_2$ppy)Pt(acac) (2.71 eV),[30] with similar radiative and nonradiative rate constants in solution.

Difluorophenylpyridine is the emissive ligand of the canonical sky blue phosphor bis-difluorophenylpyridinato iridium picolinate (Firpic), ubiquitous in the OLED field. However, fluorinated aromatics such as Firpic are unstable to reduction,[31] leading to more rapid breakdown of organo-fluorine containing OLED devices. The Bzp ligand system displays similar emission characteristics to the F$_2$ppy system, without potential dehalogenative degradation pathways under electrical stimulation. We expect to investigate several permutations of platinum and iridium complexes of this ligand in OLED devices. Furthermore, we anticipate that the synthetic advances reported herein may lead to increased investigation of complex heterotriphenylenes in liquid crystals, organic electronics, and other fields.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01693.

> Experimental procedures and characterization (PDF)
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> Crystallographic data for **5** (CIF)
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> Crystallographic data for **5**Pt(dpm) (CIF)

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Notes

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