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Substituent Effect on the Circularly Polarized Luminescence of C₁-Symmetric Carbene-Copper(I) Complexes

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Dedicated to the memory of François Mathey

The substituent effect on the magnitude of the circularly polarized luminescence (CPL) of ^{Ment}CAAC-Cu-X (X=F, Cl, Br, I, BH₄, B₃H₈; CAAC=cyclic (alkyl)(amino)carbenes) complexes is experimentally investigated. This study examines seven pairs of enantiomeric complexes with small anionic substituents (halides, borohydrides, hydride). The complexes are fully characterized, including single crystal X-ray diffraction studies, and chiroptical measurements show that small covalent anions induce a larger CPL magnitude. These results demonstrate that the magnitude of the CPL can be manipulated without making any modifications to the chiral ligand.

The emission of light with preferential circular polarization has promising applications in advanced security inks,^[1] three-dimensional displays,^[2] spintronic devices,^[3] and biological probes.^[4] At the molecular level, two main categories of emitters exhibit circularly polarized luminescence (CPL). CPL is quantified by g_{lum} given as $2(I_L - I_R)/(I_L + I_R)$ where I_L and I_R are the intensity of the left-polarized emission, and the right-polarized emission, respectively (for all compounds, $-2 \leq g_{lum} \leq +2$). The best CPL emitters are typically based on lanthanides. Thanks to their luminescence arising from f-f transitions, lanthanide complexes are well suited to generate emission with high dissymmetry factors ($g_{lum} = 0.1-1.0$).^[5] Alternatively, small organic molecules are in principle more synthetically tunable, but their dissymmetry factors are generally much lower ($g_{lum} = 10^{-3}-10^{-2}$).^[6]

The use of transition metals for CPL is more limited, with examples of zinc,^[7] rhenium,^[8] iridium,^[9] and platinum.^[10] The use of chromium(III) complexes, which mimic the luminescence of lanthanides, has led to strong dissymmetry factors (g_{lum} up to 0.2).^[11] Evaluating other metals for CPL is attractive to

provide sustainable alternatives and fundamental understanding on all the factors implicated in the generation of CPL.

We have previously reported that simple copper(I) complexes supported by enantiopure cyclic (alkyl)(amino)carbenes derived from menthol exhibited modest CPL (Figure 1, $|g_{lum}| = 1.2 \times 10^{-3}$).^[12] Interested in knowing if the circularly polarized luminescence could be modulated by simple modifications of the substituents without reengineering the chiral support, we decided to incorporate substituents with varying atom size and electronegativity to study any effects on CPL due to significant differences in bond lengths and angles. We synthesized the halide series [CAAC-Cu-X (X=F, Br, I)] adapting previously reported syntheses (Figure 2). The complexes with larger halides (X=Br, I) were obtained by coordination of the free carbenes with the corresponding copper halide salts.^[13] The copper fluoride complexes were obtained by protonation of the copper mesityl with HF-NEt₃.^[14] Single crystals were grown from THF/pentane. The X-ray crystal structures of the Br and I derivatives are shown in Figure 3. All CAAC-Cu-X species were linear, two-coordinate Cu(I) complexes. The C-X bond distances are elongated across the series (F < Cl < Br < I) consistent with the increase of the atomic radius of the halides (Table 1).

Akin to the previously reported CAAC-Cu-Cl,^[12] the absorption spectra of the halide series showed two maxima at 280 nm and 350 nm which can be attributed to ligand $\pi-\pi^*$ absorption and metal-to-ligand charge transfer, respectively (Figure 4).^[15] For the CAAC-Cu-F complex, the low-energy absorption maximum was blue shifted by 25 nm. All of the copper-halide

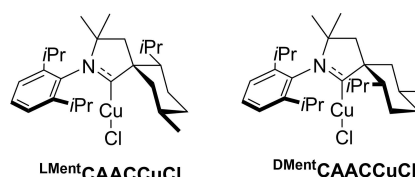


Figure 1. Previously reported CAAC-supported Cu(I) complexes exhibiting circularly polarized luminescence.

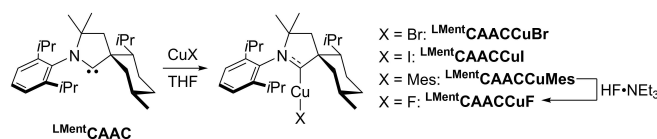


Figure 2. Synthesis of ^{LMent}CAAC-Cu-X complexes. The synthesis of the enantiomers is performed in the same way using ^{DMent}CAAC.

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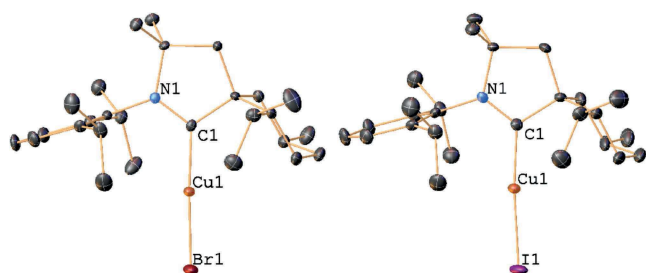


Figure 3. Structure of ^(D)MentCAACCuBr (left) and ^(D)MentCAACCuI (right) in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

Table 1. Select structural and photophysical data.

X	C–Cu [Å]	Cu–X [Å]	∠C–Cu–X [°]	λ _{em} [nm]	Φ [%]	g _{lum} [× 10 ^{−3}]
I	1.895	2.407	175.8	604	0.8	Negl.
BH ₄ [−]	1.891	2.116	170.3	538	1.4	0.3
B ₃ H ₈ [−]	1.911	2.030 ^[c]	178.9 ^[c]	536	6.2	0.4
Br	1.887	2.228	176.0	576	3.8	0.8
F ^[a]	1.889	2.106	176.8	555	1.8	1.2
F ^[b]	1.865	1.808	176.6	623	2.1	1.8

[a] Data from Ref. [12]. [b] XRD data from Ref. [14]. [c] To the center of the B–B vertex.

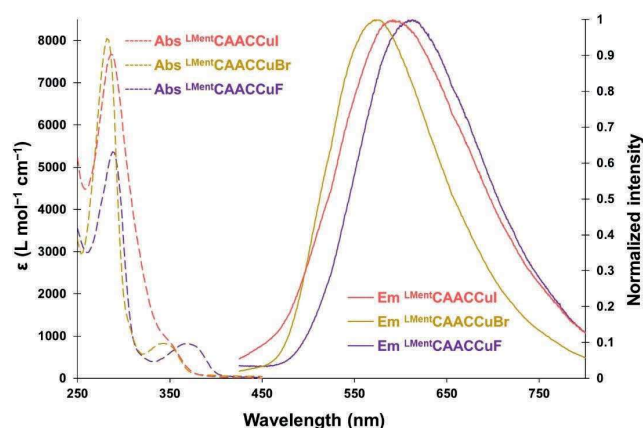


Figure 4. UV/Vis absorption and normalized emission spectra of CAAC-Cu-X (X=I, Br, F) in solution in THF (1.2×10^{-4} mol L^{−1}). Excitation at 275 nm.

CAAC-Cu-X complexes were luminescent and exhibited a broad emission peak centered at 623, 576, and 604 nm (X=F, Br, and I; respectively). The quantum yields for these complexes are relatively low, measured at 2.1%, 3.8%, and 0.8% (X=F, Br, and I; respectively). The luminescence lifetimes were in the order of microseconds (Table S2), consistent with previously reported analogous CAAC-Cu-X complexes.^[16] When exposing the solution to dry air, a decrease in emission intensity was observed. This sensitivity to oxygen and the scale of the lifetimes indicates the emission is phosphorescence (Figure S48).

The electronic circular dichroism (ECD) spectra of the halides depicted these two maxima at 270 nm and 350 nm as well. The CAAC-Cu-F complex shows a |g_{abs}| maximum of 7.8×10^{-4} and 10.1×10^{-4} , the CAAC-Cu-Br complex of 7.7×10^{-4} and

11×10^{-4} and the CAAC-Cu-I complex of 6.8×10^{-4} and 10.3×10^{-4} . And they all show a change in sign at 282 nm when going from 270 nm to 350 nm (Figures S38–S40). These values are comparable to the previously reported CAAC-Cu-Cl.

Circularly polarized luminescence for the halides series was obtained in THF solutions (Figure 5, $c = 5.0 \times 10^{-3}$ mol L^{−1}). All spectra obtained for each pair of enantiomers showed the expected mirror image spectra. Surprisingly, almost no CPL was observed for the complexes with the largest iodine anion. The copper bromide complexes showed lower dissymmetry factors ($|g_{lum}| = 0.8 \times 10^{-3}$) compared to the copper chloride complexes ($|g_{lum}| = 1.2 \times 10^{-3}$). Following the trend, the copper fluoride complexes showed the largest dissymmetry factors ($|g_{lum}| = 1.8$). Correlations between size of the substituent and dissymmetry factors, as well as between Cu–X bond distance and dissymmetry factors were therefore observed. It was also observed that both solvent polarity and concentration had a negligible effect on g_{lum} (Figure S36, S37).

To further support the correlation between size and CPL magnitude, we explored other small monoanionic substituents. We turned to borohydrides, which are among the smallest anionic substituents available. We synthesized two different types of small monoanionic borohydrides (BH₄[−] and B₃H₈[−]; Figure 6). The CAAC-Cu-B (B=BH₄[−] or B₃H₈[−]) were obtained from CAAC-Cu-Br by substitution of the bromide with excess borohydrides (NaBH₄ or KBH₃). Single crystals of the complexes were grown from slow diffusion of pentane into a concentrated 2-MeTHF solution, and slow diffusion of pentane into a

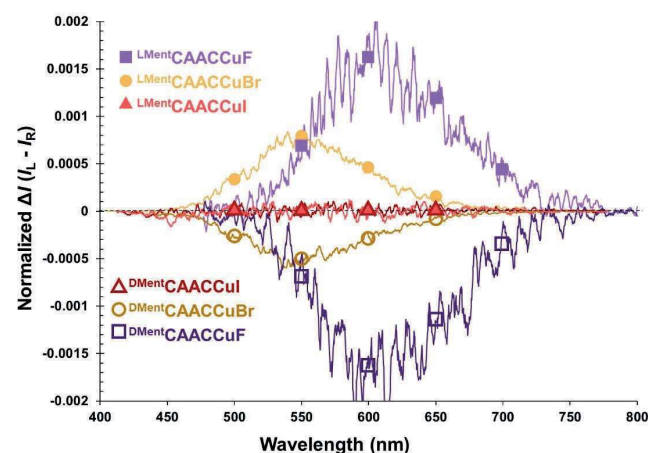


Figure 5. Circularly polarized luminescence spectra of CAAC-Cu-X (X=I, Br, F) in solution in THF (5.0×10^{-3} mol L^{−1}). Excitation at 355 nm.

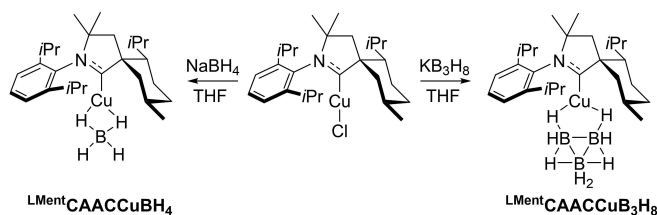


Figure 6. Synthesis of ^(D)MentCAAC-Cu-borohydride complexes. The synthesis of the enantiomers is performed in the same way using ^(D)MentCAAC.

concentrated THF solution, respectively. The CAAC-Cu-BH₄ crystallized as a monomeric two-coordinate Cu(I) with a η^2 -BH₄ ligand (Figure 7, left). In the ¹H and ¹¹B NMR, a broad quartet ($\delta = -0.60$ ppm, $^1J_{B-H} = 85$ Hz) and a quintet ($\delta = -39.12$ ppm, $^1J_{B-H} = 85$ Hz) are observed, indicating rotation of the borohydride on the NMR timescale. The CAAC-Cu-B₃H₈ also crystallizes as a monomeric complex (Figure 7, right), this is the first crystallographic characterization of a Cu-B₃H₈ compound to date.^[17] The B₃H₈ ligand is coordinated in its typical bidentate binding mode.^[18] The B₃ core forms an isosceles triangle in which two of the edges are bridged by a hydride. Each boron atom is also bound to two terminal hydrides and binding to the metal occurs through one of the terminal hydrides attached to the non-bridged B–B edge. In the ¹H and ¹¹B NMR, the octahydrotriborate signals are broad ($\delta = 0.75$ ppm, FWHM ~ 120 Hz; $\delta = -35.7$ ppm, FWHM ~ 150 Hz, respectively).

The absorption spectra of the copper-borohydride complexes differ from their halide analogues, with a slightly broader absorption band centered at about 300 nm (Figure 8). The complexes are also luminescent and both emit at 540 nm (~60 nm blue-shifted from the halides). While the quantum yields for the CAAC-Cu-BH₄ complexes are on par with the halides ($\Phi = 1.6\%$), the quantum yields for the CAAC-Cu-B₃H₈ complexes are higher ($\Phi = 6.2\%$). The emission lifetimes are

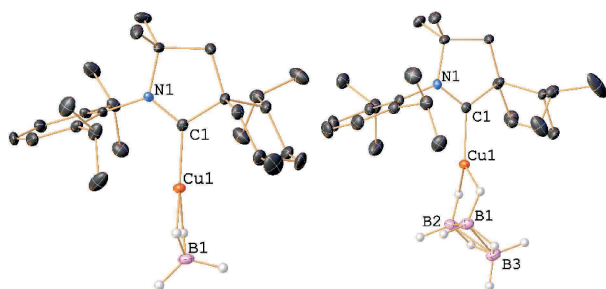


Figure 7. Structure of ^{LMent}CAACCuBH₄ (left) ^{DMent}CAACCuB₃H₈ in the solid state. Hydrogen atoms, except those on the borohydride ligands, are omitted for clarity. Only one molecule present in the asymmetric unit is drawn for clarity. Thermal ellipsoids are drawn at 50% probability.

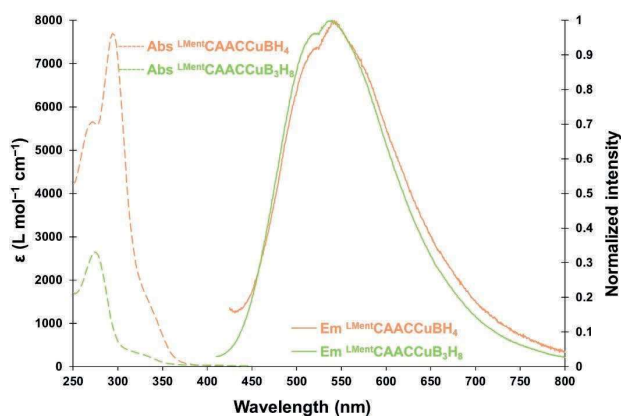


Figure 8. UV/Vis absorption and normalized emission spectra of CAAC-Cu-X (X=BH₄, B₃H₈) in solution in THF (1.2×10^{-4} mol L⁻¹). Excitation at 270 nm.

also longer for CAAC-Cu-B₃H₈ when compared to CAAC-Cu-BH₄ (5.7 μ s vs 0.60 μ s, respectively).

ECD spectra depicted two maxima at 270 nm and 330 nm for borohydride complexes as well. The CAAC-Cu-BH₄ shows a maximum $|g_{abs}|$ of 10.5×10^{-4} for both wavelengths (Figure S41), while CAAC-Cu-B₃H₈ shows a maximum of 2.5×10^{-4} and 3.7×10^{-4} (Figure S42). As in the case of the halide complexes, a change of sign was observed at 282 nm.

The CAAC-Cu-BH₄ complexes (Figure 9) showed drastically diminished CPL with $g_{lum} = 0.3 \times 10^{-3}$. The CAAC-Cu-B₃H₈ complexes showed similar dissymmetry factors ($g_{lum} = 0.4 \times 10^{-3}$). These results suggest that although comparable in size with fluoride, the lack of a strong covalent interaction between the copper atom and the borohydrides may prevent the generation of strong CPL.

To associate covalency and small size, we turned to the next logical small monoanionic substituent: hydride.^[19] Although characterized as a dimer in the solid state, we envisioned that, in dilute solution, the monomer could exist. Unfortunately, the [CAAC-Cu-H]₂ complex was only very weakly luminescent (Figure S46) and CPL could therefore not be reliably detected.

To gain further experimental insights, the redox potentials of CAAC-Cu(I)-X complexes were determined by cyclic voltammetry. In all cases, irreversible reduction and oxidation features were observed (Figures S50–S55). These features are reminiscent of similar complexes reported in the literature.^[13,16] Utilizing the oxidation and reduction potentials the energies of HOMO/LUMO levels and corresponding band-gaps (Table S1) were calculated.^[20] As expected, these values are in line with similar complexes previously reported.^[13,16]

We have demonstrated that the magnitude of the circularly polarized luminescence in CAAC-Cu(I)-X complexes could be varied by the nature of the X ligand without modifying the chiral backbone. While most substituents provided similar or diminished CPL activity compared to the original chloride ligand, higher dissymmetry factors up to 1.8×10^{-3} were obtained with X=F. These results are very promising especially when considering the recent progress in luminescent CAAC-Cu-X chemistry.^[12,15,21] With the field of CPL-active molecular copper

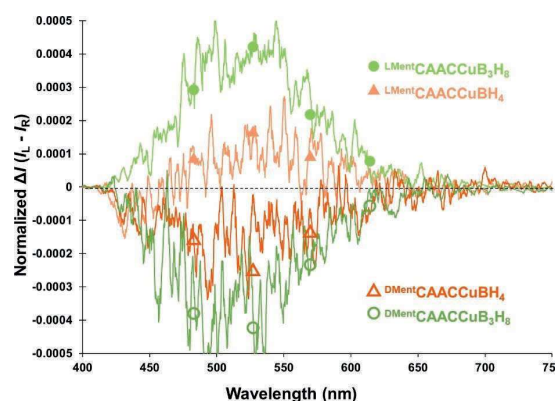


Figure 9. Circularly polarized luminescence spectra of CAAC-Cu-X (X=BH₄, B₃H₈) in solution in THF (5.0×10^{-3} mol L⁻¹). Excitation at 355 nm.

complexes still in its infancy, our results provide the first data points towards better understanding of the structure-CPL activity relationship.

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Conflict of Interest

The authors declare no conflict of interest.

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