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Control of emission colour with N-heterocyclic carbene (NHC) ligands in phosphorescent three-coordinate Cu(i) complexes†

Valentina A. Krylova, Peter I. Djurovich, Brian L. Conley, Ralf Haiges, Matthew T. Whited, Travis J. Williams and Mark E. Thompson*

A series of three phosphorescent mononuclear (NHC)–Cu(i) complexes were prepared and characterized. Photophysical properties were found to be largely controlled by the NHC ligand chromophore. Variation of the NHC ligand leads to emission colour tuning over 200 nm range from blue to red, and emission efficiencies of 0.16–0.80 in the solid state.

Phosphorescent Cu(i) complexes are an emerging class of luminescent materials based on an inexpensive and abundant metal.1 The ability to tune chemical and photophysical properties in a desirable and predictable way is highly important when considering potential applications of Cu(i)-based phosphors. The typical strategy to modulate the excited state properties of these and related luminescent materials is usually achieved through variation of the coordinating ligand(s).2 To date the types of ligands most commonly used to prepare phosphorescent Cu(i) complexes are diimines or organophosphines and their derivatives.3 Alternatively, N-heterocyclic carbenes (NHC) are an attractive class of ligands as they are electron-withdrawing ligand(s).2 To date the types of ligands most commonly used to prepare phosphorescent Cu(i) complexes are diimines or organophosphines and their derivatives.4 Alternatively, N-heterocyclic carbenes (NHC) are an attractive class of ligands as they are electronically and sterically tunable and form strong bonds with transition metals giving robust complexes.4 However, while NHCs have been employed as either chromophoric or ancillary ligands in luminescent Ir and Pt complexes5 they have been rarely used as chromophoric ligands in Cu(i) complexes.6

We have recently used NHC ligands to prepare phosphorescent 3-coordinate Cu(i) complexes (NHC)Cu(N=N), where N=N denotes a neutral diimine or monoanionic pyridyl-azolate ligand.7 The monodentate NHC ligand, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr), employed in these complexes has both a large π–π* energy gap and high triplet energy, therefore the emission energy in these derivatives is controlled by variations in the N=N ligand.

Herein, we report a series of luminescent (NHC)Cu(N=N) complexes 1–3 (Fig. 1), where the NHC ligand is principally involved in the excited state and demonstrate a wide range emission colour tunability through modification of carbene moiety. In particular, we systematically lowered the energy gap of 1 by benzannulation of imidazolyldiene ring to make 2 and further introduced nitrogen atoms to form the pyrazinyl moiety in 3. In addition, we utilize an anionic non-conjugated N=N ligand, i.e. di(2-pyridyl)dimethylborate (py2BMe2) that possesses high triplet energy to serve as an ancillary ligand.8 To the best of our knowledge the py2BMe2 ligand, unlike the isoelectronic di(1-pyrazolyl)borates (pz2BR2, R = H, alkyl, aryl),9 has never been used to prepare luminescent transition metal complexes. We have found that (NHC)Cu complexes with the py2BMe2 ligand are more robust and luminescent than the pyrazolyl-borate congeners.

The (NHC)Cu(py2BMe2) complexes were obtained from their respective (NHC)CuCl precursors upon addition of a stoichiometric amount of sodium di(2-pyridyl)dimethylborate in tetrahydrofuran at RT. Complexes 1–3 are stable in solid state and in solution under anaerobic conditions. Complex 1 can be sublimed under vacuum and is stable for hours in solution, while 2 and 3 decompose slowly under aerobic conditions in solution and blacken in the solid state.
after 24 h exposure to air. Evidently, the isopropyl groups at ortho positions of phenyl groups of the NHC ligand in 1 impart greater stability of the \((\text{NHC})\text{Cu}(\text{pz}_2\text{BMe}_2)\) complexes than in 2 and 3. We also prepared complexes analogous to 1 and 2 using the \(\text{pz}_2\text{BMe}_2\) ligand instead of \(\text{pz}_2\text{BMe}_2\). While the analog to 1, \((\text{IPr})\text{Cu}(\text{pz}_2\text{BMe}_3)\), can be isolated and fully characterized (see ESI†), the congener to 2 decomposed rapidly upon exposure to air and was not examined further.

X-ray diffraction analyses confirmed monomeric three-coordinate structures for complexes 1–3. Complex 2 has two unique structures in the unit cell that have similar geometric parameters. The coordination geometry in complexes 1–3 can be described as Y-shaped with the sum of bond angles around copper close to 360° (359.98° in 1, 357.72° in 2 and 358.64° in 3). The Cu–N–C–B–C–N ring formed upon chelation of the \(\text{pz}_2\text{BMe}_2\) ligand adopts a boat-shaped conformation similar to that reported in metal complexes bearing related di(2-pyridyl)borate ligands.8,10 The relative orientations of NHC and \(\text{pz}_2\text{BMe}_2\) ligands in crystals differ within the series. In complex 1 the ligands are arranged with the pyridyl rings situated opposite the aryl rings of the NHC ligand across a crystallographic mirror plane that bisects the \(\text{CNHC–Cu}\) and B atoms. In contrast, the \(\text{pz}_2\text{BMe}_2\) ligand in 2 and 3 is oriented about \(\text{CNHC–Cu}\) bond so that the two pyridyl rings are situated above and below a plane defined by the \(\text{NHC–NHC}\) and \(\text{CNHC}\) atoms. The Cu–N\(_{\text{pz}}\) bond lengths in 1 are 2.0288(15) Å and slightly shorter in 2 (1.9929(16) Å and 1.9997(16) Å) and 3 (2.0109 Å and 2.0141 Å). The \(\text{CNHC–Cu–Npy}\) angles are 132.78(4)° in 1–3, and vary from 134.32(7)° and 129.27(2)° in 2 to 135.06(4)° and 128.15(5)° in 3. The \(\text{CNHC–Cu}\) distances in 1–3 (1.8678(19)–1.8952(2) Å) are within the range for reported \(\text{CNHC–Cu}\) bonds.11

In solution, \(^1\)H NMR data indicates rapid boat-to-boat interconversion of the \(\text{pz}_2\text{BMe}_2\) ligand as resonances of methyl groups attached to boron atom appear as one broad singlet both at room temperature and at −40 °C in acetonitrile. Although the \(^1\)H NMR data do not allow us to assess if there is free rotation about the \(\text{CNHC–Cu}\) bonds in solution, the chemical shift for the protons ortho to the pyridyl nitrogens gives insight into the preferred molecular conformation. This resonance appears at \(\delta = 8.36 \text{ ppm}\) in the protonated \(\text{pz}_2\text{BMe}_2^–\) ligand, whereas upon coordination to copper in 1 it is shifted markedly upfield to \(\delta = 7.3 \text{ ppm}\) due to shielding by the diamagnetic ring current from the adjacent aryl rings of the NHC ligand. In contrast, the same resonance undergoes a much smaller shift upon coordination in 2 and 3, appearing at \(\delta = 7.97 \text{ ppm}\) and \(\delta = 8.05 \text{ ppm}\), respectively. Thus, the \(^1\)H NMR data in solution correlate with the relative ligand orientation found in crystalline state; co-planar for 1, perpendicular for 2 and 3.

Photophysical data for complexes 1–3 are summarized in Table 1. The UV-visible absorption spectra for complexes 1–3 in dichloromethane are shown in Fig. 2. High energy bands at 290 nm in 1 (\(\sim 7000–14 200 \text{ M} \text{ cm}^{-1}\)), 310 nm in 2 (\(\sim 6500–19 000 \text{ M} \text{ cm}^{-1}\)) and 340 nm in 3 (\(\sim 4000–13 400 \text{ M} \text{ cm}^{-1}\)) are assigned to spin-allowed ligand centered (LC) transitions on both the NHC and \(\text{pz}_2\text{BMe}_2\) ligands. Lower energy bands, not observed in absorption spectra of precursors (see ESI†), are assigned to charge transfer (CT) transitions. In complex 1 the CT bands appear at 316 nm (\(\varepsilon = 6100 \text{ M}^{-1} \text{ cm}^{-1}\)) with a shoulder at 360 nm (\(\varepsilon = 1300 \text{ M}^{-1} \text{ cm}^{-1}\)). A comparison between the absorption spectrum of 1 to that of \((\text{IPr})\text{Cu}(\text{pz}_2\text{BMe}_3)\) (see ESI†) shows the LC band is unchanged in energy in both derivatives, whereas the CT bands shift to higher energy and lower intensity (\(\lambda_{\max } = 305 \text{ nm}, \varepsilon = 2000 \text{ M}^{-1} \text{ cm}^{-1}\) and \(\lambda_{\max } = 330 \text{ nm}, \varepsilon = 1000 \text{ M}^{-1} \text{ cm}^{-1}\)) in the latter complex. The bathochromic shift for the low energy bands in 1 indicates that the \(\text{pz}_2\text{BMe}_2\) ligand participates in these transitions, although some CT character involving the Ir ligand may contribute as well. Upon expansion of \(\pi\)-system of the NHC ligand in 2 the CT band becomes more distinct and intense (\(\lambda_{\max } = 346 \text{ nm}, \varepsilon = 9100 \text{ M}^{-1} \text{ cm}^{-1}\)). Substitution of the two CH-groups with nitrogens in 3 leads to a marked red shift and increase in molar absorptivity (\(\lambda_{\max } = 422 \text{ nm}, \varepsilon = 10 300 \text{ M}^{-1} \text{ cm}^{-1}\)). Thus, these bands in 2 and 3 are unambiguously assigned to CT transitions involving NHC ligands.

Table 1 Photophysical data for complexes 1–3

<table>
<thead>
<tr>
<th>Absorbance, (a) (\lambda) (nm) (\varepsilon) (10(^3) M(^{-1}) cm(^{-1}))</th>
<th>Emission at room temperature(b)</th>
<th>Emission at 77 K(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\lambda_{\max}) (nm)</td>
<td>(\tau) (µs)</td>
</tr>
<tr>
<td>1</td>
<td>268 (14.2), 316 (6.1), 360 sh (1.3)</td>
<td>476</td>
</tr>
<tr>
<td>2</td>
<td>257 sh (19.3), 346 (9.1)</td>
<td>570</td>
</tr>
<tr>
<td>3</td>
<td>271 (13.3), 305 (7.4), 422 (10.3)</td>
<td>638</td>
</tr>
</tbody>
</table>

\(a\) In dichloromethane. \(b\) In solid state.
lifetimes of an order of magnitude or more.\textsuperscript{9,12} Complexes 1–3, however, show only a modest increase in emission lifetimes upon cooling as emission lifetimes measured at 77 K are in the range of 17–36 μs (Table 1). The relatively small increase in lifetime at 77 K is inconsistent with processes typically associated with TADF and suggests instead that emission measured both at room temperature and 77 K is from a state that is principally triplet in character. The behavior also implies that the radiative rate constant for the lowest triplet state is significantly enhanced in 1–3. This unusual temperature dependence on the emission lifetime is being currently investigated in greater detail at lower temperatures.

The observed bathochromic shift of emission energy in 1–3 upon expanding the size of the π-system of a ligand chromophore and N-substitution is consistent with a decrease in separation between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Computational analyses of the ground and excited state properties performed using density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations compare favorably with the experimental observations. The calculated wavelength and oscillator strength of the lowest singlet transitions progresses from 41 to 45%. The HOMO–LUMO gap is thus progressively smaller for 1 (\(\Delta E_{\text{H-L}} = 4.27\) eV), 2 (\(\Delta E_{\text{H-L}} = 3.98\) eV) and 3 (\(\Delta E_{\text{H-L}} = 3.15\) eV).

The lowest vertical singlet and triplet excitations obtained from TD-DFT calculations are mainly HOMO \(\rightarrow\) LUMO transitions (see ESI†). On the basis of the MO description given above the lowest lying transition for complex 1 can be ascribed as (M + L)ILCT admixed with intraligand π \(\rightarrow\) π* (pyBMe\(_2\)) (ILCT) character, whereas for complexes 2 and 3 the transition is principally metal-ligand to NHC-ligand charge transfer [(M + L)CT]. The calculated spin density surfaces for the triplet electronic geometries and triplet spin density contour plots (isovalue: 0.004 e\(\text{a}_0^{-3}\)). Hydrogen atoms are omitted for clarity.

Fig. 3 (A) HOMO and LUMO plots and energies for 1–3. (B) Optimized triplet geometries and triplet spin density contour plots (isovalue: 0.004 e\(\text{a}_0^{-3}\)).

To emphasize the importance of proper ligand design to achieve efficient room temperature phosphorescence from this family of Cu(II) compounds, we prepared complex 4 where the π-system of the NHC ligand was expanded by annulation of imidazolylidene with a peri-naphthyl moiety (Fig. 4, full characterization is given in ESI†). For this derivative, the intensity of the lowest lying CT absorption band centered at 450 nm is low...
those of third row transition metal complexes. Taking into account electronic and steric tunability of the NHC ligands, these findings introduce a new versatile method to control the photophysical properties of luminescent Cu(i) complexes.

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Notes and references