Exploiting Synergy Between Ligand Design and Counterion Interactions to Boost Room Temperature Phosphorescence from Cu(I) Compounds

Rajarshi Mondal, a Issiah B. Lozada, a Rebecca L. Davis, a J. A. Gareth Williams b* and David E. Herbert a*

a Department of Chemistry and the Manitoba Institute for Materials, University of Manitoba, 144 Dysart Road, Winnipeg, Manitoba, R3T 2N2, Canada;

* david.herbert@umanitoba.ca

b Department of Chemistry, Durham University, Durham, DH1 3LE, U.K.;

*j.a.g williams@durham.ac.uk
**ABSTRACT**

The structural and photophysical properties of three sets of emissive copper complexes of the form [(P^N)2Cu]X are presented. Here, P^N represents a bidentate ligand based on phenanthridine (3,4-benzoquinoline) incorporating a phosphine unit at the 4-position, of which three examples are investigated, namely (4-diphenylphosphino)phenanthridine (L1), (4-diphenylphosphino)(2-methyl)phenanthridine (L2) and (2,6-dimethyl)(4-diphenylphosphino)phenanthridine (L3). For each P^N-coordinating ligand, the corresponding homoleptic copper(I) complex (1-X, 2-X, 3-X) has been prepared as both the hexafluorophosphate and tetraphenylborate salt (X = PF_6^- or BPh_4^-). The identity of the counterion was found to have a profound and unexpected impact on the emission properties of the powder samples, amplifying the effects of P^N ligand modification and enabling emission tuning from orange to yellow. These effects can be attributed to different molecular packing, and to the impact of ligand structure and ionic interactions on distortions in the excited state relative to the ground state. The results have been interpreted with the help of density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations.
INTRODUCTION

The design of new emissive molecules based on low-cost and abundant metals including copper is central to increasing the sustainability of light-emitting devices, photosensitizers and imaging agents.\(^1\) To fully realize the potential of luminescent Cu(I) coordination complexes, strategies to tune emission wavelengths and optimise photophysical properties, such as lifetimes and quantum yields, are critical. One prominent strategy is to use ligand design to prevent molecular distortions of tetrahedral Cu(I) complexes in the excited state that can lead to competitive non-radiative decay. For example, methylation ortho to the nitrogen donors in bidentate \(N^N\) phenanthroline frameworks has been shown to considerably reduce the apparent Stokes shift of emission and boost quantum yields of Cu(I) complexes containing such ligands, accompanied by elongation of the emission lifetimes.\(^4\) These outcomes are associated with the influence of the methyl groups in restricting the flattening of the structure away from \(D_{2d}\) symmetry towards \(D_{2h}\). This effect is not universal, however; for example, the impact of ligand ortho methylation in Cu(I) complexes supported by 8-(diphenylphosphino)-2-methylquinoline ligands is minimal.\(^5\) A related approach is the use of rigid media,\(^6\) packing-effects,\(^7,\)\(^8\) or inter-ion interactions\(^9-\)\(^12\) to control excited state reorganization. As these approaches are usually invoked independently in the literature, we were curious as to whether these tactics could be used in a complimentary fashion. Namely, in instances where the impact of one strategy on its own is limited, could combining ligand modification and solid-state effects enhance photophysical properties to potentially expand the reach of these design strategies,
similar to the recently reported synergistic activation of room temperature phosphorescence in organic materials.\textsuperscript{13}

Here, we report a case study using homoleptic Cu(I) complexes of bidentate $P^N$-coordinating ligands based on a phenanthridine unit substituted at the 4-position with a diphenylphosphine moiety: \textbf{1X} (\textbf{1} = [(\textit{L1})\textit{2}Cu]\textsuperscript{+}), \textbf{2X} (\textbf{2} = [(\textit{L2})\textit{2}Cu]\textsuperscript{+}), \textbf{3X} (\textbf{3} = [(\textit{L3})\textit{2}Cu]\textsuperscript{+}), where \textit{X} = PF$_6^-$ or BPh$_4^-$ in each case. Emission from Cu(I) complexes of both mixed $P^P/N^N$ ligand sets\textsuperscript{14-18} and bidentate $P^N$-coordinating ligands\textsuperscript{19-24} has been widely explored. The $P^N$ ligand \textbf{L1} is the parent 4-(diphenylphosphino)phenanthridine, a benzannulated analog of the phosphine/quinoline ligand utilized by Tsukuda, Tsubomura and coworkers.\textsuperscript{5}. \textbf{L2} and \textbf{L3} both incorporate a methyl substituent in the 2-position \textit{para} to the nitrogen donor, while \textbf{L3} carries an additional methyl \textit{ortho} to N, making it reminiscent of the \textit{ortho}-methylated phenanthrolines mentioned above.\textsuperscript{4} The complexes all display moderately intense orange-yellow photoluminescence in the solid-state. In investigating the photophysical properties of powder samples, we discovered a strong effect of the counterion on the emission properties that responds differently to subtle changes in ligand architecture.

The $\pi$-extended $P^N$ donor \textbf{L3} was synthesized similarly to \textbf{L1}\textsuperscript{25} and \textbf{L2}\textsuperscript{26} The tricyclic frame of the phenanthridine moiety was prepared via a one-pot, Pd-catalyzed cross-coupling/condensation of the appropriately substituted aniline with 2-acetylphenylboronic acid (Scheme 1). \textbf{L3} was then accessed via lithium-halogen exchange between 4-bromo-2,6-dimethylphenanthridine and sec-butyllithium, followed by quenching with Ph$_2$PCl. Evidence for the assembly of the phenanthridine core could
be discerned in the downfield shift of the “imine-like” C_6 resonance in the^{13}\text{C}^{1\text{H}} NMR spectrum at 157.3 ppm (cf. L\textbf{1}: 152.8 ppm; L\textbf{2}: 151.8 ppm).

Mixing solutions of \textbf{L1-L3} with suspensions of CuBr gave increasingly homogeneous orange solutions of [(L)\text{Cu}]_2(\mu-\text{Br})_2 dimers, previously described for L\textbf{1}\textsuperscript{25} and L\textbf{2}.\textsuperscript{26} Full characterization details of [(L\textbf{3})\text{Cu}]_2(\mu-\text{Br})_2 are provided in the Supporting Information. The solid-state structure of [(L\textbf{3})\text{Cu}]_2(\mu-\text{Br})_2 shows a bent, butterfly-like orientation to the Cu_2Br_2 sub-unit with an intermetallic distance of 2.6793(4) Å and a ‘head-to-head’ orientation of the two P^N ligands in which the nitrogen donors are on the same side of the Cu_2Br_2 core (Figure S1). In comparison, the equivalent halide-bridged dimers of [(L\textbf{1-\textbf{L2}})\text{Cu}]_2(\mu-X)_2 (X = Cl, Br, I) are all ‘head-to-tail’, with longer Cu-Cu distances.\textsuperscript{25, 26} The presence of \textit{ortho} methyl groups adjacent to the phenanthridine nitrogens thus appears to override the steric preferences of the PPh\textsubscript{2} units to avoid each other in the solid-state. Addition of a second equivalent of the P^N ligand, followed by metathesis with NaPF\textsubscript{6} or NaBPh\textsubscript{4} in tetrahydrofuran, gave bright yellow/green suspensions, from which the targeted [(L)\text{Cu}]X salts could be isolated as light yellow solids. The Cu(I) complexes are soluble in most organic solvents, and were fully characterized in solution by multi-nuclear NMR spectroscopy, and in the solid-state by elemental analysis and single-crystal X-ray diffraction. A symmetric ligand environment was observed for both bound ligands for all six complexes by NMR spectroscopy.

In the solid-state, the complexes adopt the distorted tetrahedral geometry expected of four-coordinate Cu(I) with bulky ligand sets (exemplified by the BPh\textsubscript{4}^- series in Figure 1; see Figure S2 for PF\textsubscript{6}^- salts). Comparing bond distances, all complexes show
very similar metal-ligand interactions (Table 1). Examining the bond angles, the differences imposed by relatively small changes in ligand sterics (i.e., replacing H with CH$_3$) become evident. While the bite angles (N1-Cu1-P1, for example) remain invariant as a result of the rigid sp$^2$ aromatic ligand backbone, the interligand angles are significantly perturbed in moving from 1X to 3X. Interestingly, these differences are exacerbated in changing from PF$_6^-$ to BPh$_4^-$. Thus, $\tau$ metrics$^{27}$ suggest that L1 and L2, bearing no additional sterically imposing substituents close to Cu, favour a distorted sawhorse geometry in their Cu(I) complexes ($\tau \sim 0.55$) when paired with a PF$_6^-$ counterion, but enforce more of a distorted tetrahedral ligand arrangement ($\tau \sim 0.63$-0.69) as BPh$_4^-$ salts. These distortions are caused by unequal P-Cu-P vs N-Cu-N angles, and larger dihedral angles between the Cu-P1 vectors and the plane formed by the Cu-P2-N2 sub-unit of the second P$^N$ ligand compared with the equivalent dihedral angle formed by the Cu1-N1 bond/Cu-P2-N2 plane (Table S1).

The inequivalence of these angles is smallest in 3X. In particular, the N-Cu-N angles are much larger for 3X, owing to the presence of the ortho methyl groups. Increased steric demand close to the donor nitrogen in L3 thus disfavours distortion from an idealized tetrahedral geometry for both BPh$_4$ and PF$_6$ salts. More pronounced are the rocking distortions$^4$ (Figure 1b), as well as a marked bending of the Cu-N bond out of plane with the phenanthridine ligand in 3X; the dihedral angle of the Cu-N vector with the plane formed by the phenanthridine moiety reaches 21° in 3X, compared with an arrangement much closer to coplanarity in 1X/2X ($\sim$0-5°). Comparing 3BPh$_4$ and 3PF$_6$, the N-Cu-N angles are similar, but the P-Cu-P angles are much smaller in 3BPh$_4$. Space-
filling diagrams reveal that these geometric constraints result from more intimate inter-ion contacts for the BPh$_4^-$ salts (Figure 1c).

Absorption spectra of the Cu(I) complexes in CH$_2$Cl$_2$ solution at room temperature (Figure S3) show strong absorbance in the UV (250-300 nm; $\varepsilon \sim 35 \times 10^3$ M$^{-1}$cm$^{-1}$), with two distinct but weaker bands at $\sim$340 nm which also appear in the spectra of the proligands (Figure S4). The major difference between the absorption profile of the ligands and their Cu(I) complexes is the longer wavelength tail in the complexes, attributable to relatively weak, spin-allowed, charge-transfer transitions ($^{1}$CT), in which the phenanthridine heterocycle serves as the CT acceptor. By analogy to homoleptic [(N$^N$N)$_2$Cu]$^+$ complexes, we assign these as metal-to-ligand charge-transfer ($^{1}$MLCT) in character, the donor orbitals being of predominantly metal-based $d$ character with participation from the phosphine-metal bonding pairs. Close examination of the peaks around $\sim$341 and $\sim$357 nm revealed only a small bathochromic shift for all BPh$_4^-$ complexes, with the sets of spectra otherwise indistinguishable.

Electrochemical analysis of all three complexes showed irreversible redox events at similar potentials vs FcH$^{0/+}$ (FcH = (η$^5$-C$_5$H$_5$)$_2$Fe; Figure S5). Comparing the onset of the reduction events for 1-3, a slight cathodic shift is observed with alkylation of the phenanthridinyl unit as the addition of an inductively donating methyl group renders the complexes harder to reduce (1PF$_6^-$ $\sim$ -2.14 V, 2PF$_6^-$ $\sim$ -2.22 and 3PF$_6^-$ $\sim$ -2.36 V vs FcH$^{0/+}$). This impact of alkylation is regio-specific: alkylation at the 6-position in 3PF$_6^-$ results in a more negatively shifted reduction potential relative to 1PF$_6^-$, compared to alkylation at the 2-position in 2PF$_6^-$.

This is likely a consequence of the LUMO being
structured with lobes localized at the C=N sub-unit in the 6-position (Figure S41). The Cu(I/II) oxidation event is affected according to the same trend as the reduction peaks but in the opposite direction, with a slight anodic shift upon alkylation that is also regiospecific (1PF₆ ~0.76 V, 2PF₆ ~0.74 and 3PF₆ ~0.69 vs FcH⁰⁰⁹). As a result of these offsetting effects, the separation between oxidation and reduction events measured by electrochemistry is more or less equivalent for all three complexes. Using these separations to estimate the HOMO-LUMO gap shows that all complexes thus fall within a relatively narrow spread of 150 mV (Table S2), consistent with the isoenergetic lowest energy peaks observed by absorption spectroscopy. TD-DFT vertical absorption energies and the HOMO-LUMO gap estimated by DFT-determined frontier orbital energies are accordingly similar for the three cations 1⁺, 2⁺ and 3⁺ (Table S5).

The complexes are not emissive in solution at ambient temperature, even with rigorous exclusion of oxygen. In contrast, powdered samples are brightly luminescent to the eye when observed under long-wavelength UV irradiation, glowing bright yellow to orange in colour (Figure S6). The emission of the samples was therefore studied in the solid state at ambient temperature, using an integrating sphere to evaluate photoluminescence quantum yields (Φₗₐₘ) under continuous-wave excitation, and with pulsed laser diode excitation to measure the corresponding luminescence lifetimes (τ; Table 2). Broad, featureless emission peaks are observed, consistent with MLCT character to the emissive state, with maxima between 584 and 647 nm. Quantum yields hover mostly around 2%, but are significantly higher for 3BPh₄. The lifetimes are roughly of the order of 1 µs, with some variation; 3BPh₄ is again notable in that it
displays a significantly longer lifetime. PF$_6^-$ salts of Cu(I) complexes of bidentate $P^N$ ligands incorporating smaller quinolinyl $\pi$-systems, but that are otherwise directly analogous to 1PF$_6$ and 3PF$_6$, show broad emission centred at 640 nm for both complexes, with lifetimes of 0.33 and 1.0 $\mu$s, respectively.$^5$ In comparison, the emission maximum of 1PF$_6$ at room temperature is blue-shifted by 12 nm compared to 2PF$_6$, and 22 nm compared to 3PF$_6$. A similar trend in the apparent Stokes shift was observed for emission from [(L)Cu$_2$(μ-I)$_2$] dimers, with a hypsochromic shift for emission from the parent [(L1)Cu$_2$(μ-I)$_2$] relative to the alkylated [(L2)Cu$_2$(μ-I)$_2$].$^{26}$ While this same trend holds for room temperature emission from 1BPh$_4$ ($\lambda_{em} = 618$ nm) and 2BPh$_4$ ($\lambda_{em} = 647$ nm), a considerable hypsochromic shift in the opposite direction is seen for 3BPh$_4$ ($\lambda_{em} = 584$ nm), as expected from previous studies of [(N$^N$)(P$^P$)Cu(I)]$^+$ complexes with ortho-methylated phenanthroline ligands.$^{17}$ The anticipated effect of ligand substitution ortho to the coordinating nitrogen is therefore “turned on” for 1X/3X by changing the counterion from PF$_6^-$ to BPh$_4^-$.

Attributing this effect to enhanced molecular rigidity is supported by the low temperature emission spectra. In a frozen glass of EPA at 77 K, complexes 1X and 2X display orange/red luminescence whilst the brighter luminescence of 3X is green-yellow to the eye (EPA = diethyl ether / isopentane / ethanol, 2:2:1 v/v). The corresponding emission spectra are broad and structureless (Figure 5), and highlight a substantial blue shift of 3X relative to 1X and 2X (whose emission maxima are similar to one another), regardless of counterion. The substantial hypsochromic shift of the phosphorescence of 3X relative to the other complexes at low temperature, despite the absorption spectra
being so similar for all complexes, is consistent with the steric influence of the ortho methyl groups inhibiting attainment of a geometry that most stabilises the triplet state. At low temperature, ortho methylation clearly has a large impact on structural reorganization, whereas methylation para to nitrogen (i.e., in L2) does not, consistent with Cu(I) complexes of ortho-methylated phenanthroline N^N ligands.\textsuperscript{4,6} The timescale of low temperature luminescence is long, indicative of phosphorescence from a triplet state: $3\text{PF}_6$ and $3\text{BP}_4$ have identical lifetimes within the uncertainty on the measurement (740 and 730 µs, respectively). The emission of the $1\text{X}$ and $2\text{X}$ complexes is shorter, showing biexponential decay, fitting to a major component of about 150 µs and a minor of around 50 µs in each case. The origin of the biexponential nature of the decay is unclear. It may be due to inhomogeneities owing to poor solubility in the EPA glass at low temperature. However, what is clear is that the formally forbidden $T_1 \rightarrow S_0$ emission is evidently promoted by the Cu(I) centre, as the phosphorescence lifetimes of the corresponding free $P^N$ ligands are of the order of hundreds of milliseconds ($\tau = 240$, 310, and 530 ms for 1, 2, and 3, respectively; Figure S7). The temporal decay of their emission is easily visible to the naked eye.

To further investigate the origin of this effect, we optimized gas-phase geometries of the isolated cations in both the ground state ($S_0$) and first triplet excited state ($T_1$) using DFT, and probed the nature of the optical transitions with TD-DFT. Consistent with the absorption spectra, the vertical transitions to the lowest lying singlet states are very similar in energy for all three cations (Table S5). The lowest energy excitations are HOMO→LUMO/HOMO-1→LUMO+1 in character, as can be seen in the
electron/hole maps in Figure S42. Re-optimizing the geometry of each ground state as a triplet gave the geometry and free energy of the lowest lying triplet states (T1). In the T1 excited state, all three cations show elongation of Cu-P distances, which is most pronounced for 1+ (Table S3). This is consistent with participation of filled Cu-P \( \sigma \)-bonding orbitals in the MLCT excitation to vacant \( \pi^* \) acceptor orbitals on phenanthridine. The trend observed in the low temperature emission spectra could be reproduced computationally; TD-DFT calculated phosphorescence energies for 1+ and 2+ are nearly equivalent, and smaller than that calculated for 3+. A slightly larger singlet-triplet gap was calculated for 2+ compared to 1+, whilst 3+ has the smallest calculated singlet-triplet gap and smallest reorganization energy.\(^{31}\) The lowest lying triplet state of 3+ is higher in energy than for 1+/2+ and incurs the least structural reorganization upon relaxation to the ground state.

So why is this predicted impact only observed at room temperature for the BPh4− complexes? The most pronounced structural change is to the coordination geometry of the four-coordinate Cu centre. The three optimized \( S_0 \) structures have \( \tau, \) metrics of 0.57 (1+), 0.57 (2+) and 0.71 (3+), which align well with the \( \tau, \) metrics and distorted sawhorse geometries of the PF6 salts (Table 1). In the T1 state, a distinct distortion towards true sawhorse geometry is accompanied by a reduction in \( \tau, \) to 0.44 (1+), 0.44 (2+) and 0.56 (3+; Table S3). In addition, for 1+/2+ the P-Cu-P angles compress significantly from 144° in the ground state to 109° in the first excited triplet state. The same angle in the more sterically encumbered 3+ is also made more acute in the excited state (\( S_0 \): 131° vs. \( T_1 \): 108°), but as this angle is tighter in the ground state already, the change is not as
drastic. The N-Cu-N angles are relatively invariant for all three complexes, constricting by only a few degrees for $1^*/2^*$ ($S_0$: 109° vs. $T_1$: 106°) and relaxing slightly for $3^*$ ($S_0$: 119° vs. $T_1$: 121°). Thus, inclusion of 6-position methyl groups on its own is not enough to prevent significant reorganization in the emissive states at room temperature. As a result, emission from 1PF$_6$, 2PF$_6$ and 3PF$_6$ is most strongly affected by the increased degrees of freedom from an added alkyl substituent, which red-shifts emission to lower energy. Replacing PF$_6^-$ with BPh$_4^-$ leads to closer inter-ion contacts in the solid-state. As can be seen in Figure 3, to minimize motion of the large phenanthridinyl moiety, the PPh$_2$ fragment twists substantially in the $T_1$ geometry, which is hampered by the presence of the BPh$_4^-$ ion, as shown in Figure 1c. This twisting is not sufficiently inhibited by 6-alkylation alone (as in 3PF$_6$), nor by substitution of PF$_6^-$ for BPh$_4^-$ in the absence of 6-alkylation (as in 1BPh$_4$ or 2BPh$_4$). For 1BPh$_4$ and 2BPh$_4$ the presence of close inter-ion interactions on their own is not sufficient to prevent reorganization: these interactions are more substantial for the BPh$_4^-$ salts compared to PF$_6^-$ salts as the former undergo greater distortions, as evidenced by the larger changes to $\tau_1$ ($\Delta\tau_1$). The larger distortions result in lower energy emission. The combined effect of 6-position alkylation and enhanced inter-ion interactions is likely responsible for the observed boost in quantum yield of 3BPh$_4$ via reduction of non-radiative decay rates, and also accounts for the substantial blue-shift in the wavelength of emission from this complex even at ambient temperature. Thus, as seen in the case of 3X, close inter-ion interactions can compliment the impact of ligand design, amplifying photophysical properties in a synergistic fashion.
In conclusion, we have found that exploiting the synergy between ligand modification (in this case, $^N$ ligand ortho methylation) and inter-ion interactions can be used to amplify the impact of ligand design and tune emission from orange-red to quite bright yellow ($\lambda_{\text{max}}$ shifting from 647 to 584 nm) in Cu(I) complexes of bidentate, benzannulated $^N$ ligands. Yellow-emitting Cu(I) complexes are relatively rare,\textsuperscript{32-38} despite yellow being a key component for achieving white light emission in organometallic light emitting diodes (OLEDs).\textsuperscript{39} The applicability of this method for amplifying ligand effects through choice of counterion to other phosphorescent emitters is currently underway.
Scheme 1. Synthesis of proligands $L_1$, $L_2$, and $L_3$ (this work) and their Cu(I) complexes.
Figure 1. (a) Solid-state X-ray structures of the cationic fragments of 1BPh₄, 2BPh₄ and 3BPh₄. Hydrogen atoms, counterions and lattice-confined solvent molecules (2BPh₄) are omitted for clarity. (b) View highlighting rocking distortions from idealized tetrahedral geometry and bending of the Cu-N bond out of the phenanthridine ligand plane. (c) Partial space-filling diagrams for 1BPh₄ and 1PF₆.

<table>
<thead>
<tr>
<th></th>
<th>1PF₆</th>
<th>2PF₆</th>
<th>3PF₆</th>
<th>1BPh₄</th>
<th>2BPh₄</th>
<th>3BPh₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1-N1/</td>
<td>2.0538(16)</td>
<td>2.0578(18)</td>
<td>2.1251(18)</td>
<td>2.0669(16)</td>
<td>2.094(3)</td>
<td>2.0740(18)</td>
</tr>
<tr>
<td>Cu2-N3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu1-N2/</td>
<td>2.0837(15)</td>
<td>2.0951(19)</td>
<td></td>
<td>2.061(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu2-N4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.073(3)</td>
<td></td>
</tr>
<tr>
<td>Cu1-P1/</td>
<td>2.2195(5)</td>
<td>2.2016(6)</td>
<td>2.2162(6)</td>
<td>2.2328(5)</td>
<td>2.2041(10)</td>
<td>2.2229(10)</td>
</tr>
<tr>
<td>Cu2-P3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.2527(6)</td>
<td></td>
</tr>
<tr>
<td>Cu1-P2/</td>
<td>2.2115(5)</td>
<td>2.2265(6)</td>
<td></td>
<td>2.2222(10)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu2-P4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.2251(6)</td>
<td></td>
</tr>
<tr>
<td>N1-Cu1-N2/</td>
<td>109.20(6)</td>
<td>100.19(10)</td>
<td>118.93(7)</td>
<td>105.46(9)</td>
<td>101.40(11)</td>
<td>123.78(7)</td>
</tr>
<tr>
<td>N3-Cu2-N4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>105.94(11)</td>
<td></td>
</tr>
<tr>
<td>P1-Cu1-P2/</td>
<td>145.49(2)</td>
<td>146.99(4)</td>
<td>133.23(2)</td>
<td>136.73(3)</td>
<td>131.49(4)</td>
<td>126.15(2)</td>
</tr>
<tr>
<td>P3-Cu2-P4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>137.17(4)</td>
<td></td>
</tr>
<tr>
<td>N1-Cu1-P1/</td>
<td>87.31(5)</td>
<td>86.83(5)</td>
<td>85.63(5)</td>
<td>87.04(5)</td>
<td>86.70(8)</td>
<td>87.92(5)</td>
</tr>
<tr>
<td>N3-Cu2-P3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>86.14(8)</td>
<td></td>
</tr>
<tr>
<td>N2-Cu1-P2/</td>
<td>86.34(4)</td>
<td>86.65(5)</td>
<td></td>
<td>86.59(8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N4-Cu2-P4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>85.02(5)</td>
<td></td>
</tr>
<tr>
<td>N1-Cu1-P2/</td>
<td>116.41(5)</td>
<td>114.83(5)</td>
<td>114.67(5)</td>
<td>119.87(5)</td>
<td>117.95(8)</td>
<td>129.20(5)</td>
</tr>
<tr>
<td>N3-Cu2-P4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>116.76(8)</td>
<td></td>
</tr>
<tr>
<td>N2-Cu1-P1/</td>
<td>110.26(5)</td>
<td>121.21(5)</td>
<td></td>
<td>131.48(8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N4-Cu2-P3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>106.63(5)</td>
<td></td>
</tr>
</tbody>
</table>

|  \( \tau \)[a] | 0.56 | 0.54 | 0.68 | 0.64 | 0.69, 0.63 | 0.72 |

---

[a]: The value of \( \tau \) for 1BPh₄, 2BPh₄ and 3BPh₄.
\[ \tau = \delta \cdot [360-(\alpha+\beta)]/141, \] where \( \delta = \beta/\alpha \), the ratio of the second largest (\( \beta \)) to largest (\( \alpha \)) angle.\(^{27}\)

**Figure 2.** Emission spectra of 1X, 2X and 3X in the solid-state at 298 ± 3 K \( \lambda_{\text{ex}} = 425 \) nm, where X = (a) PF\(_6\) or (b) BPh\(_4\) and (c) in dilute EPA glass at 77 K, \( \lambda_{\text{ex}} = 370 \) nm.
Table 2. Emission data for 1X, 2X and 3X in the solid state at 298 ± 1 K and in dilute EPA glass at 77 K.

<table>
<thead>
<tr>
<th></th>
<th>Emission, solid state 298±1 K</th>
<th></th>
<th>Emission, EPA glass 77 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}^a$ / nm</td>
<td>$\Phi_{\text{lum}}^a \times 10^2$</td>
<td>$\tau^b$ / ns</td>
</tr>
<tr>
<td>1PF$_6$</td>
<td>607</td>
<td>2.4</td>
<td>2100</td>
</tr>
<tr>
<td>2PF$_6$</td>
<td>619</td>
<td>0.80</td>
<td>1900</td>
</tr>
<tr>
<td>3PF$_6$</td>
<td>629</td>
<td>1.7</td>
<td>1300</td>
</tr>
<tr>
<td>1BPh$_4$</td>
<td>618</td>
<td>2.9</td>
<td>710</td>
</tr>
<tr>
<td>2BPh$_4$</td>
<td>647</td>
<td>2.0</td>
<td>840</td>
</tr>
<tr>
<td>3BPh$_4$</td>
<td>584</td>
<td>8.9</td>
<td>7400</td>
</tr>
</tbody>
</table>

*(a) Recorded using an integrating sphere, $\lambda_{\text{ex}} = 425$ nm. (b) Measured by time-correlated single-photon counting, $\lambda_{\text{ex}} = 425$ nm. (c) EPA = diethyl ether/isopentane/ethanol (2:2:1 v/v). (d) Measured by multichannel scaling, $\lambda_{\text{ex}} = 370$ nm. Where two values are given, the decay follows biexponential kinetics with relative magnitudes of the two components in parenthesis.*
Figure 3. Optimized geometries and $\tau,^{27}$ metrics of the ground-state ($S_0$) and first excited triplet state ($T_1$) of $1^+$, $2^+$ and $3^+$.

ASSOCIATED CONTENT

Supporting Information. Multi-nuclear NMR spectra of all new compounds; additional UV-vis absorption and emission spectra; details of computational methods; combined crystallographic information file containing all X-ray data. CCDC 1872863-1872869 contain the supplementary crystallographic data for this paper. The data can be
obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

The following files are available free of charge:

Supporting Information File (PDF)
Combined Crystallographic Information File (CIF)

AUTHOR INFORMATION

Corresponding Authors

david.herbert@umanitoba.ca, j.a.g.williams@durham.ac.uk

ORCID

Rebecca L. Davis: 0000-0002-0679-6025
J. A. Gareth Williams: 0000-0002-4688-3000
David E. Herbert: 0000-0001-8190-2468

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources
The following sources are gratefully acknowledged: Natural Sciences Engineering Research Council of Canada for a Discovery Grant to DEH (RGPIN-2014-03733); the Canadian Foundation for Innovation and Research Manitoba for an award in support of an X-ray diffractometer (CFI #32146); the University of Manitoba for start-up funding (DEH) and GETS support (RM, IBML). The Association of Commonwealth Universities (ACU) is thanked for a University of Manitoba Titular Fellowship (2016–17) to JAGW.

ACKNOWLEDGMENTS

We are grateful to Prof. Mazdak Khajehpour for access to a UV-Vis spectrometer.

References