Luminescence and Nonlinear Optical Properties in Copper(I) Halide Extended Networks

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S Supporting Information

ABSTRACT: The syntheses, structures, and luminescence properties of a series of copper(I) halide coordination polymers, prepared with mono- and bidentate N-heteroaromatic ligands, are reported. These metal—organic coordination networks form $[Cu_2I_2L]_n$ for bidentate ligands (where L = pyrazine (1), quinazoline (2)) and $[CuIL]_n$ for monodentate ligands (where L = 3-benzoylpyridine (3) and 4-benzoylpyridine(4)). Both sets of compounds exhibit a double-stranded stair— Cu_2I_2 —polymer, or "ladder" structure with the ligand coordinating to the metal in a bidentate (bridging two stairs) or monodentate mode. The copper bromide analogues for the bidentate ligands were also targeted, $[Cu_2Br_2L]_n$ for L = pyrazine (5) with



the same stair structure, as well as compositions of $[CuBr(L)]_n$ for L = pyrazine (6) and quinazoline (7), which have a different structure type, where the -Cu-Br- forms a single-stranded "zigzag" chain. These copper halide polymers were found to be luminescent at room temperature, with emission peaks ranging from ~550 to 680 nm with small shifts at low temperature. The structure (stair or chain), the halide (I or Br), as well as the ligand play an important role in determining the position and intensity of emission. Lifetime measurements at room and low temperatures confirm the presence of thermally activated delayed fluorescence, or singlet harvesting for compounds 1, 2, and 7. We also investigated the nonlinear optical properties and found that, of this series, $[CuBr(quinazoline)]_n$ shows a very strong second harmonic generating response that is ~150 times greater than that of α -SiO₂.

INTRODUCTION

Luminescent materials have gained a great deal of attention because of potential applications including chemo-sensors, light-emitting diodes (LEDs), display devices, and biological probes.^{1,2} There has long been interest in the study of univalent group 11 transition-metal complexes because of their intriguing structural and photophysical properties.³ Copper, which is abundant and inexpensive, is known to form both complexes and coordination polymers that are highly emissive even at room temperature.⁴⁻⁶ Recently, luminescent Cu(I) halide complexes have been found to produce efficient electroluminescence in thin film devices.⁵ In addition, the integration of organic-inorganic hybrids into thin film devices⁷ has been demonstrated for metal halide amine perovskite materials⁸ and successfully used in photovoltaic cells.⁹ Copper halides and pseudohalide have been of interest for vapochromism¹⁰ and, more recently, for copper-based organic LEDs materials.¹¹ The interest is due to the thermally activated delayed fluorescence (TADF), which has been shown to give fast and efficient luminescence.¹²⁻¹⁴ The potential for novel devices is inspiring, and has renewed interest in the luminescent copper halide systems.

The structural chemistry of compounds formed from Cu(I), X (halide), and organo-amines is quite rich because of the lack of stereochemical preference of the d^{10} electronic config-

uration.^{3,15} Cu(I) metal centers are particularly attractive due to their ability to assemble into coordination polymers and similar networks.¹⁵ The structure of these copper–organic frameworks largely depends on the nature of the organic ligand and the halide, but the synthetic conditions used (solvent and temperature) are also quite important. Although there are examples where the halide has structure-directing abilities,^{16,17} the coordination properties of the organic ligands often controls the dimensionality of the resulting polymer.^{4,18} We found that, for the same set of components (Cu(I), X, L), different compositions and structures can be stabilized depending on whether the synthesis is hydrothermal or from organic solvents. These building blocks have provided insight into the formation of network structures.¹⁵

Despite the rich structural diversity, there are some commonly observed structures of copper(I) halides (Cu–X) in combination with mono- and bidentate ligands (L).^{3,15,19} Some frequently observed structural motifs for Cu–X include [CuXL]₄ tetramers, a single-stranded polymer chain (zigzag of -CuX-),²⁰ and the double stranded "stair" ($-Cu_2X_2-$) polymer.^{15,21,22} Clusters are more commonly found with

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monodentate ligands, while both chains and stairs can be formed with mono or bidentate ligands.²³ We have previously investigated halide–pseudohalide copper polymer compounds using hydrothermal synthesis.¹⁷ We discovered novel structures such as a mixed halide and cyanide polymeric structure, $[Cu_3Cl_2CN(pyrazine)]_n$, which exhibits three coordinate cyanide.¹⁷ This structure contrasts with the halide-only polymer, $[Cu_2X_2(pyrazine)]_n$, which exhibits the common double-stranded "stair" structure for X = Cl, Br, and I. This framework structure forms the basis for the compounds investigated here.

Of the luminescent copper halides, perhaps the most systematically studied system is the tetrameric cubane structure [CuIL]₄, for monodentate ligands, such as pyridine (py).^{22,24,25} This structure has been described as a Cu_4 tetrahedron with a larger I_4 tetrahedron surrounding it³ and is strongly luminescent as both a solid²⁶ and in solution.²⁷ The emissive state in this system is predominantly metal-centered.³ Ford also investigated the luminescence of copper halide polymers, demonstrating that both the chain and ladder structures are emissive, and highlighting the role of the halogen in halogenligand charge transfer (XLCT) was thought to be significant.¹ Ford argued that inorganic-organic hybrids that undergo this type of electron-transfer process are likely to exhibit nonlinear optical properties and demonstrated this for the first time in $[CuI(acetyl-pyridine)_2]_n$ chain polymer.³ By contrast, Araki discovered the ligand plays an important role in the luminescence properties of a series of mixed ligand, $Cu_2X_2(PPh_3)L$ (where L = aromatic amine), dimeric complexes that form chains in the solid state.²⁸ These compounds are luminescent through the full spectrum of color depending on the choice of aromatic organoamine. Thus, by modifying the double-stranded $[Cu_2X_2L]_n$ stair structure and the $[CuX(L)]_n$ chain structure using select ligands from this series, we sought to determine whether the emission energy could be tuned analogously in the copper halide coordination polymers. Although less attention has been placed on the luminescence of coordination polymers,^{3,28,29} there are advantages of hybrid inorganic-organic materials due to enhanced thermal stability and emission tunability,³⁰ which makes them suitable for commercial applications.³¹

In this investigation, we synthesized a series of copper(I)iodide coordination polymers and selected bromide analogues and investigated their photophysical properties. The focus was on polymers with the $-Cu_2I_2-$ double-stranded ladder or stair backbone and include $[Cu_2I_2L]_n$, for bidentate ligands L = pyrazine (pyz, 1), quinazoline (quinz, 2), and $[CuIL]_n$ for monodentate ligands L = 3-benzoylpyridine (3-bzpy, 3) and 4benzoylpyridine (4-bzpy, 4). We were interested in elucidating the role of the halide by preparing bromide analogues of each compound; however, the analogous structure type was not always observed. In the case of [Cu₂X₂ (pyz)], this compound can be prepared for all of the halides X = Cl, Br, I, and here we report the luminescence properties of the Br and I systems. In the case of the copper bromide, reaction with quinazoline formed a different structure type, with the single-stranded "zigzag" chain of copper bromide $[CuBr(quinz)]_n$ (7). We include $[CuBr(pyz)]_n$ (6) to compare the properties of the single-stranded chain structures with the double-stranded stair in the Cu-Br-pyz series. For this series of compounds, only two have unreported structures, so we include the crystal structures of $[Cu_2I_2(quinz)]_n$ (2) and $[CuI(3-bzpy)]_n$ (3). The luminescence at both room temperature and low temperature

(77 K), as well as the lifetime measurements, are reported for all compounds. We explored the nonlinear optical (NLO) properties for all compounds with non-centrosymmetric space groups and found the $[CuBr(quinz)]_n$ to have the most significant properties.

EXPERIMENTAL SECTION

General Information. Acetonitrile, copper(I) iodide, copper(I) bromide, quinazoline, pyrazine, dimethylaminopyridine, and 3-benzoylpyridine were obtained from Sigma-Aldrich. 4-Benzoylpyridine was obtained from Alfa Aesar. All materials were used as received.

Synthesis. $[Cu_2l_2(pyz)]_n$ (1). A solution of pyrazine (0.0400 g, 0.5 mmol) in CH₃CN (20 mL) was added to a CH₃CN (20 mL) solution of CuI (0.1904 g, 1.0 mmol). Yellow solid appeared when the solution was stirred, which was isolated by vacuum filtration. The product was washed with acetone and recrystallized in hot CH₃CN. The resulting yellow block crystals were found to emit a bright orange color under UV light. IR (cm⁻¹): 1637 (s), 1477 (m), 1416 (vs), 1157 (m), 1120 (m), 1049 (m), 804 (m), 451 (m). Anal. Calcd for C₄H₄N₂Cu₂I₂: C, 10.42; H, 0.87; N, 6.08; Found: C, 10.63; H, 0.83; N, 5.87%. Percent yield 76%.

 $[Cu_2I_2(quinz)]_n$ (2). A solution of CuI (0.1904 g, 1.0 mmol) in CH₃CN (25 mL) was added to a CH₃CN solution (25 mL) of quinazoline (0.0650 g, 0.5 mmol). Red-orange powder formed when the solution was stirred. The product was collected by vacuum filtration, washed with acetone, and recrystallized from hot CH₃CN. The crystals were found to emit an orange color under UV light. IR (cm⁻¹): 1713 (s), 1617 (s), 1576 (s), 1561 (w), 1488 (s), 1378 (s), 1302 (m), 1208 (s), 1151 (w), 1137 (m), 1085 (m), 965 (m), 785 (s), 750 (s), 647 (m), 633 (m), 487 (m). Anal. Calcd for C₈H₆N₂Cu₂I₂: C, 19.0; H, 1.13; N, 5.29; Found: C, 18.79; H, 1.06; N, 5.43%. Percent yield 83%.

 $[Cul(3-bzpy)]_n$ (3). A solution of CuI (0.1904 g, 1.0 mmol) in CH₃CN (10 mL) and a solution of 3-benzoylpyridine (0.1832 g, 1.0 mmol) in CH₃CN (5 mL) were added to form a fluffy, bright yellow powder. The product was collected by vacuum filtration and washed with acetone. Recrystallization in hot CH₃CN afforded the formation of fine, yellow needles that emit an intense yellow color under UV light. IR (cm⁻¹): 1662 (vs), 1593(s), 1577 (w), 1448 (m), 1418 (m), 1319 (s), 1286 (vs), 1195 (w), 1157 (w), 1031 (w), 941 (w), 927 (w), 827 (w), 790 (w), 744 (w), 707 (vs), 687 (w), 655 (m). Anal. Calcd for C₁₂H₉NOCuI: C, 38.57; H, 2.43; N, 3.75; Found: C, 38.34; H, 2.32; N, 3.71%. Percent yield 63%.

 $[Cul(4-bzpy)]_n$ (4). To a CH₃CN (20 mL) solution of CuI (0.1904 g, 1.0 mmol), a solution of 4-benzoylpyridine (0.1832 g, 1.0 mmol) in CH₃CN (20 mL) was added. Immediate formation of an orange precipitate was observed when the solution was stirred. The product was collected via vacuum filtration and washed with acetone. Recrystallization in hot CH₃CN resulted in the formation of orange needles that were found to emit red luminescence under UV light. IR (cm⁻¹): 1657 (vs), 1596 (w), 1548 (w), 1446 (m), 1411 (s), 1321 (vs), 1281 (vs), 946 (m), 747 (m), 694 (vs), 647 (s). Anal. Calcd for C₁₂H₃NOCuI: C, 38.57; H, 2.43; N, 3.75; Found: C, 38.38; H, 2.28; N, 3.62%. Percent yield 91%.

 $[Cu_2Br_2(pyz)]_n$ (5). CuBr (0.173 g, 1.2 mmol), pyrazine (0.048 g, 0.6 mmol), and 8 mL of HBr (0.26M) were combined in a hydrothermal bomb. After 5 h at 150 °C, the reaction vessel was cooled at 0.2 °C/ min to room temperature. The yellow crystals were filtered off in air and washed with acetone. They were luminescent under UV light as a bright yellow color. IR (cm⁻¹): 1476 (m), 1409 (vs), 1156 (m), 1113 (m), 1047 (m), 800 (m), 448 (m). Anal. Calcd for C₄H₄N₂Cu₂Br₂: C, 13.09; H, 1.10; N, 7.63; Found: C, 13.34; H, 1.17; N, 7.61%. Percent yield 53%.

 $[CuBr(pyz)]_n$ (6). A solution of pyrazine (0.0400 g, 0.5 mmol) in CH₃CN (20 mL) was added to a CH₃CN (20 mL) solution of CuBr (0.143 g, 1.0 mmol). Orange solid appeared when the solution was stirred, which was isolated by vacuum filtration. The product was washed with acetone and recrystallized in hot CH₃CN. The resulting orange block crystals were found to emit a bright red color under UV

light. IR (cm⁻¹): 1477 (m), 1416 (vs), 1159 (m), 1117 (m), 1054 (m), 804 (m), 450 (m). Anal. Calcd for $C_4H_4N_2CuBr$: C, 21.49; H, 1.80; N, 12.53; Found: C, 21.15; H, 1.70; N, 12.19%. Percent yield 78%.

[*CuBr*(quinz)]_n (7). A solution of CuBr (0.0717 g, 0.5 mmol) in CH₃CN (25 mL) was added to a CH₃CN (25 mL) solution of quinazoline (0.0651 g, 0.5 mmol). The metallic orange platelike crystals that came out were isolated via vacuum filtration and washed with CH₃CN. The product was luminescent under UV light as a red color. IR (cm⁻¹): 1615 (s), 1572 (m), 1487 (s), 1384 (vs), 1306 (m), 1206 (w), 1155 (w), 928 (w), 791 (vs), 748 (vs), 648 (w), 633 (m), 486 (m). Anal. Calcd for C₈H₆N₂CuBr: C, 35.12; H, 2.21; N, 10.24; Found: C, 35.12; H, 2.18; N, 10.18%. Percent yield 39%.

Characterization. All the copper(I) halide polymers were characterized by IR and elemental analysis. Infrared spectra were measured in the range of 450–4000 cm⁻¹ as pressed KBr pellets on a Nicolet 380 FTIR spectrometer. Elemental analysis (C, H, and N content) was performed on a PerkinElmer 2400 microanalyzer, using acetanilide as standard. Phase purity was supported using powder X-ray diffraction using a Rigaku Ultima IV powder diffractometer with Cu K α radiation, under a range of 20–80° 2 Θ .

Photophysical Characterization. The photoluminescence data were obtained in a Fluorolog-3 spectro-fluorimeter (Horiba FL3–22-iHR550), with 1200 grooves/mm excitation monochromator gratings blazed at 330 nm and 1200 grooves/mm emission monochromator gratings blazed at 500 nm. An ozone-free xenon lamp of 450 W (Ushio) was used as a radiation source. The excitation spectra corrected for instrumental function were measured between 250 and 600 nm. The emission spectra were measured in the range of 450–850 nm in front face mode at 22.5°. All emission spectra were corrected for instrumental function. The emission decay curves were obtained using a TCSPC system and a Horiba NanoLED model N-370 (peak wavelength = 370 ± 10 nm, ~4 pJ/pulse) as excitation source. All spectra were measured on solid samples.

Nonlinear Optical Properties. The powdered material (~200 mg) was sieved into different particle size ranges (<20, 20–45, 45–63, 63–75, 75–90, and 90–125 μ m) and subsequently placed in separate fused silica tubes. To compare with a known second-harmonic generating (SHG) material, a standard, α -SiO₂, was also ground and sieved into the same particle size range. Powder SHG measurements were performed on a modified Kurtz-NLO56 system equipped with a pulsed Nd:YAG laser having an output of 1064 nm. Phase-matching information was determined, and the SHG efficiency of the sample was reported with respect to α -SiO₂.

Single-Crystal X-ray Crystallography. A suitable needlelike crystal was mounted on a Mitegen micromount for single-crystal X-ray diffraction analysis. Intensity data were collected on a Bruker D8 Venture diffractometer equipped with a Photon 100 CMOS detector using Mo K α radiation ($\lambda = 0.71073$ Å) at 100 K. The data were integrated using the APEX2 suite of software, and absorption corrections were calculated using SADABS/TWINABS. The structures were solved using direct methods and refined by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were located in calculated positions and refined isotropically. Crystallographic details can be found in the Supporting Information. The cif files for (2) and (3) were deposited in the Cambridge Structural Database with CCDC numbers 1496395 and 1496396, respectively.

Computational Methods. Density functional theory (DFT) calculations were performed with the Gaussian 09/D.01 package,³² using the geometric parameters of $[CuI(3-bzpy)]_n$ and $[CuI(4-bzpy)]_n$ obtained from X-ray diffraction analysis. The structures were extended to include at least two CuI units. Single-point calculations were performed with B3LYP³³ functional level of theory and 3-21G* basis set for all atoms.³⁴ The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) figures were generated with ChemCraft.³⁵

RESULTS AND DISCUSSION

Synthesis. We synthesized a series of Cu–I compounds with the ligands illustrated in Figure 1 under both hydrothermal



Figure 1. Mono- and bidentate ligands used in the series of Cu(I) coordination polymers.

and acetonitrile conditions. These N-heteroatomic aromatic ligands were selected from those used in the previously reported series $Cu_2X_2(PPh_3)(L)$ on the basis of the spectral range of emission and their ability to form a polymer network (chains or stairs). Copper(I) halide coordination polymers have been reported from both hydrothermal synthesis³⁶ and from organic solvents.^{15,18} Hydrothermal conditions are ideal for crystal growth, and aqueous Cu(I) can be stabilized under these conditions by the presence of organoamines. We have previously been unable to grow single crystals of $[Cu_2I_2(pyz)]_n$ hydrothermally, but the structure was reported from the hydrothermal synthesis of Cu(II) with pyrazine carboxylate by zur Loye.³⁹ We prepared this compound directly from CuI and pyrazine in acetonitrile, similar to most of the compounds reported here. In some systems both approaches form the same compounds, but frequently either the stair or the chain compound is exclusively found for a given method.

For most of our syntheses, whether hydrothermal or from organic solvents, the stoichiometry of reagents does not dictate the product stoichiometry. In most cases variation of the metal/ halide/ligand ratio did not change the product composition for either method. This is in contrast to the Cu/X system with the ligand 4.4'-bipyridyl, in which the stoichiometry of the product [CuXL] or $[(CuX)_2L]$ could be controlled by the reagent ratio of CuX/L.40 The effect of the synthetic conditions can be illustrated by the two series of compounds, where L includes the bidentate ligands pyrazine and quinazoline. In the series with pyrazine, using hydrothermal synthesis it was possible to form the stair structures $[Cu_2X_2(pyz)]_n$ for X = Cl, Br, and I, but none of the chain compounds $[CuX(pyz)]_n$. Using acetonitrile as the solvent, the iodide also formed the stair structure $[Cu_2I_2(pyz)]_n$, but for bromide only the chain structure $[CuBr(pyz)]_n$ could be prepared. In the case of quinazoline, we found that the stair compound $[Cu_2I_2(quinz)]_n$ was also easily stabilized from either hydrothermal or organic solvents but never the chain compound $[CuI(quinz)]_n$. For bromide with quinazoline, the chain compound [CuBr- $(quinz)]_n$ could only be formed from acetonitrile, and it was not possible to crystallize the stair structure $[Cu_2Br_2(quinz)]_n$ using either method. In most general terms, we found that the chain compounds form under acetonitrile conditions, while the stair compounds were more easily crystallized hydrothermally. We were, however, unable using any method to prepare $[CuI(pyz)]_{n}$, $[CuI(quinz)]_{n}$, or $[Cu_2Br_2(quinz)]_{n}$, creating gaps in the series of compounds reported here. The inability to isolate these compounds suggests that the stair structure is more stable for the iodide complexes, while the chain structure is more stable for the bromide. By contrast, using the monodentate ligands benzoylpyridine (bzpy), we were unable to isolate any chain compounds for the iodide or bromide using either method. Although we were able to prepare bromide

analogues of the stair structures from acetonitrile with this ligand, they did not luminesce and are not included here.

Structure. The focus of these studies is on two structure types, namely, the stair and the chain compounds, which have been nicely summarized previously for mono- and bidentate ligands.⁴¹ Inconveniently, the stoichiometry of the product does not indicate structure. In the case of monodentate ligands the metal/halide/ligand stoichiometry 1:1:1 could structurally be a dimer or stair type of polymer $(Cu_2X_2L_2)$ or tetramer $(Cu_4X_4L_4)$. For example, pyridine can form either a cubane cluster $[CuIpy]_4$ or the stair polymer $[CuIpy]_n$ depending on the conditions (e.g., the tetramer is favored at low temperatures).⁴² The structure of $[CuIpy]_n$ is quite similar to the double-stranded stair structure with pendant monodentate ligands as illustrated in Figure 2 (right). For the copper halide



Figure 2. Crystal structures of compounds $[Cu_2I_2quin]_n$ (2, left) and $[CuI(3-bzpy)]_n$ (3, right). Both have the bidentate amine-bridging $-Cu_2I_2$ - ladder, but the ligand is bidentate for quinz and monodentate for 3-bzpy.

organoamine complexes reported here there were only two different structure types, double-stranded stair structure illustrated in Figure 2 and the zigzag chain structure shown in Figure 3. One advantage for the photophysical studies is that



Figure 3. Crystal structure of the linear chain compounds for pyrazine [CuBr(pyz)] (6, left) and quinazoline, [CuBr(quinz)] (7, right).

generally the structure can be preserved with different halides, while for the cluster compounds the structure can change substantially with a change in halide.³ It is possible to form either structure with monodentate or bidentate organoamine ligands as presented in Table 1.³⁹ This table summarizes the structure type, bonding mode, Cu–Cu bond distance, aromatic ring distance, and space group for the known structures. All compounds were characterized by elemental analysis and

powder X-ray diffraction to confirm the powders were single phased, and the patterns were matched with diffraction patterns generated from the single-crystal structures. Several views of the extended network structures for all the compounds (1-7) are shown in the Supporting Information (Figures S8–S19).

For the two unreported structures we include select crystallographic information in Table 2. We found quinazoline

Table 2. Crystallographic Information for Compounds 2 and3

	$Cu_2I_2(quinz)$ 2	CuI(3-bzpy) 3
space group	$P\overline{1}$	C2
a (Å)	4.2068(8)	15.744(3)
b (Å)	8.8327(17)	4.0635(6)
c (Å)	15.339(3)	18.279(4)
α (deg)	92.608(6)	90
β (deg)	91.696(6)	92.191(5)
γ (deg)	100.988(6)	90
V (Å ³)	558.51(18)	1168.6(4)
$R_{ m f}$	0.0831	0.0318

compound $[Cu_2I_2(quinz)]_n$ (2) to have the common doublestranded stair structure with the stairs linked with the bidentate ligand as illustrated in Figure 2 (left). The copper is fourcoordinate (to three iodine and the nitrogen of one ligand) in a distorted tetrahedral geometry. We also report the structure of benzoylpyrazine compound $[CuI(3-bzpy)]_n$ (3). This compound is isostructural with the previously reported [CuI(4- $[bzpy]_n$ (4) shown in Figure 2 (right). Both have the same double-stranded stair, with only monodentate coordination of the ligand. In the case of the $[CuI(3-bzpy)]_{u}$, the two rings of the benzoylpyridine are not coplanar and form a herringbone stack between the ladders. Both compounds were found to have relatively short Cu-Cu bond lengths, less than the van der Waals radius of 2.85 Å ($[Cu_2I_2(quinz)]_n$ had the shortest Cu-Cu distance of 2.65 Å, and $[CuI(3-bzpy)]_n$ shortest distance was 2.68 Å). Another structural feature relevant for the optical properties is the distance between the aromatic rings, which were in the weak limit of greater than 3.5 Å. Quenching of emission could result from π stacking, as reported for *trans*stilbazole polymers with copper iodide.²

Luminescence Studies. The emissive excited states observed in copper halide compounds include metal-centered, metal-to-ligand charge transfer (MLCT), and halide-to-ligand charge transfer (XLCT). Previous luminescence studies of copper halide chains and stair compounds investigated by Ford found that the emission energy was influenced by the polarizability of the halide and the electronic properties of the ligand.⁴³ By contrast, for cluster compounds a cluster-centered excited state of d-s character (³CC) was present and was found to be influenced by the Cu–Cu bond length.³ Generally, all of the compounds investigated here exhibit

Table 1. Structural Information for All Compounds Investigated

	$Cu_2I_2(pyz)$ 1	$Cu_2I_2(quinz)$ 2	CuI(3-bzpy) 3	CuI(4-bzpy) 4	$Cu_2Br_2(pyz)$ 5	CuBr(pyz) 6	CuBr(quinz) 7
structure type	stair	stair	stair	stair	stair	chain	chain
ligand bonding mode	bidentate	bidentate	monodentate	monodentate	bidentate	bidentate	bidentate
aromatic rings (Å)	4.134	3.486	4.064	4.178	3.868	3.986	3.756
		4.207					3.876
space group	$P\overline{1}$	$P\overline{1}$	C2	P21/c	$P\overline{1}$	P2/c	$Pca2_1$
refcode	AGIYEU0155			KALNOA ⁵⁶	WOWYOW ¹⁷	VEVFUX ¹⁵	HUWCEH ⁵⁷

	compound	structure type	Cu–Cu bond (Å)	$\lambda_{\rm exc}~({\rm nm})$	$\lambda_{\rm em}$ 298 K (nm) ^{<i>a</i>}	$\lambda_{\rm em}$ 77 K (nm) ^{<i>a</i>}	$\tau_{298 \text{ K}}^{a} (\mu \text{s})$	$ au_{77\ \mathrm{K}}{}^{a}(\mu\mathrm{s})$
1	$[Cu_2I_2(pyz)]$	stair	2.756	400	663	614	$0.944 \pm 0.011 \ (0.32)$	$12.3 \pm 0.3 (0.91)$
							$0.175 \pm 0.001 \ (0.47)$	
							$0.028 \pm 0.004 \ (0.21)$	$32.0 \pm 1.5 (0.09)$
2	$[Cu_2I_2(quinz)]$	stair	2.739	390	608	626	$0.823 \pm 0.017 \ (0.18)$	$12.1 \pm 0.3 \ (0.90)$
			2.654				$0.165 \pm 0.002 \ (0.62)$	
							$0.021 \pm 0.004 \; (0.20)$	30.9 ± 2.1 (0.10)
3	[CuI(3-bzpy)]	stair	2.6819	390	537	545	$1.051 \pm 0.006 \ (0.64)$	$11.1 \pm 0.3 (1.00)$
							$0.244 \pm 0.007 \ (0.36)$	
4	[CuI(4-bzpy)]	stair	2.818	270	637	650	$0.934 \pm 0.033 \ (0.14)$	*
			2.895				$0.194 \pm 0.002 \ (0.86)$	
5	$[Cu_2Br_2(pyz)]$	stair	2.814	420	586	570	$3.24 \pm 0.03 (1.00)$	$15.6 \pm 0.3 (1.00)$
6	[CuBr(pyz)]	chain		390	648	690	$1.19 \pm 0.14 \ (0.33)$	$8.0 \pm 0.1 (1.00)$
							$0.20 \pm 0.03 \ (0.67)$	
7	[CuBr(quinz)]	chain		270	620	646	$1.058 \pm 0.002 \ (0.43)$	$8.2 \pm 0.1 (1.00)$
							$0.183 \pm 0.003 \ (0.49)$	
							$0.026 \pm 0.003 \ (0.08)$	

Table 3. Solid-State Luminescence Data for Compounds 1-7

^aReported as the 0–0 phonon peak from deconvolution of the emission spectra into their vibrational components.



Figure 4. Room-temperature (solid) and 77 K (dashed) solid-state emission spectra of $[Cu_2X_2(pyz)]_n X = Br$ (5, green) and I (1, black).

luminescence due to XLCT (at room temperature and 77 K) in the range of 550–680 nm. In Table 3, we report the excitation, emission wavelengths, emission lifetimes, and Cu–Cu distances for compounds 1–7. Although $[CuI(3-bzpy)]_n$ has the highestenergy emission and shortest Cu–Cu bond (2.68 Å), collectively there is no trend between the copper–copper bond length and the emission energy, indicating a reduced role of metal-centered bonding in the luminescence properties.

Bromide versus lodide. To probe the role of the halide, we aimed to compare coordination polymers with the same structure and ligand, with either bromide or iodide. Our example is for the stair structure with pyrazine as the bridging ligand, and their emission spectra are shown in Figure 4. After deconvolution, the 0–0 transition of $[Cu_2I_2(pyz)]_n$ is located at 663 nm and for $[Cu_2Br_2(pyz)]_n$ at 586 nm. The shift to lower energy for the heavier iodide analogue is consistent with what one would expect based on polarizability or, alternatively, electronegativity. This is in contrast to the emissive properties of two previously reported stair polymers with the monodentate ligand pyridine $[CuI(py)]_n$, which shows an emission maximum at 437 nm, while the $[CuBr(py)]_n$ has a peak at 509 nm.⁴⁴ The explanation for this reversal in trend is thought to be due to the halide ionicity, or ligand field strength in the case of [CuX(dtpb)] (dtpb = 1,2-bis (*o*-ditolylphosphino)benzene).⁴⁵ What is also notable here is that the luminescence appeared weaker for bromide analogues, while in several cases the chloride analogue lacked any observable emission.

Luminescence Lifetime Measurements. The emission decay curves for the $[Cu_2I_2(pyz)]_n$, $[Cu_2I_2(quinz)]_n$, and [CuBr(quinz)], complexes (Figures S22, S23, and S24, Table 3) show three lifetime components, with the shortest in the 1-50 ns range attributed to fluorescence. The longer lifetime components, with similar magnitudes as those observed for the $[CuI(3-bzpy)]_{w}$ $[CuI(4-bzpy)]_{w}$ and $[CuBr(pyz)]_{n}$ complexes (Figures S25, S26, and S27, Table 3) and for the $[Cu_2Br_2(pyz)]_n$ complex (Figure S28, Table 1), are shorter than what would be expected for phosphorescence (10-1000 μ s) and can be attributed to TADF or singlet harvesting.⁴ In this process, after intersystem crossing $(S_1 \rightarrow T)$ the S_1 level is thermally repopulated if the singlet-triplet energy gap is ~1000 cm^{-1} (or 0.15 eV) as suggested by our calculations.¹¹ For larger energy separations $(1 \times 10^3 \text{ cm}^{-1})$, only triplet emission is observed at room temperature. The TADF mechanism also explains the overlap between excitation and emission, which is characteristic of "pure" fluorescence transitions accompanied by a relatively long fluorescence lifetime. TADF is very attractive for organic LED applications due to the possibility of obtaining high electroluminescence efficiencies along with short, when compared to phosphorescent materials, emission lifetimes.^{13,14,45,47} The emission lifetime depends on the rigidity of the structure and the energy gap between the excited and ground states. In the present case, the rigidity of the structure is a factor that contributes to increase the emission lifetimes due to the polymeric nature of the complexes (Figures 2 and 3).



Figure 5. Room-temperature (solid) and 77 K (dashed) solid-state emission spectra of compounds $[CuI(3-bzpy)]_n$ (3, green), $[Cu_2I_2$ (quinz)] $_n$ (2, blue), and $[CuI(4-bzpy)]_n$ (4, black).



Figure 6. Room-temperature solid-state emission spectra of compounds $[Cu_2Br_2 (pyz)]_n$ (5, green), $[CuBr(quinz)]_n$ (7, blue), and $[CuBr(pyz)]_n$ (6, black).

The direct dependence of the emission lifetime on the energy gap between excited and ground states was demostred by Kato and co-workers.⁴⁸ This dependence explains the shorter emission lifetime values obtained with our compounds when compared with several reported blue emitters.^{49,50} In addition, the lifetimes measured here are similar to those of orange and red emitters reported by Steffen and co-workers also attributed to TADF.¹¹

To confirm that TADF is responsible for the observed emission behavior, the excitation and emission spectra were obtained at 77 K (Figures 4 and 5). We note that we do not have temperature-dependent structural information for any of these compounds to determine whether there are structural distortions or symmetry changes as a function of temperature. Two compounds, $[Cu_2I_2(pyz)]_n$ and $[Cu_2Br_2(pyz)]_n$ had emission energies with hypsochromic shift at low temperature (the energy difference between the room-temperature and lowtemperature peaks is \sim 500 cm⁻¹), similar to that observed for the chains of dimers, $\{Cu_2X_2(PPh_3)(L)\}$ ²⁸ All other compounds exhibited a bathochromic shift, in the range of 823-1310 cm⁻¹ (the difference between the high- and lowtemperature peaks is similar to that observed for the phosphine copper dimers reported by Deaton).¹³ In the case of the bzpy ligands it is possible to observe the vibrational splitting in the spectra of both isomers $[CuI(3-bzpy)]_n$ and $[CuI(4-bzpy)]_n$ with energies of 1134 and 1324 cm⁻¹, respectively, which is close to one of the vibrational modes of these complexes (see Experimental Section). Finally, the decrease in temperature decreases the probability of the thermally activated ${}^{3}T \rightarrow {}^{1}S_{1}$ conversion that is reflected in the increase of the lifetime up to tens of microseconds (Figures S8-S13 and Table 3), which is

characteristic of phosphorescence.⁵⁰ The energy shifts in combination with the lifetime measurements suggest there is more than one emission level, and they are close enough in energy for TADF.

Chain versus Stair Structure. We anticipated that the structure, whether stair or chain polymer, should influence the luminescence properties. Thus, we were interested in comparing systems with the same ligand and the same halide but different structure type. The example from our work is for copper, bromide, and pyrazine, forming either the $[Cu_2Br_2(pyz)]_n$, which has the stair structure type and the 0-0 transition at 586 nm, in contrast to the $[CuBr(pyz)]_n$ with the chain structure that shows its 0-0 transition at 648 nm. The emission spectra for these two compounds, as well as $[CuBr(quinz)]_n$, are shown in Figure 6. The emission at longer wavelengths for the chain structure can also be observed by comparing the acetyl-pyridine (acpy) polymers with the stair structure, $[CuI(acpy)]_n$ (emission maximum at 612 nm), with the chain structure, $[CuI(acpy)_2]_n$ (emission maximum at 700 nm). We postulate, as discussed below, that the HOMO is based on a mix of the metal and halogen orbitals, while the LUMO is dominantly π^* ligand orbitals. The higher energy of the stair may be a result of stabilization of the HOMO due to delocalization through the stair structure increasing the energy separation between HOMO and LUMO.

Ligand Binding Mode. One approach to determining the effect of the ligand was to compare coordination polymers with the same structure, same halide, and ligands differing only as to whether they are monodentate or bidentate. There are several possibilities, but our focus was on the comparison between pyridine and pyrazine. For the iodide example, the $[CuI(py)]_n$

with the stair structure was reported to have its emission maximum at 437 nm,³ whereas $[Cu_2I_2(pyz)]_n$ also has a stair structure but with a bridging pyrazine and 0–0 transition at 663 nm. In the case of bromide for the same system, the previously reported $[CuBr(py)]_n$ with the stair structure has an emission maximum at 509 nm. However, the $[Cu_2Br_2(pyz)]_n$ also has a stair structure with the bridging pyrazine and shows 0–0 transition at 586 nm. Both examples suggest that the bridging ligand has a shifted LUMO, and that potentially delocalization lowers the LUMO giving a lower-energy emission for the bridged ligands.

Ligand Electronic Structure. Of all the components that affect the emission energy of the copper halide polymers, we found that the electronic structure of the ligand was most important. We selected the ligands based on the emission reported for the $[Cu_2(\mu-Br)_2(PPh_3)_2(L)]_{\infty}$ complexes, which varied between ~579 and 707 nm. The energy of emission of these complexes decreased in the order 3-bzpy > quinz >4-bzpy > pyz. The same energy of emission order was found for these ligands in the $[Cu_2I_2L]_n$ series. The range of emission energies (540 nm-660 nm) is also close but slightly shifted compared with the bromide compounds. Perhaps the most striking example of the ligand effect is for the closely related benzoylpyridine isomers 3-bzpy and 4-bzpy, which differ only in whether the noncoordinating benzoyl substitutes meta or para on the pyridine ring. In this example, $[CuI(3-bzpy]_n has its 0-0]$ phonon transition at 537 nm, whereas the one of [CuI(4bzpy]_n is red-shifted to ~637 nm. This is the strongest argument for the role of the ligand electronics in the emission spectra. For this particular pair, we performed the molecular orbital calculations to determine the properties of the HOMO and LUMO by the DFT method on Gaussian 09. The geometry was taken from the crystal structures, and the fragment included in the calculation was two -Cu-I-units and two ligands. The calculated energy levels were similar to those of previously investigated copper iodide complexes in that the HOMO is dominantly based on the copper 3d and iodide 4p orbitals, whereas the LUMO is primarily based on the π^* of the aromatic amine (see Figure 7). The low overlap between the donating and accepting orbitals often leads to a low energy gap between S_1 and T_1 as observed by Steffen.¹¹ For the two compounds compared here, the calculated HOMO-LUMO difference was 2.05 eV or 600 nm for $[CuI(3-bzpy)]_n$ compared with 537 nm experimentally and 1.74 eV or 712 nm for $CuI(4-bzpy)]_n$ compared with 637 nm observed experimentally. Both values are ~ 60 nm too low in energy, but the trend is consistent. These calculations are supported by studies by Araki, who found that the emission energy in the $[(Cu_2Br_2(PPh_3)_2(L_2)]$ for L = 3-bzpy, 4-bzpy also using DFT methods found similar frontier orbitals, where the excited state was due to charge transfer from the metal to the π^* of the Nheteroaromatic ligand with mixing of the halogen adding XMLCT. Charge transfer to an antibonding LUMO should cause a geometrical change, involving bond change and large Stokes shift. Our shifts are <7000-10000 cm⁻¹ similar to that observed by Pike.^{41,46} Larger Stokes shifts (12 000-14 000 cm⁻¹) have been observed for tetranuclear clusters.⁴¹

Nonlinear Optical Properties. Materials possessing noncentrosymmetric space groups have the potential to emit SHG light upon laser irradiation.^{51,52} In addition to structural constraints, the presence of a charge transfer transition has also been identified as an important electronic feature that leads to second-order NLO response.⁴⁴ Alignment along a specific



Figure 7. Molecular orbital calculation for $[CuI(3-bzpy)]_n$ (left) and $[CuI(4-bzpy)]_n$ (right). Above are the HOMO (left) orbitals illustrating the combination of metal and iodide, and the LUMO (right) orbitals illustrating the contribution of the π^* aromatic amine orbitals.

direction of related chromophores has been observed to increase SHG efficiencies in organic salts.⁵³ Ford investigated the NLO properties of non-centrosymmetric $[CuX(L)]_n$ (X = Cl, Br, I; L = pseudoaromatic η^1 nitrogen donor ligands) with single-stranded and ladder-type structures to determine the structural and electronic properties that contribute to the SHG.³ On the basis of these studies, the conclusions were: (1)the SHG efficiencies do not follow the intensity of emissions, (2) the MLCT process alone does not control the second-order NLO activity, and (3) chain compounds appear to exhibit stronger NLO than ladders.⁴⁴ We investigated the second-order NLO of several compounds reported here, using an incident nonresonant wavelength of 1064 nm, taking quartz (α -SiO₂) as the reference material. The NLO values for copper halide polymers reported previously ranged from 23 to 45 times that of quartz.43 The strongest SHG we observed was for the $[CuBr(quinz)]_n$ (7; see Figure 8). This compound crystallizes in the space group $Pca2_1$ and emits in the red, with a $\lambda_{em} = 620$ nm. The SHG was shown to be phase matchable, and ~100 times larger response compared to α -SiO₂.⁵⁴ The structure type is similar to the chain structures reported previously, in which the copper is bonded to two ligands. The structures subtly differ in that the quinazoline compound reported here has ligands that bridge two chains. Nonetheless, our results are a modest improvement over those reported previously.

CONCLUSION

In this series of copper bromide and iodide organoamine coordination polymers we have reported the crystal structure of two new compounds, namely, $[Cu_2I_2(quinz)]_n$ (2) and $[CuI(3-bzpy)]_n$ (3). Both coordination polymers have the frequently observed double-stranded stair formed by $-Cu_2I_2-$ units. We have also investigated the luminescence properties of several stair-type coordination polymers, finding that the emission is



Figure 8. SHG curve for CuBr(quinz). Phase matchable and ~150 times larger than α -SiO₂ for 45–63 μ m particle size.

most likely due to a (M + X)LCT. While the structure and halide are important for the emission energies, it appears that the electronic structure of the ligand has the strongest impact. The copper iodides have the advantage of being air-stable, and although we have not investigated the electroluminescent properties, these materials exhibit TADF and may be of potential interest in organic LEDs. In screening the non-centrosymmetric structures, we discovered one of the strongest NLO responses observed in the copper halide organoamine systems in the chain structure $[CuBr(quinz)]_n$ (7).

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b01879.

Crystal structure, powder X-ray diffraction pattern, and full emission spectra (PDF)

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Notes

The authors declare no competing financial interest.

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