# **Inorganic Chemistry**

pubs.acs.org/IC

# From Short-Bite Ligand Assembled Ribbons to Nanosized Networks in Cu(I) Coordination Polymers Built Upon Bis(benzylthio)alkanes (BzS(CH<sub>2</sub>)<sub>n</sub>SBz; n = 1-9)

Adrien Schlachter, Antony Lapprand, Daniel Fortin, Carsten Strohmann, Pierre D. Harvey,\* and Michael Knorr\*



**ABSTRACT:** With the objective to establish a correlation between the spacer distance and halide dependence on the structural features of coordination polymers (CPs) assembled by the reaction between CuX salts (X = Cl, Br, I) and dithioether ligands  $BzS(CH_2)_nSBz$  (n = 1-9; Bz = benzyl), a series of 26 compounds have been prepared and structurally investigated. A particular attention has been devoted to the design of networks with extremely long and flexible methylene spacer units between the SBz donor sites. Under identical conditions, CuI and CuBr



Article

react with BzSCH<sub>2</sub>Bz (L1) affording respectively the one-dimensional (1D) CPs  $\{Cu(\mu_2-I)_2Cu\}(\mu-L1)_2\}_n$  (CP1) and  $\{Cu(\mu_2-I)_2Cu\}(\mu-L1)_2\}_n$  $Br_2Cu_{\mu-L1_2}(CP2)$ , which incorporate  $Cu_{\mu_2-X_2}Cu$  rhomboids as secondary building units (SBUs). The hitherto unknown architecture of two-dimensional (2D) layers obtained with CuCl (CP3) differs from that of CP1 and CP2, which bear inorganic -Cl-Cu-Cl-Cu-Cl- chains interconnected through bridging L1 ligands, thus forming a 2D architecture. The crystallographic characterization of a 1D CP obtained by reacting CuI with 1,3-bis(benzylthio)propane (L2) reveals that  $[{Cu(\mu_2-I)_2Cu}(\mu-L2)_2]_n$ (CP4) contains conventional Cu<sub>2</sub>I<sub>2</sub> rhomboids as SBUs. In contrast, unusual isostructural CPs [{Cu( $\mu_2$ -X)}( $\mu_2$ -L2)]<sub>n</sub> (CP5) and (CP6) are obtained with CuX when X = Br and Cl, respectively, in which the isolated Cu atoms are bridged by a single  $\mu_2$ -Br or  $\mu_2$ -Cl ion giving rise to infinite  $[Cu(\mu_2-X)Cu]_n$  ribbons. The crystal structure of the strongly luminescent three-dimensional (3D) polymer  $[\{Cu_4(\mu_3-I)_3(\mu_4-I)(\mu-L3)_{1,5}]_n$  (CP7) issued from reacting 2 equiv of CuI with BzS(CH<sub>2</sub>)<sub>4</sub>SBz (L3) has been redetermined. **CP7** features unusual  $[(Cu_4I_3)(\mu_4-I)]_n$  arrays securing the 3D connectivity. In contrast, mixing CuI with an excess of L3 provides the nonemissive material  $[{Cu(\mu_2-I)_2Cu}(\mu-L3)_2]_n$  (CP8). Treatment of CuBr and CuCl with L3 leads to  $[{Cu(\mu_2-Br)_2Cu}(\mu-L3)_2]_n$ (CP9) and the 0D complex [{Cu( $\mu_2$ -Cl)<sub>2</sub>Cu}( $\mu$ -L3)<sub>2</sub>] (D1), respectively. The crystallographic particularity for CP9 is the coexistence of two topological isomers within the unit cell. The first one, CP9-1D, consists of simple 1D ribbons running along the *a* axis of the unit cell. The second topological isomer, CP9-2D, also consists of  $[Cu(\mu_2-Br)_2Cu]$  SBUs, but these are interconnected in a 2D manner forming 2D sheets placed perpendicular to the 1D ribbons. Four 2D CPs, namely,  $[{Cu_4(\mu_3-I)_4}(\mu-L4)_2]_n$  (CP10),  $[{Cu(\mu_2-I)_2Cu}(\mu-L4)_2]_n$  (CP11),  $[{Cu(\mu_2-Br)_2Cu}(\mu-L4)_2]_n$  (CP12), and  $[{Cu(\mu_2-Cl)_2Cu}(\mu-L4)_2]_n$  (CP13), stem from the self-assembly process of CuX with BzS(CH<sub>2</sub>)<sub>6</sub>SBz (L4). A similar series of 2D materials comprising  $[{Cu<sub>4</sub>(\mu_3-I)<sub>4</sub>}(\mu-L5)_2]_n$  (CP14),  $[\{Cu(\mu_2-I)_2Cu\}(\mu-LS)_2]_n$  (CP15),  $[\{Cu(\mu_2-Br)_2Cu\}(\mu-LS)_2]_n$  (CP16), and  $[\{Cu(\mu_2-Cl)_2Cu\}(\mu-LS)_2]_n$  (CP17) result from the coordination of  $BzS(CH_2)_7SBz$  (L5) on CuX. Ligation of CuX with the long-chain ligand  $BzS(CH_2)_8SBz$  (L6) allows for the X-ray characterization of the luminescent 2D [{ $Cu_4(\mu_3-I)_4$ }(\mu-L6)\_2]\_n (CP18) and the isostructural 1D series [{ $Cu(\mu_2-X)_2Cu$ }(\mu-L6)\_2]\_n **CP19** (X = I), **CP20** (X = Br) and **CP21**(X = Cl). Noteworthy,  $BzS(CH_2)_9SBz$  (L7) bearing a very flexible nine-atom chain generated the crystalline materials 2D [{ $Cu_4(\mu_3-I)_4$ }(\mu-L7)\_2]\_n (CP22) and the isostructural 1D series [{ $Cu(\mu_2-X)_2Cu$ }(\mu-L6)\_2]\_n **CP23** (X = I), **CP24** (X = Br), and **CP25** (X = Cl), featuring nanometric separations between the cubane- or rhomboid-SBUs. This comparative study reveals that the outcome of the reaction of CuX with the shorter ligands  $BzS(CH_2)_nSBz$  (n = 1-4) is not predictable. However, with more flexible spacer chains  $BzS(CH_2)_nSBz$  (n = 6-9), a clear structural pattern can be established. Using a 1:1 CuX-to-ligand ratio,  $[{Cu(\mu_2-X)_2Cu}(\mu-L4-7)_2]$  CPs are always formed, irrespectively of L4–L7. Employing a 2:1 CuX-tocontinued...

Received: November 7, 2019



Α

ligand ratio, only CuI is able to form networks incorporating  $Cu_4(\mu_3-I)_4$  clusters as SBUs. All attempts to construct polynuclear cluster using CuBr and CuCl failed. The materials have been furthermore analyzed by powder X-ray diffraction, Raman spectroscopy, and thermogravimetric analysis, and the photophysical properties of the emissive materials have been studied.

# ■ INTRODUCTION

The coordination chemistry of long chain diphosphine ligands of type  $R_2P(CH_2)$ ,  $PR_2$   $(n \ge 5)$  has intrigued coordination chemists since the 1970s as their flexibility induces various coordination modes such as  $\eta^1$ -mondentate, chelating, or *trans*spanning upon complexation onto transition metals.<sup>1-8</sup> For instance, selected examples of discrete molecular complexes and large macrocycles ligated by with 1,8-bis(diphenylphosphino)octane (dppo) include the monosubstituted  $[(\eta^5-indenyl)Fe (CO)_2(\eta^1 \text{-dppo})$  [BF<sub>4</sub>], dimeric [{( $\eta^5$ -indenyl)Fe(CO)\_2}( $\mu$ dppo)]<sub>2</sub>[BF<sub>4</sub>]<sub>2</sub>, dinuclear [( $\mu$ -bpym)Cu<sub>2</sub>( $\mu$ -dppo)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (bpym = 2,2'-bipyrimidine), and macrocyclic species cis- $[Mo_2(CO)_8(\mu-dppo)_2]^{.9-11}$  However,  $Ph_2P(CH_2)_8PPh_2$  has also been used as an assembling ligand to construct polymers networks such as one-dimensional (1D)  $[IAu(\mu-dppo)Au]_{1/2}$  $[ClAu(\mu-dppo)AuCl]_n$  and 1D  $[Ag_{12}(SCy)_{12}(\mu-dppo)]_n$ <sup>12</sup> Note that with CuI and  $Ph_2P(CH_2)_nPPh_2$  (*n* = 1, 2, 3, 4, 5, 6), only discrete zero-dimensional (0D) complexes are formed.<sup>14-20</sup> Chart 1 presents some selected examples of such (CuI), clusters as well as some molecular metal complexes and CPs ligated by dppo.

Conversely, the coordination chemistry of acyclic long chain dithioether ligands  $RS(CH_2)_nSR$  ( $n \ge 6$ ; R = alkyl, aryl), which should also confer a high degree of flexibility, has been much less explored than that of their diphosphine counterparts. Among the scarce examples are the investigation of Murray and Levason on the preparation of insoluble  $[PdX_2(PhS(CH_2)_8SPh)]$  (X = Cl, Br, I) complexes, for which a polymeric structure has been suggested.<sup>21</sup> The reduction of  $[AuCl_4]^-$  in the presence of

PhS(CH<sub>2</sub>)<sub>8</sub>SPh is reported to produce the dinuclear complex  $[ClAu(\mu-PhS(CH_2)_8SPh)AuCl]^{22}$  The dicationic cyclopentadienvliron arene complex  $[(\eta^5-C_5H_5)Fe(\eta^6-C_6H_4Cl)-S (CH_2)_8S-(\eta^6-C_6H_4Cl)Fe(\eta^5-C_5H_5)]^{2+}$  has been used as a building block for the synthesis of organometallic oligomers.<sup>23</sup> Reaction of the  $(CH_2)_8$ -containing ligand 1,8-bis(8thioquinolyl)octane (C8TQ) with AgCF<sub>3</sub>CO<sub>2</sub> afforded the two-dimensional (2D) brick-wall CP [Ag<sub>2</sub>(C8TQ)- $(CF_3CO_2)_2]_n$ , composed of thio-bridged helical chains, racemically aligned and further connected by the (CH<sub>2</sub>)<sub>8</sub> spacers.<sup>24</sup> In the case of CuX salts, one report indicated that the reaction of 1,12-diphenyl-5,8-dioxa-2,11-dithiadodecane with CuI leads to a luminescent 2D framework of composition  $[(Cu_4I_4)(BzS(CH_2)_2O(CH_2)_2O(CH_2)_2SBz)_2]_n$ <sup>25</sup> Cu<sub>4</sub>I<sub>4</sub>- and Cu<sub>2</sub>I<sub>2</sub>-containing CPs have recently been obtained by treatment of CuI with the rigid ligand 4,4'-bis(ethylthiomethyl)biphenyl incorporating an aromatic biphenyl unit with its C10 spacer chain.<sup>26</sup> For other CuI-containing CPs with a long chain dithioether ligand incorporating heteroelements within the spacer chain, two examples exist, 1,4-bis((methylthio)propanoyl)piperazine<sup>27</sup> and 1,4-bis(2-methylthioethoxy)benzene.<sup>28</sup> Although the motivation to design networks assembled by thioether ligands was mainly driven by structural aspects and the interesting photophysical properties such as high emission quantum yields and triplet-triplet annihilation, other applications in material sciences and catalysis are emerging.<sup>29,30</sup>

In the context of our ongoing systematic study on the impact of the spacer length and rigidity of acyclic dithioether ligands on the nuclearity of the (CuX) cluster core, dimensionality of the

Chart 1. Overview of Literature-Known  $Ph_2P(CH_2)_nPPh_2$  Diphosphine Complexes and CPs Which Are Related to Dithioether-Containing Complexes Ligated by  $RS(CH_2)_nSR$ 



https://dx.doi.org/10.1021/acs.inorgchem.9b03275 Inorg. Chem. XXXX, XXX, XXX–XXX CDIT

#### pubs.acs.org/IC

	350	0					
polymer	geometry	cluster	ligand		dimensionality	shortest distance Cu…Cu (Å)	mean distance Cu…Cu (Å)
CP1	rhomboid	$Cu_2I_2$	BzSCH <sub>2</sub> SBz	L1	1D	2.7742(6) <sup>a</sup>	2.7305(6)
						$2.6867(6)^{b}$	
CP2	rhomboid	$Cu_2Br_2$	BzSCH <sub>2</sub> SBz		1D	2.8829(7)	2.8829(7)
CP3	chain	CuCl	BzSCH <sub>2</sub> SBz		2D	4.2016(8)	4.2016(8)
CP4	rhomboid	$Cu_2I_2$	BzS(CH <sub>2</sub> ) <sub>3</sub> SBz	L2	1D	3.092(4)	3.092(4)
CP5	chain	CuBr	$BzS(CH_2)_3SBz$		1D	4.1169(10)	4.1169(10)
CP6	chain	CuCl	BzS(CH <sub>2</sub> ) <sub>3</sub> SBz		1D	3.9595(14)	3.9595(14)
CP7	cubane	$\mathrm{Cu}_4\mathrm{I}_4$	$BzS(CH_2)_4SBz$	L3	3D	2.7013(5)	2.7897(6)
CP8	rhomboid	$Cu_2I_2$	$BzS(CH_2)_4SBz$		2D	2.796(3)	2.796(3)
CP9-1D	rhomboid	$Cu_2Br_2$	$BzS(CH_2)_4SBz$		1D	3.0159(5)	3.0159(5)
CP9-2D	rhomboid	$Cu_2Br_2$	$BzS(CH_2)_4SBz$		2D	2.9951(6)	2.9951(6)
D1	rhomboid	$Cu_2Cl_2$	$BzS(CH_2)_4SBz$		0D	2.9083(9)	2.9083(9)
CP10	cubane	$Cu_4I_4$	$BzS(CH_2)_6SBz$	L4	2D	2.7034(12)	2.7316(12)
CP11	rhomboid	$Cu_2I_2$	$BzS(CH_2)_6SBz$		2D	2.828(3)	2.828(3)
CP12	rhomboid	$Cu_2Br_2$	$BzS(CH_2)_6SBz$		2D	2.9597(3)	2.9597(3)
CP13	rhomboid	$Cu_2Cl_2$	$BzS(CH_2)_6SBz$		2D	2.9570(14)	2.9570(14)
CP14	cubane	$Cu_4I_4$	$BzS(CH_2)_7SBz$	L5	2D	2.679(6)	2.6898(32)
CP15	rhomboid	$Cu_2I_2$	$BzS(CH_2)_7SBz$		2D	2.7415(8)	2.7415(8)
CP16	rhomboid	$Cu_2Br_2$	$BzS(CH_2)_7SBz$		2D	2.7081(4)	2.7081(4)
CP17	rhomboid	$Cu_2Cl_2$	$BzS(CH_2)_7SBz$		2D	2.695(4)	2.695(4)
CP18	cubane	$Cu_4I_4$	$BzS(CH_2)_8SBz$	L6	2D	2.7098(19)	2.7230(11)
CP19	rhomboid	$Cu_2I_2$	$BzS(CH_2)_8SBz$		1D	2.8479(5)	2.8479(5)
CP20	rhomboid	$Cu_2Br_2$	$BzS(CH_2)_8SBz$		1D	3.0091(15)	3.0091(15)
CP21	rhomboid	$Cu_2Cl_2$	$BzS(CH_2)_8SBz$		1D	2.9297(10)	2.9297(10)
CP22	cubane	$Cu_4I_4$	BzS(CH <sub>2</sub> ) <sub>9</sub> SBz	L7	2D	2.639(5)	2.745(5)
CP23	rhomboid	$Cu_2I_2$	$BzS(CH_2)_9SBz$		1D	2.7773(6)	2.7773(6)
CP24	rhomboid	$Cu_2Br_2$	$BzS(CH_2)_9SBz$		1D	2.9178(8)	2.9178(8)
CP25	rhomboid	$Cu_2Cl_2$	$BzS(CH_2)_9SBz$		1D	2.8883(11)	2.8883(11)
<sup><i>i</i></sup> Ribbon A. <sup><i>b</i></sup>	Ribbon <b>B</b> .						

## Table 1. List of Ligands, Coordination Polymers, Their Codes Used, and Resulting Cu-Cu Parameters

network, and other topological features, 31-33 we recently reported in detail the coordination of the short-bite dithioether ligands ArSCH<sub>2</sub>SAr (Ar = Ph, p-Tol, m-Tol, o-Tol, p-anisyl, p- $BrC_6H_4$ , 5-tert-butyl-2-methyl $C_6H_3$ , 2-tert-butyl-4-methyl $C_6H_3$ ) toward CuI.<sup>34</sup> Despite the electronic and steric variation of the substitution pattern on the aryl, invariably in all cases, 1D CPs of the type  $[{Cu_4(\mu_3-I)_4}(\mu-ArSCH_2SAr)_2]$  incorporating tetranuclear closed-cubane Cu<sub>4</sub>I<sub>4</sub> clusters were isolated. Conversely, 2D [{Cu( $\mu_2$ -I)\_2Cu}{ $\mu$ -PhS(CH<sub>2</sub>)\_3SPh}<sub>2</sub>]<sub>n</sub> and [Cu<sub>4</sub>I<sub>4</sub>{ $\mu$ -PhS- $(CH_2)_3SPh_2]_n$  networks formed upon by varying the CuI-to-PhS(CH<sub>2</sub>)<sub>3</sub>SPh ratio. A double interpenetrated 2D network  $[{Cu(\mu_2-I)_2Cu}{\mu-PhS(CH_2)_4SPh}_2]_n$  resulted from treatment of CuI with  $PhS(CH_2)_4SPh$ . Mixing CuI and the dithioether in a 2:1 ratio resulted in the formation of  $[Cu_4I_4{\mu-PhS (CH_2)_{s}SPh_{2}$ , in which cubane-like  $Cu_4(\mu_3-I)_4$  clusters are linked by bridging PhS(CH<sub>2</sub>)<sub>5</sub>Ph ligands affording a 1D necklace CP similar to that of  $[Cu_4I_4\{\mu_2-PhSCH_2SPh\}_2]_n$ . However, a ribbon-like 1D CP with the composition [{Cu( $\mu_2$ -I)<sub>2</sub>Cu}{ $\mu$ -PhS(CH<sub>2</sub>)<sub>5</sub>SPh}<sub>2</sub>]<sub>n</sub> incorporating rhomboid Cu<sub>2</sub>I<sub>2</sub> units was produced upon treatment of CuI with this ligand in a 1:1 ratio.

In order to develop a systematic method for this seemingly unpredictable outcome of the assembly process, we studied the impact of a long spacer dithioether, which should confer a high degree of flexibility. Indeed, our work on ArS(CH<sub>2</sub>)<sub>n</sub>SAr ligands with variable spacer lengths going from ArSCH<sub>2</sub>SAr to the highly flexible ArS(CH<sub>2</sub>)<sub>8</sub>SAr, we were intrigued by the impact of a systematic variation of the spacer length in the BzS-(CH<sub>2</sub>)<sub>1-9</sub>SBz series. A particular attention has been devoted to the juxtaposition of the rigid short-bite BzSCH<sub>2</sub>SBz to the  $BzS(CH_2)_{s=0}SBz$  ligand incorporating long aliphatic flexible octane and nonane chains between the two S-donor sites. This endeavor was motivated by expected formations of porous CPs or metal-organic frameworks (MOFs), in which due to the nanometric separation between the inorganic  $(CuX)_n$  connection nodes, cavities and voids should be present and accessible for guest molecules. The crystallogenesis of interpenetrated and entangled networks was also anticipated. The choice of using benzylic SCH<sub>2</sub>Ph is motivated by two reasons: (i) the steric constraint around the S-donor is reduced compared to SAr, and (ii) a benzyl group enhances the donor propensity of the sulfur atom (although less than a purely aliphatic R substituent), reinforcing the stability of the dative S-Cu bond and thus obtaining more robust materials. This strengthened affinity of SBz versus SAr vis-à-vis Cu(I) permits even their bonding to CuCl, whose coordination fails when using  $\operatorname{ArS}(\operatorname{CH}_2)_n \operatorname{SAr}$  as ligands. We now report the very surprising effect of an *a priori* innocent switch from *p*-Tol<sup>33-36</sup> to the isomeric Bz-substituent on both the nuclearity and dimensionality of the CPs. The structures of the investigated ligands along with the resulting dimensionalities and type of secondary building units (SBUs) of the CPs are summarized in Table 1.

# RESULTS AND DISCUSSION

**Reaction of Cul, CuBr, and CuCl with BzSCH<sub>2</sub>SBz (L1).** *Reaction of Cul with L1.* The short-bite ligand L1 has previously been used in the past by several research groups. Indeed, its coordination on simple mononuclear complexes such as  $[(C_5H_5)Fe(CO)_2(\kappa^{1}-L1)]^+$  has been reported.<sup>37,38</sup> Its resemblance with the widespread short-bite ligand bis-(diphenyl-phosphino)methane (dppm) is notable as it also forms the L1-bridged dinuclear complex  $[CIPd(\mu_2-L1)_2PdCl]$ , which also converts to an A-frame complex upon addition of  $MeO_2CC\equiv CCO_2Me.^{39}$  The assembly of a 1D CP built upon dinuclear  $[Ag(\mu_2-L1)_2Ag]^{2+}$  interconnected by bridging  $CIO_4^$ counterions has been obtained by Bu et al. by the reaction of  $AgClO_4$  with L1.<sup>40</sup> We and other groups have extensively investigated the coordination of a series of aromatic ArSCH<sub>2</sub>SAr dithioethers with CuI and invariantly isolated 1D CPs of composition  $[Cu_4I_4\{\mu-ArSCH_2SAr\}_2]_n$  or macrocyclic complexes incorporating tetranuclear clusters of the closed cubane type as connecting nodes.<sup>31,34,41</sup>

We were intrigued whether the reaction of L1, which is isomeric with the previously investigated *p*-TolSCH<sub>2</sub>STol-*p* ligand, with CuI in MeCN would also produce a similar  $[Cu_4I_4\{\mu$ -BzSCH<sub>2</sub>SBz $\}_2]_n$  neck-lace-type chain CP. However, air-stable colorless crystals of a material having a 1:1 CuI-to-L1 ratio were isolated in 72% yield regardless of the CuI-to-ligand ratio. The X-ray analysis shows the formation of a 1D CP  $\{Cu(\mu_2-I)_2Cu\}(\mu-L1)_2]_n$  (CP1) (Figure 1, Scheme 1) consisting of centrosymmetric dinuclear rhomboid  $Cu(\mu_2-I)_2Cu$  units spanned by L1 ligands.



**Figure 1.** View of the two independent ribbons of **CP1** along the *a* axis. Selected bond lengths [Å] and angles [°] at 100 K: Cu1–S1 2.3416(6), Cu1–S2 2.3183(6), Cu2–S3 2.3105(6), Cu2–S4 2.32878(7), Cu1–I1 2.6053(4), Cu1–I1# 2.6226(5), Cu2–I2 2.6107(5), Cu2–I2# 2.6226(4), Cu1–Cu1# 2.7742(6) Cu2–Cu2# 2.6867(6); S1–Cu1–S2 101.10(2), S3–Cu2–S4 99.06(2), S1–Cu1–I1 109.382(18), S1–Cu1–I# 113.507(18), S3–Cu2–I2 109.695(18), S3–Cu2–I2# 104.862(19), S4–Cu2–I2 112.485(19), S4–Cu2–I2# 110.49(2), I2–Cu2–I2# 118.221(14), I1–Cu1–I1# 115.903(13), Cu1–I1–Cu1# 64.098(13), Cu2–I2–Cu2# 61.777(14). Symmetry transformations used to generate equivalent atoms: #1 3 – x, 2 – y, 1 – z. #2 1 + x, y, z. #3 – 1 + x, y, + z. #4 1 – x, 1 – y, –z.

At first glance, this 1D architecture does not seem spectacular since it has been previously reported for several other flexible  $RS(CH_2)_nSR$  ligands and CPs such as  $[{Cu(\mu_2-I)_2Cu}_{\mu-CyS(CH_2)_4SCy}_2]_n$  (dCu····Cu = 3.0089(15) Å) and  $[{Cu(\mu_2-I)_2Cu}_{\mu-PhS(CH_2)_5SPh}_2]_n$  (dCu····Cu = 3.0089(15) Å), as well as for  $[{Cu(\mu_2-I)_2Cu}_{\mu-C_6H_{11}CH_2SCH_2C}(=O)$ -NC<sub>4</sub>H<sub>8</sub>S}<sub>2</sub>]<sub>n</sub>, formed by the self-assembly of CuI with the carbonyl-functionalized dithioether 2-(cyclohexythio)-1-thiomorpholino-ethanone ligand.<sup>33,42,43</sup> We also recently described



the structure of the 1D CP  $[{Cu(\mu_2-I)_2Cu}_{\mu_2}-methyldithia$  $ne_{2}]_{n}$ , spanned by rigid 2-methyldithiane heterocycles featuring a CH<sub>2</sub>SCH(Me)SCH<sub>2</sub> motif, in which like in L1, the two S donor sites are separated by a single C atom as a spacer.<sup>4</sup> However, a closer look reveals the coexistence of two independent ribbons (A and B) running along the a axis. Their main difference is the Cu-Cu distance. For ribbon A, the Cu1-Cu1 distance of 2.7742(6) Å is close to the van der Waals radii of two Cu atoms  $(2 \times 1.4 \text{ Å})$ , whereas in ribbon B, the separation between the two metals is 2.6867(6) Å, which is markedly shorter and may be considered bonding. A quite similar value has been reported for the 1D CP  $[(Me_2S)_2{Cu_2(\mu_2-I)_2}]_n$  in which the metal centers within the rhomboid cluster are separated by 2.684(1) Å.<sup>45</sup> Noteworthy, the extreme difference between the Cu-Cu separations of CP1 and those in  $[{Cu(\mu_2-I)_2Cu}_{\mu_2}-methyldithiane}_2]_n$  (3.367) Å)<sup>44</sup> stresses the structural flexibility of the Cu( $\mu_2$ -I)<sub>2</sub>Cu motif. We have recently structurally characterized the 2D CP  $[{Cu(\mu_2-I)}_2Cu}{\mu-E-PhS(CH_2CH=CHCH_2)SPh}_2]_n$  in which the square-grid network is built upon alternating 2D layers with an ABAB sequence and contains rhomboid  $Cu_2(\mu_2$ -I)<sub>2</sub> units as SBUs.<sup>46</sup> Remarkably, layer A contains exclusively dinuclear units with short Cu…Cu separations (2.6485(7) Å), whereas the B layer exhibits Cu-Cu distances of 2.8133(8) Å. Noteworthy to the best of our knowledge, no other 1D (CuI). CP in which two isomeric forms of ribbons coexist as seen in CP1.

Reactions of CuBr and CuCl with L1. For comparison purposes, a CH<sub>3</sub>CN solution of L1 was also treated with an equimolar amount of CuBr. At 5 °C, colorless crystals of composition  $[{Cu(\mu_2-Br)_2Cu}(\mu-L1)]_n$  (CP2) formed and were isolated in 69% yield (Scheme 1). The crystallographic analysis revealed that this material, crystallizing in the monoclinic crystal system with space group  $P12_1/n_1$ , has a very similar architecture with CP1 (Figure 2).

This 1D scaffold of **CP2** exhibits, in an identical manner, dinuclear  $Cu(\mu_2\text{-Br})_2Cu$  rhomboids, which are linked by two bridging dithioethers (Figure 2), but the Cu<sup>•••</sup>Cu contact is somewhat longer than that of ribbon **A** of its  $\mu_2$ -iodide analogue [2.8829(7) vs 2.7742(6) Å]. The Cu–X–Cu angle is wider than that for **CP1** (71.507(15)° vs 64.089(13)°). Noteworthy, the Cu<sup>•••</sup>Cu's are lengthening upon changing X = I (**CP1**) for Br (**CP2**), whereas the reverse trend is noted for the isostructural [{Cu( $\mu_2$ -X)\_2Cu}{ $\mu$ -PhS(CH2)\_SPh}\_2]\_n CPs [dCu<sup>•••</sup>Cu<sup>•</sup> (X = I) 2.9190(3) versus (X = Br) 3.0089(15) Å].<sup>33</sup>

The structural arrangement within the ribbon in **CP2** is also comparable with that of  $[Cu(\mu_2-Br)_2Cu\{\mu-p-EtSCH_2C_6H_4C_6H_4CH_2SEt-p\}_2]_n$  in which two 2,2'-bis-



**Figure 2.** View of the infinite ribbon of **CP2** running along the *a* axis and incorporating dinuclear  $Cu(\mu_2\text{-}Br)_2Cu$  motifs. Selected bond lengths [Å] and angles [°]: Cu–S1 2.2876(7), Cu–S2 2.2924(7), Cu–Br 2.4466(5), Cu–Br# 2.4871(4), Cu····Cu 2.8829(7); S1–Cu–S2 129.56(2), S1–C1–S2 111.91(14), S1–Cu–Br 105.23(2), S1–Cu1–Br# 114.76(2), Cu–Br–Cu 71.507(15), Cu–S1–C1 108.89(9), Cu–S2–C1 106.69(9). Symmetry transformations used to generate equivalent atoms: #1 –1 + *x*, *y*, *z*. #2 1 – *x*, 1 – *y*, 1 – *z*.

(ethylthiomethyl)biphenyl ligands bind dinuclear Cu( $\mu_2$ -Br)\_2Cu SBUs giving rise to an infinite 1D strand (dCu····Cu = 2.918 Å), and [{Cu( $\mu_2$ -Br)\_2Cu}<sub>2</sub>{ $\mu$ -PhS(CH<sub>2</sub>)<sub>5</sub>SPh}<sub>2</sub>]<sub>n</sub> (dCu····Cu = 2.9130(3) Å).<sup>47,48</sup> Note that the similar structure of [{Cu( $\mu_2$ -Br)\_2Cu}{ $\mu$ -BzS(CH<sub>2</sub>)<sub>8</sub>SBz}<sub>2</sub>]<sub>n</sub> (**CP20**) is presented below.

L1 was also reacted with CuCl in an equimolar manner using a MeCN/MeOH (90/10) mixture as solvent. A yellowish crystalline product could be isolated upon storage at 5 °C, which was analyzed to have a 1:1 composition [(CuCl)( $\mu$ -L1)] CP3 according to elemental analysis (Scheme 1). X-ray-suitable single crystals (orthorhombic, *Pbca*) were grown from MeCN (the PXRD pattern of CP3 is provided in Figure S6). The architecture of 2D polymeric CP3 differs considerably from that of the CuI and CuBr materials. No [{Cu( $\mu_2$ -Cl)<sub>2</sub>Cu}] SBUs are present, but instead inorganic -Cl-Cu-Cl-Cu-Cl- chains (Figure 3). The 4.2002 Å separation between the  $\mu_2$ -Cl-bridged Cu atoms is far too loose for any Cu···Cu interaction between two adjacent Cu centers. These -Cl-Cu-Cl-Cu-Cl- chains

running along the *a* axis are interconnected through bridging L1 ligands, thus forming a 2D sheet architecture. The coordination around each crystallographic equivalent Cu center is tetrahedral consisting of two Cl atoms S atoms. We are not aware of any 2D CuCl thioether CPs featuring such an architecture, but two examples of 1D CPs with similar -Cl-Cu-Cl-Cu-Cl-backbones have been reported (see also below for the related 1D-polymer, notably **CP6**).<sup>49,50</sup>

**Reactions of Cul, CuBr, and CuCl with BzS(CH<sub>2</sub>)<sub>3</sub>SBz (L2).** *Reaction of Cul with L2.* The ligand 1,3-bis(benzylthio)-propane  $(L2)^{51}$  has previously been used by Bu et al. to prepare a 2D Ag(I) CP [Ag(L2)<sub>1.5</sub>]NO<sub>3</sub> by the reaction of AgNO<sub>3</sub> with this dithioether.<sup>52</sup> The reactivity of L2 *vis-à-vis* the entire CuX series is now investigated (Scheme 2).

Mixing CuI and L2 in a 1:1 ratio allowed for the isolation of a 1D CP of composition  $\{Cu(\mu_2-I)_2Cu\}(\mu-L2)_2\}_{\mu}$  (CP4; Figure 4). The crystal structure of this air-stable colorless material consists of centrosymmetric {Cu( $\mu_2$ -I)<sub>2</sub>Cu} SBUs interconnected through bridging L2 molecules giving rise to a 1D chain like in CP1. The most striking difference concerns the very loose Cu----Cu contacts largely surpassing those of ribbons A and B of **CP1**, even reaching those of the aforementioned [{Cu( $\mu_2$ -I)<sub>2</sub>Cu}{ $\mu$ -CyS(CH<sub>2</sub>)<sub>4</sub>SCy}<sub>2</sub>]<sub>n</sub> (3.0922 vs 3.0089(15) Å). This lengthening cannot likely be correlated with an increased flexibility of the ligand, since in the related 1D CPs [{Cu( $\mu_2$ -I)<sub>2</sub>Cu}{ $\mu$ -BzS(CH<sub>2</sub>)<sub>m</sub>SBz}<sub>2</sub>]<sub>n</sub> (CP19 m = 8, CP23 m = 9; see below), the Cu---Cu separation shortens again despite the high flexibility of the long alkane chain. In line with this considerable lengthening, the Cu-I-Cu angle is more widened than that of ribbon A of CP1 [64.098(13) versus  $71.70(16)^{\circ}]$ . The relative orientation of the ribbons in the packing is presented as Figure S1.

*Reactions of CuBr and CuCl with L2.* A different architecture is unexpectedly depicted for the materials obtained when mixing equimolar amounts of L2 with CuBr and CuCl in MeCN solution (Scheme 2). In both cases, colorless compounds of composition [{Cu( $\mu_2$ -X)}( $\mu_2$ -L2)]<sub>w</sub> respectively CP5 and CP6, are obtained. The crystal structures confirm the 1:1 copper-toligand ratio of these two isostructural compounds shown (Figure 5 and Figure 6). The structural arrangement is quite different from that of CP4 in terms of connectivity of the Cu atoms within the ribbons. These connectivities are not associated with the



**Figure 3.** (Left) View down the *c* direction on an *ab* layer of the 2D framework of  $[(CuCl)(\mu-L1)]_n$  (**CP3**). The benzyl groups are not shown for clarity. Selected bond lengths [Å] and angles [°]: Cu–S1 2.3431(19), Cu–S2 2.2787(19), Cu–Cl 2.291(2), Cu–Cl# 2.372(2); S1–Cu–S2 107.04(7), S1–C16–S2 112.0(3), S1–Cu–Cl 107.55(8), S1–Cu1–Cl# 112.50(8), Cu–Cl–Cu 128.53(8), Cu–S1–C16 99.8 (92), Cu–S2–C16 110.1(2). Symmetry transformations used to generate equivalent atoms: #1 1/2 – *x*, 1/2 + *y*, *z*. #2 1/2 + *x*, 3/2 – *y*, 1 – *z*. (Right) Perspective view down the *a* direction on a *bc* layer of the 2D network of **CP3**.

Article

# Scheme 2. Reactions of CuX with L2 in MeCN Forming CP4-CP6





**Figure 4.** View of a segment of the 1D ribbon of **CP4** running along the *b* axis. Selected bond lengths [Å] and angles [°] at 170 K: Cu–S1 2.303(3), Cu–S4 2.336(3), Cu–I 2.6299(17), Cu–I# 2.6500(16), Cu—Cu# 3.0922; S1–Cu–S4 99.41 (12), S1–Cu–I 101.25(9), S1–Cu–I# 126.60(1), S4–Cu–I 101.00(9), S4–Cu–I# 122.03(10), I–Cu–I# 108.30(6), Cu–I–Cu# 71.70(16). Symmetry transformations used to generate equivalent atoms: #1 *x*, 1 + *y*, *z*. #2 2 – *x*, 1 – *y*, –*z*.



**Figure 5.** View of a segment of the 1D ribbon of **CP5** running along the *b* axis. Selected bond lengths [Å] and angles [°] at 173 K: Cu–S1 2.3088(13), Cu–S2 2.3649(14), Cu–Br 2.4670(9), Br–Cu# 2.4743(19); S1–Cu–S2 94.58(5), S1–Cu–Br 103.72(16), S1–Cu–Br# 126.82(5), Br–Cu–Br# 110.48(3), Cu–Br–Cu# 112.85(2). Symmetry transformations used to generate equivalent atoms: #1 -x, -1/2 + y, 1 - z #2 x, 1 + y, z.

form of the Cu( $\mu_2$ -X)Cu rhomboids, as encountered in the Brand Cl-containing 1D CPs **CP2**, **CP20**, **CP21**, **CP24**, and **CP25** (see below). Instead, isolated Cu atoms interconnected via a single  $\mu_2$ -halide ligand. The most salient feature of these infinite Cu-X-Cu-X-Cu-X arrays is the unusual alignment of the CuX units, which are bridged only by a single  $\mu_2$ -halide ligand, similar to the bonding scheme observed in **CP3**. The most reminiscent 1D material from the literature is [{Cu( $\mu_2$ -Cl)}( $\mu$ -1,3-dithiolane)]<sub>n</sub> featuring a similar architecture.<sup>53</sup> Another rare



**Figure 6.** View of a segment of the 1D ribbon of **CP6** running along the *b* axis. Selected bond lengths [Å] and angles [°] at 173 K: Cu–S1 2.339(2), Cu–S2 2.3759(19), Cu–Cl 2.339(2), Cl–Cu# 2.342(2); S1–Cu–S2 94.98(7), S1–Cu–Cl 106.07(8), S1–Cu–Cl# 126.27(9), Cl–Cu–Cl# 111.87(5), Cu–Cl–Cu# 115.51(7). Symmetry transformations used to generate equivalent atoms: #1 *x*, -1 + y, *z*. #2 1 – *x*, 1/2 + y, 1 - z.

example of a 1D CP built with CuCl is  $[(THT)_3 \{Cu_2(\mu_2 - Cl)_2\}]_n$  (THT = tetrahydrothiophene), but the latter contains distinct Cu( $\mu_2$ -Cl)Cu rhomboids.<sup>45</sup>

With the aim to synthesize a network incorporating highernuclear Cu<sub>4</sub>Br<sub>4</sub> clusters related to Cu<sub>4</sub>I<sub>4</sub>-containing materials such as **CP7**, **CP10**, and **CP14** (Table 1), we also treated CuBr with **L3** in a 3:1 ratio. Unfortunately, no Cu<sub>4</sub>Br<sub>4</sub>-containing compound could be isolated; solely the 1:1 adduct [{Cu( $\mu_2$ -Br)<sub>2</sub>Cu}{ $\mu$ -L3}<sub>2</sub>]<sub>n</sub> (**CP5**) was produced. The comparison of the PXRD patterns of the materials resulting from the reactions performed in a 3:1 or 1:1 CuBr-to-L2 ratios unambiguously revealed that, in contrast to the CuI case, there is no impact on the product composition (Figure 7).

Reactions of Cul, CuBr and CuCl with BzS(CH<sub>2</sub>)<sub>4</sub>SBz (L3). Reaction of Cul with L3. Shortly after our investigation on the reactivity of PhS(CH<sub>2</sub>)<sub>4</sub>SPh toward CuI yielding the double interpenetrated 2D CP [{Cu<sub>4</sub>( $\mu_3$ -I)<sub>4</sub>}{ $\mu$ -PhS(CH<sub>2</sub>)<sub>4</sub>SPh}<sub>2</sub>]<sub>m</sub><sup>3</sup> Chen et al. reported in 2009 the X-ray structure of the 3D CP  $[{Cu_4(\mu_3-I)_3(\mu_4-I)}{\mu-BzS(CH_2)_4SBz}_{1.5}]_n$ , CP7, obtained by treatment of 1,4-bis(benzythio)butane L3 with CuI (Scheme 3).<sup>54</sup> The most salient feature of this nonporous 3D material exhibiting a rare 4(6).6(4) topology is the occurrence of tetranuclear CuI clusters of the closed cubane type, which are not only interconnected together by their ligands (like in the  $\mu_2$ brided 1,4-bis(phenylthio)butane-containing CP [{Cu<sub>4</sub>( $\mu_3$ -I)<sub>4</sub>}{ $\mu$ -PhS(CH<sub>2</sub>)<sub>4</sub>SPh}<sub>2]<sub>n</sub></sub>,<sup>32</sup> but also through  $\mu_4$ -iodo ligands forming a 1D  $-Cu_4I_4-Cu_4I_4$  – chain. The ladder motif of CP7 leads to a 2D hexagonal structure due to the three anchoring points of the tetrahedral cluster motif; here three Cu atoms out



**Figure 7.** PXRD patterns of the products obtained by treatment of CuBr with L2 in a 3:1 ratio and 1:1 ratio and comparison of the experimental PXRDs of CP5 with the simulated pattern.

of four are coordinated to S-donors inducing the formation of a hexagonal sheet (Figure 8, bottom). The fourth position on the cluster is used for a pentahedral connectivity between the closed cubanes, again forming an infinite array of cubanes  $[(Cu_4I_3)(\mu_4-I)]_n$  along the *c* axis, thus making a 3D material defined as  $[(Cu_4I_3)(\mu_4-I)(\mu-L3)_{1.5}]_n$ . This feature makes this material fall into a different category where the SBU is not a distinct cluster nor a multinuclear unit but a polycluster  $(Cu_4I_4)_n$ -containing inorganic chain.

As the original structure reported by Chen et al. has been recorded at 293 K, we have resynthesized this material by mixing

#### pubs.acs.org/IC

CuI and L3 in a 2:1 ratio and determined the structure at 173 K to get more accurate data for an advanced photophysical investigation of this strongly luminescent material (below). The low-temperature structure is very similar to that at 293 K (i.e., no phase transition), but has been refined choosing a trigonal crystal system with space group  $P\overline{3}$  (Z = 2) instead of a hexagonal one with Z = 4 as previously used by Chen. At 293 K, the Cu-Cu distances within the cluster range from 2.725(1) to 2.898(1) Å with mean intermetallic distances of 2.811 Å. The mean Cu-Cu distance shrinks slightly to 2.7897(6) Å at 173 K, just somewhat below the sum of the van der Waals radii of two Cu atoms.

In the original paper of Chen et al., the authors stated briefly that treatment of CuI with an excess of L3 just resulted in some oily residue, which was not further analyzed.<sup>54</sup> When this experience was repeated using an exact 1:1 ratio, a minor amount of nonemissive crystals along with luminescent crystals of CP7 was noticed under UV light at 364 nm. This material turned out to be the main product when using a 3-fold excess of L3, and the X-ray data revealed the presence of  $[{Cu(\mu_2-I)_2Cu}(\mu-L3)_2]_n$  (CP8), crystallizing in the triclinic space group  $P\overline{1}$ . A 2D network was formed incorporating centrosymmetric  $Cu(\mu_2-I)_2Cu$  SBUs, which are interconntected in the *ab* direction with other SBUs through bridging BzS(CH<sub>2</sub>)<sub>4</sub>SBz ligands (Figure 9). The Cu…Cu separation of 2.796(3) Å falls at the limit of the sum of the van der Waals radii of two Cu atoms,

# Scheme 3. Reactions of CuX with L3 in MeCN Forming CP7-CP9 and D1





**Figure 8.** Top: Perspective view down the *c* direction on an *ab* layer of the 3D framework of  $[(Cu_4I_3)(\mu_4-I)(\mu-L3)_{1.5}]_n$  (CP7) recorded at 173 K. Bottom: View of a segment of the inorganic 1D ribbon making part of the 3D network of CP7 running along the *c* axis. Selected bond lengths (Å) and angles (deg): Cu1–Cu1 2.8779(5), Cu1–Cu1# 2.8780(5), Cu1–Cu4 2.7013(5), Cu1–S1 2.2946(2), Cu1–I1 2.7027(4), Cu1–I4 2.7099(3), Cu1–I4 2.6443(3), Cu4–I4 2.6443(3); S1–Cu–S2 119.07(3), S1–Cu–I 106.44(2), S1–Cu–I# 97.23(2), I–Cu–I# 113.209(12), Cu–I–Cu# 66.970(12). Symmetry transformations used to generate equivalent atoms: #11 – *x*, 1 – *y*, 2 – *z*. #2 *y* – *x*, 1 – *x*, *z*. #3 1 – *y*, 1 + *x* – *y*, *z*. #4 *x*, *y*, -1 + *z*.



**Figure 9.** View of an *ab* layer of the 2D network of  $[\{Cu(\mu_2-I)_2Cu\}\{\mu-BzS(CH_2)_4SBz\}_2]_n$  (**CP8**). Selected bond lengths [Å] and angles [°] at 173 K: Cu–S1 2.312(3), Cu–S2 2.299(2), Cu–I 2.6044(15), Cu–I# 2.6690(12), Cu–Cu# 2.796(3); S1–Cu–S2 119.44(11), S1–Cu–I 107.04(6), S1–Cu–I# 100.38(6), S2–Cu–I 112.63(7), S2–Cu–I# 101.06(6), I–Cu–I# 115.98(5), Cu–I–Cu# 64.02(5). Symmetry transformations used to generate equivalent atoms: #1 2 - *x*, 1 - *y*, 1 - *z*. #2 1 - *x*, -*y*, 1 - *z*. #3 1 - *x*, 1 - *y*, 1 - *z*.

which will be compared below to those for other structurally related 2D networks obtained using  $BzS(CH_2)_nSBz$  ligands.

Reactions of CuBr and CuCl with L3. Concurrently, when performing the reaction in MeCN solution in a 1:1 ratio, large amounts of air-stable, colorless materials crystallizing in the triclinic space group  $P\overline{1}$  were isolated (Scheme 3, Figure 10). Surprisingly, the X-ray data of this  $[{Cu(\mu_2-Br)_2Cu}_{\mu-L3}_2]_n$ (CP9) material revealed the coexistence of two topological isomers within the unit cell (Figure S2). The first one, CP9-1D, consists of simple 1D ribbons running along the *a* axis of the unit cell. The structural features are reminiscent to those discussed above for  $[{Cu(\mu_2-Br)_2Cu}_2{\mu-L1}_2]_n$  (CP2), but the Cu···Cu distances are significantly elongated (2.8829(7) vs 3.0159(5) Å). The second topological isomer, CP9-2D, consists also of  $[Cu(\mu_2-Br)_2Cu]$  SBUs but interconnected in a 2D manner to form sheets placed perpendicular to the 1D ribbons. In CP9-2D, the Cu…Cu distances are somewhat shorter compared to those for **CP9–1D** (2.9951(6) vs 3.0159(5) Å), but nonetheless these are considerably longer than those for CP2 and match well those of the 2D  $[{Cu(\mu_2-Br)_2Cu}{\mu-BzS(CH_2)_6SBz}_2]_n$  CP12 (dCu - Cu = 2.957(3) Å, below).

The occurrence of two topological isomers within the same unit cell of a crystalline lattice is quite scare. One case is the coexistence of a mononuclear species  $[{(S=)P[N(Me)N=}]$  $CHIm]_3 \cdot Zn$  (NO<sub>3</sub>)<sub>2</sub> and a 20-membered dinuclear metallamacrocycle [{(S = )P[N(Me)N = CHIm]<sub>3</sub>·Zn}<sub>2</sub>](NO<sub>3</sub>)<sub>4</sub> (Im = imidazoloyl) in the same unit cell.<sup>55</sup> Li et al. also obtained, by mixing  $Cd(BF_4)_2$  with 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene (bbtz), the 3D CP  $[Cd_3(bbtz)_6(H_2O)_6](BF_4)_6 \cdot 1.75 H_2O_1$ constructed with entangled 1D ribbons of rings and a planar 2D(4,4) network.<sup>56</sup> A third and more relevant example is found in the material produced by the reaction of the 14-membered crown ether dibenzo-O<sub>2</sub>S<sub>2</sub> macrocycle toward CuI. This complexation afforded a mixture of the molecular dinuclear  $\begin{array}{l} \text{conplex} \left[ Cu_2 I_2(\text{dibenzo-}O_2 S_2)_2 \right] \text{ and a double-stranded 1D CP} \\ \left[ \left\{ Cu_2 I_2(\text{dibenzo-}O_2 S_2)_2 \cdot 2\text{MeCN} \right\} \right]_n \cdot 5^7 \text{ To the best of our} \end{array} \right]$ knowledge, there are however so far, no other examples describing a coexistence of thioether-assembled 1D and 2D topological isomers. To probe the impact of a variation of the CuBr-to-L3 ratio on the dimensiality and nuclearity of the network, L3 was also treated with a 2-fold excess of CuBr. However, like in the case of L2, again only the formation of the 1:1 adduct CP9 was demonstrated.

We recently reported the abnormal triplet energy migration of a 3D CP  $[Cu_2Cl_2(EtS(CH_2)_4SEt)_4]_n$  obtained by complexation of the very related ligand 1,4-bis(ethylthio)butane on CuCl.<sup>58</sup> With this in mind, the reaction of CuCl with L3 in a MeCN solution in a 1:1 ratio was also performed. Surprisingly, a discrete molecular dinuclear complex crystallizing in the monoclinic space group  $P2_1/n$  was isolated as sole product. The molecular structure of this formally 0D compound  $[{Cu(\mu_2-Cl)_2Cu}(\mu_2-Cl)_2Cu}$ L3)<sub>2</sub>] D1 consists of a centrosymmetric  $Cu(\mu_2-Cl)_2Cu$  core, which is doubly bridged by two L3 ligands in a chelating manner, the Cu…Cu separation being 2.9083(9) Å (Figure 11). We are not aware of any other dinuclear  $Cu(\mu_2-Cl)_2Cu$  thioether compound of this type, but related 0D complexes with unsaturated SC<sub>4</sub>S backbones such as  $[{Cu(\mu_2-Br)_2Cu}(\mu BzSCH_2C \equiv CCH_2SBz)_2$  and  $[{Cu(\mu_2-X)_2Cu}(\mu-BzSCH_2C (H) = C(H)CH_2SB_2)_1^{[2]}(X = Br, I)$  have previously been described by us.<sup>32,35,46,59</sup> This finding indicates that this type of discrete complexes can be formed regardless the flexibility of the  $SC_4S$  linker  $(-CH_2C \equiv CCH_2-, -CH_2C(H) = C(H)CH_2-,$  $-CH_2CH_2CH_2CH_2-$ ) and the nature of the halide.



**Figure 10.** (Left) View of the ribbon-shaped 1D form of **CP9–1D** incorporating dinuclear  $Cu(\mu_2$ -Br)\_2Cu motifs. Selected bond lengths [Å] and angles [°]: Cu1–S1 2.2878(5), Cu1–S2 2.3056(6), Cu1–Br1 2.4889(4), Cu1–Br1# 2.4781(6), Cu1…Cu1# 3.0159(5); S1–Cu1–S2 113.26(2), S1–Cu1–Br1 111.727(16), S1–Cu1–Br1# 112.590(17), S2–Cu1–Br1 105.672(18), S2–Cu1–B1r# 107.287(16), Br1#–Cu1–Br1 105.765(11), Cu1–S1–C4 105.46(6), Cu1–S2–C12 106.42(8). (right) View on a 2D layer down the *c* axis of the second topologic isomer of **CP9–2D**. Selected bond lengths [Å] and angles [°]: Cu2–S3 2.3057(6), Cu2–S4 2.2806(6), Cu2–Br2 2.5100(4), Cu2–Br2# 2.5383(2), Cu2…Cu2 2.9951(6); S3–Cu2–S4 130.52(2), S3–Cu2–Br2 103.465(18), S3–Cu2–Br# 115.437(6), S(2)–Cu(2)–Br 102.432(6), S(2)–Cu(2)–Br# 118.584(6), Br#–Cu(1)–Br 108.323(8), Br#–Cu2–Br 108.121(8), Cu(1)–Br–Cu(2) 71.778(7), Cu(1)–S(1)–C(1) 105.32 (3), Cu(2)–S(2)–C(7) 113.49(3). Symmetry transformations used to generate equivalent atoms: #1–1+*x*, *y*, *z*. #2 1–*x*, –*y*, –*z*. #3 1–*x*, 1–*y*, –*z*. #4 2–*x*, –*y*, 1–*z*. #5 –*x*, 1–*y*, –*z*.



**Figure 11.** Molecular structure of **D1** at 173 K incorporating the dinuclear  $Cu(\mu_2-Cl)_2Cu$  motif. Selected bond lengths [Å] and angles [°]: Cu–S1 2.3210(8), Cu–S2 2.3016(9), Cu–Cl 2.3920(8), Cu–Cl# 2.4471(9), Cu-...Cu 2.9083(9); S1–Cu–S2 129.56(2), S1–C1–S2 116.71(3), S1–Cu–Cl 103.94(3), S1–Cu–Cl# 105.70(3), Cu–Cl-Cu 73.87(2), C1–S1–C5 97.17(14), C4–S2–C12 98.93(14). Symmetry transformations used to generate equivalent atoms: #1 –*x*, 1 - y, –*z*.

**Reactions of Cul, CuBr, and CuCl with BzS(CH<sub>2</sub>)<sub>6</sub>SBz (L4).** *Reaction of Cul with L4.* Intrigued by the structural diversity encountered with the reaction of CuX salts with L3, we extended our investigation to the more flexible 1,6-bis-(benzylthio)hexane ligand L4.<sup>60</sup> This flexible dithioether has never been used as a ligand in coordination chemistry so far. To probe whether the CuI-to-L ratio impacts the resulting CP as encountered for L3, CuI was reacted with L4 in 1:1 and 2:1 ratios (Scheme 4). Moreover, we were intrigued whether the unusual formation of  $\mu_4$ -type iodo-bridged cluster arrays as found for CP7 could be reproduced using L4.

With a 2:1 ratio, a colorless, air-stable solid was isolated, and its intense emission under UV light (364 nm) suggests the presence of polynuclear clusters as luminescent SBUs. An X-ray diffraction analysis confirmed indeed the formation of this type of SBU inside a 2D CP [{Cu<sub>4</sub>( $\mu_3$ -I)<sub>4</sub>}( $\mu$ -L4)<sub>2</sub>]<sub>n</sub> (CP10). The resulting square-grid architecture is not unprecedented as it was

Scheme 4. Reaction of CuX with L4 in MeCN Forming CP10–CP13



previously observed for  $[{Cu_4(\mu_3-I)_4}{\mu^{-n}BuS-(CH_2)_4SBu^n}_2]_n$ .<sup>61</sup> All four Cu atoms are crystallographically nonequivalent within the { $Cu_4(\mu_3-I)_4$ } SBUs. The Cu–Cu bond lengths range from 2.7032(10) to 2.7543(12) Å, and the mean Cu---Cu distance at 100 K is 2.7316(11) Å. The separation between the midpoints of two cluster units along the edge is ~13.797 Å, and the diagonal is about 19.513 Å (Figure 12). Likewise, when L3 reacts with CuI, the resulting CPs architecture also depends on the stoichiometry used. Indeed, the 1:1 ratio affords a nonemissive material crystallizing in the triclinic space group  $P\overline{1}$ . This colorless product was crystallographically characterized as a 2D CP of composition [{Cu( $\mu_2$ - $I_{2}Cu^{2}(\mu-L4)_{2}_{n}$  (CP10) (Scheme 4, Figure 12). The CP11 network is built upon centosymmetric rhomboid  $Cu(\mu_2-I)_2Cu$ SBUs, which are interconntected in 2D with other SBUs through bridging  $BzS(CH_2)_6SBz$  ligands. The Cu···Cu separation within the SBUs is 2.828(3) Å, which is markedly shorter than that for CP9-2D (2.828(3) versus 2.9951(6) Å). The purity of the



**Figure 12.** View on the *ab* plane of the 2D network of  $[\{Cu_4(\mu_3-I)_4\}\{\mu-BzS(CH_2)_6SBz\}_2]_n$  (**CP10**). H atoms and benzyl groups are omitted for clarity. Selected bond lengths [Å] at 100 K: Cu1–S1 2.3206(16), Cu2–S2 2.3162(16), Cu3–S3 2.3278(17), Cu4–S4 2.3103(16), Cu1–Cu2 2.7543(12), Cu1–Cu3 2.7220(10), Cu1–Cu4 2.7032(10), Cu2–Cu3 2.7497(10), Cu2–Cu4 2.7202(10), Cu3–Cu4 2.7398(11), Cu1–I1 2.7423(9), Cu1–I2 2.7130(8), Cu1–I4 2.6250(8), Cu2–I1 2.6937(9), Cu2–I2 2.6944(9), Cu2–I3 2.6490(8), Cu3–I2 2.6399(8), Cu3–I3 2.6893(9), Cu3–I4 2.7085(10), Cu4–I1 2.6396(8), Cu4–I3 2.7075(9), Cu4–I4 2.7087(9); symmetry transformations used to generate equivalent atoms: #1 *x*, 1 + *y*, *z*. #2 1 + *x*, *y*, *z*. #3 +*x*, -1 + *y*, + *z*. #4 -1 + *x*, +*y*, +*z*.

phases was addressed for both **CP10** and **CP11** by the comparison of the calculated and experimental PXRD patterns (Figure S7).

Reactions of CuBr and CuCl with L4. Using analogous reaction conditions, CuBr and CuCl were treated with L4 in a 1:1 ratio and produced air-stable crystalline solids in yields ranging from 65 to 75%. However, as also noticed for other CuBr and CuCl dithioether complexes, the solutions turn dark green progressively due to some slow oxidation to Cu(II) species upon exposure to air. The crystal structure determinations of the materials obtained with CuBr and CuCl reveal the presence of 2D materials  $[{Cu(\mu_2-Br)_2Cu}(\mu-L4)_2]_n$  (CP12) and  $[{Cu(\mu_2-Br)_2Cu}(\mu-L4)_2]_n$  $Cl_2Cu_1^2(\mu-L4)_2_n^2$  (CP13) isostructural (triclinic,  $P\overline{1}$ ) with their iodo analogue CP11 (Figure 13 and Figure 14). The homogeneity of the phases (crystals vs powders) has been checked by PXRD. The isomorphous properties of CP11, CP12 (Figure 13), and CP13 (Figure 14) offer an opportunity to comment on the evolution of the metric parameters within this  $[{Cu(\mu_2-X)_2Cu}(\mu-L4)_2]_n$  series. The Cu···Cu distances increase from 2.828(3) to 2.957(3) Å going from I to Br and remain almost constant for X = Cl(2.9570(14) Å). The Cu-X-Cu angles evolve from 64.48(5) (X = I), 72.258(5) (X = Br) to  $75.68(5)^{\circ}$  (X = Cl); the mean Cu–S bond lengths are not particularity affected upon increasing the electronegativity of the bridging halide (respectively 2.308(3), 2.2861(3) and 2.2866(15) Å). This evolution of the Cu…Cu distances is opposite to that for the 1D [{Cu( $\mu_2$ -X)\_2Cu}( $\mu_2$ -2-methyl-1,3-



**Figure 13.** View of a layer of the 2D network of  $[{Cu(\mu_2-I)_2Cu}{\mu-BzS(CH_2)_6SBz}_2]_n$  (**CP11**). Selected bond lengths [Å] and angles [°] at 173 K: Cu–S1 2.308(3), Cu–S2 2.305(3), Cu–I 2.6395(13), Cu–I# 2.6628(14), Cu–Cu# 2.828(3); S1–Cu–S2 126.22(11), S1–Cu–I 104.48(7), S1–Cu–I# 107.76(8), S2–Cu–I 101.93(8), S2–Cu–I# 101.53(7), I–Cu–I# 115.52(5), Cu–I–Cu# 64.48(5). Symmetry transformations used to generate equivalent atoms: #1 1 – *x*, 1 – *y*, 1 – *z*. #2 2 – *x*, 2 – *y*, 2 – *z*. #3 1 – *x*, 1 – *y*, 2 – *z*.



Figure 14. View of a *bc* layer of the 2D network of  $[{Cu(\mu_2-Br)_2Cu}{\mu-BzS(CH_2)_6SBz}_2]_n$  (CP12). The phenyl groups are not shown. Selected bond lengths [Å] and angles [°] at 100 K: Cu–S1 2.2883(3), Cu–S2 2.2839(3), Cu–Br 2.48825(19), Cu–Br# 2.5313(2), Cu-···Cu# 2.957(3); S1–Cu–S2 131.583(11), S1–Cu–Br 100.517(9), S1–Cu–Br# 99.155(9), S2–Cu–Br 106.819(9), S2–Cu–Br# 109.155(9), Br–Cu–Br# 107.741(6), Cu–Br–Cu# 72.258(5). Symmetry transformations used to generate equivalent atoms: #1 1 – *x*, 1 – *y*, 1 – *z*. #2 2 – *x*, 1 – *y*, –*z*. #3 1 – *x*, –*y*, 1 – *z*.

dithiane)<sub>2</sub>]<sub>*n*</sub> series recently investigated by us.<sup>44</sup> Indeed, the nonbonding Cu···Cu contacts of the [{Cu( $\mu_2$ -X)\_2Cu}] rhomboids shorten systematically from 3.367 to 3.176 Å going from I to Br and reach 3.0517(8) Å for X = Cl.<sup>44</sup> This trend is also observed for the [{Cu( $\mu_2$ -X)\_2Cu}{ $\mu$ -L5}<sub>2</sub>]<sub>*n*</sub> series CP15-CP17 (see below).

**Reactions of Cul, CuBr and CuCl with BzS(CH<sub>2</sub>)<sub>7</sub>SBz (L5).** *Reaction of Cul with L5.* In order to probe the impact of the R-group on SR (aliphatic vs aromatic) on the architecture of the networks, the hitherto unknown ligand L5 (1,7-bis-(benzylthio)heptane) was prepared. L5 was obtained as viscous oil, and like L4, the outcome of the reaction with CuI depends



**Figure 15.** View down the *a* axis of a *bc* layer of the 2D network of  $[{Cu(\mu_2-Cl)_2Cu}{\mu-BzS(CH_2)_6SBz}_2]_n$  (CP13). Selected bond lengths [Å] and angles [°] at 173 K: Cu–S1 2.2866(15), Cu–S2 2.2866(15), Cu–Cl 2.3752(14), Cu–Cl# 2.4444(15), Cu-···Cu# 2.9570(14); S1–Cu–S2 131.06(6), S1–Cu–Cl 106.96(5), S1–Cu–Cl# 108.39(6), S2–Cu–Cl 103.82(5), S2–Cu–Cl# 99.52(5), Cl–Cu–Cl# 104.32(5), Cu–Cl–Cu# 75.68(5). Symmetry transformations used to generate equivalent atoms: #1 2 - *x*, 1 - *y*, -*z*. #2 1 - *x*, -*y*, 1 - *z*. #3 1 - *x*, 1 - *y*, 1 - *z*.

upon the metal-to-ligand ratio employed (Scheme 5). A colorless, strongly luminescent material of composition





 $[{Cu_4(\mu_3-I)_4}{\mu-BzS(CH_2)_7SBz}_2]_n$  (CP14) was produced when using a 2:1 ratio. Because of twinning and disorder problems of the alkyl chains of L5, the quality of the crystal structure of CP14 is somewhat inferior to that for the other structures. Nonetheless, the crystallographic data allow for concluding the formation of a 2D network with the incorporation of cubane-type [{Cu\_4(\mu\_3-I)\_4}] clusters, in which each Cu atom is ligated by one S donor (Figure 16).

Similar to the 2D network of CP10, the architecture of CP14 consists of square-grid frames. Because of the incorporation of an additional methylene group within the spacer chain (C7 vs C6), the separation between the midpoints of two cluster units increases now to ~14.522 Å and the diagonal distance to ~20.538 Å. Similarly to the  $Cu_4I_4$  SBUs found in CP10, all four Cu atoms are crystallographically nonequivalent in which the Cu-Cu bond lengths range from 2.679(6) to 2.703(7) Å. Despite the higher recording temperatures, the mean Cu--Cu distance at 173 K of CP14 is shorter than that of its C6-analogue **CP10** at 100 K (2.6898(32) versus 2.7316(11) Å; i.e., one can anticipate that the mean Cu…Cu distance should shrink further upon cooling to 100 K). The Cu-I bond length covers a broader range than those of **CP10** and varies from 2.501(7) to 2.959(7)Å, with a mean Cu–I bond length of 2.684(7) Å. Another 2D network architecture was obtained when reacting CuI with a slight excess of L5 in MeCN solution (Scheme 5). A layer of the resulting colorless stable material of composition [{Cu( $\mu_2$ -I)<sub>2</sub>Cu}{ $\mu$ -BzS(CH<sub>2</sub>)<sub>7</sub>SBz}<sub>2</sub>]<sub>n</sub> (CP15), crystallizing in the orthorhombic space group Pbca, is shown in Figure 17.

*Reactions of CuBr and CuCl with* **L5**. As for the CuI salt, the reactions of both CuBr and CuCl with **L5** in equimolar amounts provides 2D CPs of composition  $[{Cu(\mu_2-Br)_2Cu}{{\mu-L5}_2]_n}$  (CP16) and  $[{Cu(\mu_2-Cl)_2Cu}{{\mu-L5}_2]_n}$  (CP17), which are isostructural to CP15 and crystallizing in the orthorhombic space group *Pbca* (Figure 18 and Figure 19). The layers incorporate centrosymmetric Cu( $\mu_2$ -X)\_2Cu rhomboids as SBUs. In full contrast with the  $[{Cu(\mu_2-X)_2Cu}{{\mu-L4}_2}_n$  series CP11–CP13, the Cu–Cu distances within the  $[{Cu(\mu_2-X)_2Cu}{{\mu-L5}_2}_n$  series CP15–CP17 shorten systematically from 2.7414(6) to 2.7081(4) to 2.6939(4) Å going from I to Br to Cl. The Cu–X–Cu angles evolve from 62.453(12) (X = I) to



14.53 Å 20.54

**Figure 16.** (Left) View of a square-grid segment of the 2D network of  $[{Cu_4(\mu_3-I)_4}{\mu-BzS(CH_2)_7SBz}_2]_n$  (CP14). The H atoms and benzyl groups are omitted for clarity. Selected bond lengths [Å] at 173 K: Cu1-S1A 2.373(114), Cu2-S2 2.373(13), Cu3A-S3 2.354(13), Cu4-S4A 2.367(13), Cu1-Cu2 2.703(7), Cu1-Cu3 2.690(7), Cu1-Cu4 2.679(6), Cu2-Cu3 2.680(7), Cu2-Cu4 2.693(7), Cu3-Cu4 2.701(6), Cu1-IIA 2.957(7), Cu1-I2A 2.501(7), Cu1-I3A 2.690(7), Cu2-I1A 2.686(6), Cu2-I3A 2.504(3), Cu2-I4A 2.943(8), Cu3-I2A 2.689(7), Cu3-I3A 2.946(7), Cu3-I3A 2.94 14A 2.506(7), Cu4–I1A 2.504(8), Cu4–I2A 2.959(7), Cu4–I4A 2.678(6); symmetry transformations used to generate equivalent atoms: #1 1/2 + x, 1/2 + y, z. #2 –1/2 + x, 1/2 + y, z. (Right) Labeling scheme for the Cu<sub>4</sub>I<sub>4</sub>S<sub>4</sub> SBU of **CP14** featuring four crystallographically nonequivalent Cu atoms.



Figure 17. View of the *ab* layer of the 2D network of [{Cu( $\mu_2$ -I)<sub>2</sub>Cu}{ $\mu$ -BzS(CH<sub>2</sub>)<sub>7</sub>SBz}<sub>2</sub>]<sub>n</sub> (CP15) down the *c* axis. The benzyl groups are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cu-S1 2.3274(6), Cu-S2 2.3351(6), Cu-I 2.5976(3), Cu-I# 2.6882(4), Cu-Cu# 2.7414(6); S1-Cu-S2 114.28(3), S1-Cu-I 116.761(17), S1-Cu-I# 96.866(16), S2-Cu-I# 109.151(18), S2-Cu-I 100.936(17), I-Cu-I# 117.547(12), Cu-I-Cu# 62.453(12). Symmetry transformations used to generate equivalent atoms: #11 - x, -y, 1 - z. #2 1/2 + x, 1/2 - y, 1 - z. #3 -1/2 + x, 1/2 - y, 1 - z.

65.796(9) (X = Br) to  $68.689(13)^{\circ}$  (X = Cl). The mean Cu–S bond length, respectively 2.3312(6), 2.3043(4), and 2.3014(5) Å, are not much affected by the electronegativity increase of the bridging halide. In an attempt to obtain a paramagnetic material, a slight excess of L5 was reacted with CuCl<sub>2</sub>. A progressive fading of the initially dark green color of the MeCN solution, characteristic of Cu(II) species, to light green, was observed. An X-ray diffraction study of the isolated yellowish crystals (isolated in  $\sim$ 40% yield) revealed a 2D network isostructural to that of



Article

Figure 18. View down the c axis of a layer of the 2D network of  $[{Cu(\mu_2-Br)_2Cu}{\mu-BzS(CH_2)_7SBz}_2]_n$  (CP16). The benzyl groups are omitted for clarity. Selected bond lengths (Å) and angles (deg) at 100 K: Cu-S1 2.2984(4), Cu-S2 2.3102(4), Cu-Br 2.4483(3), Cu-Br# 2.5357(3), Cu-Cu# 2.7081(4); S1-Cu-S2 115.133(16), S1-Cu-Br 117.722(14), S1-Cu-Br# 97.792(13), S2-Cu-Br 109.172(13), S2-Cu-Br# 101.301(13), Br-Cu-Br# 114.203(9), Cu-Br-Cu# 65.796(9). Symmetry transformations used to generate equivalent atoms: #1 1 - x, 2 - y, 1 - z. #2 1/2 + x, 3/2 - y, 1 - z.

CP17. So most probably, L5 acts as reducing agent explaining this Cu(II) to Cu(I) reduction. Note that other reductions of CuCl<sub>2</sub> to CuCl species in the presence of thioethers have been reported previously. For example, Tan and Ang observed that 1,3-dithiane reacts readily with CuCl<sub>2</sub> to form a paramagnetic



**Figure 19.** View of a layer of the 2D network of  $[{Cu(\mu_2-Br)_2Cu}{\mu_{BZS}(CH_2)_7SBz}_2]_n$  (**CP17**) down the *c* axis. The benzyl groups are omitted for clarity. Selected bond lengths (Å) and angles (deg) at 100 K: Cu–S1 2.2910(4), Cu–S2 2.3117(5), Cu–Cl 2.3404(4), Cu–Cl# 2.4321(4), Cu–Cu# 2.6939(4); S1–Cu–S2 114.619(16), S1–Cu–Cl# 98.592(15), S1–Cu–Cl 119.254(17), S2–Cu–Cl 109.137(16), Cu–Cl–Cu# 68.698(13). Symmetry transformations used to generate equivalent atoms: #1 1 – *x*, –*y*, 1 – *z*. #2 –1/2 + *x*, 1/2 – *y*, 1 – *z*. #3 1/2 + *x*, 1/2 – *y*, 1 – *z*.

species [CuCl<sub>2</sub>·dithiane] undergoing a spontaneous reduction to give finally [Cu<sub>2</sub>Cl<sub>2</sub>·dithiane] according to elemental analysis and magnetic measurements.<sup>62-64</sup>

**Reactions of Cul, CuBr and CuCl with BzS(CH<sub>2</sub>)<sub>8</sub>SBz (L6).** With the aim to construct CPs assembled with a dithioether containing an even longer flexible chain, the CuX salts were also reacted with  $BzS(CH_2)_8SBz$  (L6).<sup>51</sup> This 1,8-bis(benzylthio)octane ligand has so far not been used in coordination chemistry. However, the related 1,12-diphenyl-5,8-dioxa-2,11-dithiadodecane ligand bearing two oxygen atoms in the spacer chain has been employed by Park et al. for its coordination on PdCl<sub>2</sub>, HgCl<sub>2</sub>, and CuI.<sup>25,65,66</sup> In the latter case, L6 reacts with CuI in MeCN and CHCl<sub>3</sub> to form a luminescent 2D framework of composition [{Cu<sub>4</sub>( $\mu_3$ -I)\_4}{ $\mu$ -BzS-

 $(CH_2)_6O_2SBz\}_2]_n$ . The square grids are held together by closed cubane clusters, similar to that encountered for **CP10** and **CP14**. The layer structure also exhibits a slipped sheet type, where again, the benzyl substituent on the S atom, interpenetrates the cavity of the neighbor layer. The cubane  $Cu_4I_4$  clusters are located at the nodes of the square-grid with edges 14.171(2) Å long (same as the length of *a*- or *b*-axis). The layers are stacked with an ABAB sequence.

Reaction of Cul with L6. Using the same protocol employed for the preparation of the Cu<sub>4</sub>I<sub>4</sub> materials, CP10 and CP14 interconnected by C6 and C7 spacers between the two SBz groups, the self-assembly process of 1,8-bis(benzylthio)octane with 2 equiv of CuI led straightforwardly to the formation of luminescent  $[{Cu_4(\mu_3-I)_4}]{\mu-BzS(CH_2)_8SBz}_2]_n$  (CP20) (Scheme 6). CP20 crystallizes in MeCN to form yellowish airstable crystals, and the X-ray diffraction data revealed, as for CP11 and CP15, the generation of a 2D square-grid-shaped network (Figure 20). Each corner of the square grid exhibits edge lengths of ~14.394 Å (note that this separation is 14.171(2) Å for Kim's  $BzS(CH_2)_6O_2SBz$  analogue) and a diagonal distance of ~20.356 Å. CP20 is also composed of closed cubane-[{ $Cu_4(\mu_3-I)_4$ }S\_4] clusters as SBUs. In contrast with the  $Cu_4I_4$  units depicted in CP10 and CP14, all Cu atoms are crystallographically identical. However, the mean Cu…Cu distance (2.7230(11) Å) in CP20 is markedly shorter than that found in Kim's 2D CP  $[{Cu_4(\mu_3-I)_4}{\mu-BzS(CH_2)_6O_2SBz}_2]_n$ (i.e., 2.8142(16) Å at 173 K).

Despite the nanometric separation between the SBUs, no inclusion of solvent guest molecules occurs in **CP18**, contrasting with that previously noted for 2D CP  $[Cu_8I_8\{p\text{-TolS}(CH_2)_8STol-p\}_3(solvent)_2]_n$  (solvent = MeCN or EtCN), nor entanglement of the networks as depicted for the 2D CP  $[\{Cu_4(\mu_3-I)_4\}\{\mu\text{-PhS}(CH_2)_4SPh\}_2]$  was observed (Figure S3).<sup>32,67</sup> The unit cell volume of **CP18** is 5078.85 Å<sup>3</sup> with the filled space occupying 941.42 Å<sup>3</sup> (18.54%) and the void space being 4137.43 Å<sup>3</sup> (81.46%), whereas these parameters are cell volume: 5081.98 Å<sup>3</sup>, filled space: 965.14 Å<sup>3</sup> (18.99%), void space: 4116.85 Å<sup>3</sup> (81.01%) for the BzS(CH<sub>2</sub>)<sub>7</sub>SBz analogue **CP14**.

Concurrently, the treatment of **L6** with CuI in MeCN using a 1:1 ratio yields solely the 1D CP [{Cu( $\mu_2$ -I)\_2Cu}{ $\mu$ -BzS-(CH<sub>2</sub>)<sub>8</sub>SBz}<sub>2</sub>]<sub>n</sub> (**CP19**) (Scheme 6 and Figure 21). Each centrosymmetric and planar Cu( $\mu_2$ -I)<sub>2</sub>Cu SBU is interconnected to the adjacent one through two bridging **L6** ligands forming 22-membered stretched macrocycles. The 2.8479(5) Å







**Figure 20.** View of two square-grid segments making part of the 2D network of  $[\{Cu_4(\mu_3-I)_4\}\{\mu-BzS(CH_2)_8SBz\}_2]_n$  (**CP18**). The benzyl groups are omitted for clarity. Selected bond lengths (Å) and angles (deg) at 173 K: Cu–S 2.305(2), Cu–Cu#1 2.7296(15), Cu–Cu#2 2.7296(15), Cu–Cu#4 2.7098(19), Cu–I 2.6417(10), Cu–I#1 2.71540(11), Cu–I#2 2.6948(8); Cu–I–Cu#1 61.52(3), Cu#1–I–Cu#2 60.12(4). Symmetry transformations used to generate equivalent atoms: #1 x + 3/2, -y – 1/2, -z + 3/2. #2 –x + 1/2, y + 3/2, -z + 3/2. #3 –x + 1, -y + 1, z. #4 –x + 2, -y + 1, z.



Figure 21. View of a segment of the 1D ribbon of  $[\{Cu(\mu_2-I)_2Cu\}\{\mu-BzS(CH_2)_8SBz\}_2]_n$  (CP19) running along the *a* axis. Selected bond lengths [Å] and angles [°] at 173 K: Cu–S1 2.3342(5), Cu–S2 2.3284(6), Cu–I1 2.6040(3), Cu–I1# 2.6456(3), Cu–Cu# 2.8479(5); S1–Cu–S2 103.51(2), S1–Cu–I1 104.467(17), S1–Cu–I# 107.323(17), S(2)–Cu–I# 106.32(17), I1–Cu–II# 114.299(10), Cu–I–Cu# 65.701(10). Symmetry transformations used to generate equivalent atoms: #1 1 – *x*, 2 – *y*, 2 – *z*. #2 2 – *x*, 1 – *y*, 2 – *z*.

Cu···Cu separation lies midway between those of its 1D analogues CP1 and CP4 (Table 1). The separation between the midpoints of the  $Cu_2I_2$  rhomboids reaches ~14.8 Å, which falls in the nanoscale dimension. The ribbons of CP19 are arranged in an orthogonal manner in an ABAB sequence (Figure S4). The comparison between the calculated and experimental PXRD data indicates that no other phase is present in the samples (Figure S9).

**Reactions of CuBr and CuCl with L6.** Adding an equimolar amount of CuBr or CuCl to a MeCN solution of L6 provides straightforwardly the 1D polymers CP20 and CP21 (Scheme 6, Figure 22 and Figure 23), which are isostructural to their CuIanalogue CP19, which crystallize in the monoclinic space group  $P121/c_1$ . This isostructural series [{Cu( $\mu_2$ -X)<sub>2</sub>Cu}{ $\mu$ -BzS-(CH<sub>2</sub>)<sub>8</sub>SBz}<sub>2</sub>]<sub>n</sub> allows again for a systematic comparison of the impact of the bridging halide on the Cu---Cu separations within the rhomboid. Surprisingly and contrasting with the  $[{Cu(\mu_2-X)_2Cu}{\mu-BzS(CH_2)_7SBz}_2]_n$  series **CP15-CP17**, no correlation is noted since the Cu····Cu separation (at 173 K) increases K from 2.8479(5) (X = I) to 3.0091(15) Å (X = Br), but then shrinks slightly to 2.9296(10) Å for (X = Cl). Noteworthy, the dimensionality of the CP switches from 2D (**CP18**) to 1D (**CP19-CP21**).

**Reactions of Cul, CuBr and CuCl with BzS(CH<sub>2</sub>)<sub>9</sub>SBz (L7).** Aiming at enhancing the porosity of the materials, the effect of the chain length of the BzS(CH<sub>2</sub>)<sub>n</sub>SBz ligands was tested further with n = 9, and the coordination of 1,9-bis(benzylthio)nonane L7 *vis-à-vis* the entire CuX series was explored. The coordination of L7 on HAuCl<sub>4</sub> has been previously reported to yield (AuCl)BzS(CH<sub>2</sub>)<sub>9</sub>SBz(AuCl), but except for NMR and elemental analysis, no other character-ization data were provided.<sup>68</sup>

Reaction of Cul with L7. Like for L5 and L6, the resulting CPs stemming from the reaction of L7 with CuI exhibit network architectures that are dependent on the stoichiometry. Adding the ligand to a 2-fold excess of CuI in MeCN causes a rapid precipitation of a colorless, strongly luminescent, and initially oily material. This product could be finally solidified by decanting the supernatant solvent and by dissolving the residue in hot MeCN or EtCN. Its crystallographic characterization at 100 K revealed the presence of a 2D network of composition  $[{Cu<sub>4</sub>(\mu_3-I)<sub>4</sub>}{\mu-BzS(CH<sub>2</sub>)_9SBz}_2]_n$  (CP22) comprising Cu<sub>4</sub>I<sub>4</sub> clusters as SBUs (Figure 24).

A striking contrast with the occurrence of symmetric squaredgrid architecture in the planar sheets of  $[\{Cu_4(\mu_3-I)_4\}\{\mu-BzS(CH_2)_nSBz\}_2]_n$  (n = 6-8) and of  $[\{Cu_4(\mu_3-I)_4\}\{\mu-BzS-(CH_2)_6O_2SBz\}_2]_n$  is that the  $Cu_4I_4$  SBUs are no longer coplanar with the neighbored ones, thus forming distorted grids (Figure S5). The increased flexibility of the  $BzS(CH_2)_9SBz$  assembling ligand compared to the C6-C8 analogues now leads to strongly folded chains, thus distorting the grid. Consequently, an annealed grid is now almost perpendicularly orientated with respect to other one. In contrast to the  $Cu_4I_4$  units in **CP18**, all Cu atoms in **CP22** are now crystallographically different with a mean Cu-Cu distance of only 2.710(3) Å. The structure at 173 K also exhibits a change in crystal system and space group from orthorhombic *Pbca* to monoclinic,  $P12_1/c1$ , which is accom-



**Figure 22.** View of three segments of the 1D ribbon of  $[\{Cu(\mu_2-Br)_2Cu\}\{\mu-BzS(CH_2)_8SBz\}_2]_n$  (**CP20**) at 173 K running along the *a* axis. Selected bond lengths [Å] and angles [°]: Cu1–S1 2.287(2), Cu1–S2 2.311(2), Cu2–S3 2.288(2), Cu2–S4 2.301(3), Cu1–Br1 2.4499(14), Cu1–Br2 2.4304(13), Cu2–Br1 2.5114(13), Cu2–Br2 2.4967(13), Cu1-...Cu2 3.0091(15); S1–Cu1–S2 111.14(9), S3–Cu2–S4 122.78(10), S1–Cu1–Br1 105.28(7), S1–Cu1–Br2 113.79(7), Cu1–Br1–Cu2 73.81(4), Cu2–Br2–Cu2 75.27(4). Symmetry transformations used to generate equivalent atoms: #1 x - 1, y, z. #2 x + 1, y, z.



**Figure 23.** View of a segment of the 1D ribbon of [ $\{Cu(\mu_2-Cl)_2Cu\}\{\mu-BzS(CH_2)_8SBz\}_2\}_n$  (**CP21**) running along the *a* axis recorded at 173 K. Selected bond lengths [Å] and angles [°]: Cu1–S1 2.3049(16), Cu1–S2 2.2857(17), Cu2–S3 2.2882(16), Cu2–S4 2.3145(16), Cu1–Cl1 2.4143(15), Cu1–Cl2 2.3834(15), Cu2–Cl1 2.4040(15), Cu2–Cl2 2.3217(16), Cu1…Cu2 2.9296(10); S1–Cu1–S2 123.67(6), S3–Cu2–S4 111.87(6), S1–Cu1–Cl1 105.81(6), S1–Cu1–Cl2 107.73(6), Cu1–Cl1–Cu2 74.89(5), Cu2–Cl2–Cu2 77.01(5). Symmetry transformations used to generate equivalent atoms: #1 *x* - 1, *y*, *z*; #2 *x* + 1, *y*, *z*.

panied by a slight expansion of the unit cell volume from 10951.2(11) to 10996.3(19) Å<sup>3</sup>, and of the mean Cu···Cu distance to 2.745(5) Å. Even at this temperature, this intermetallic separation, along with that of **CP14**, is the shortest one within all Cu<sub>4</sub>I<sub>4</sub> containing materials synthesized in this investigation (Table 1). The porosity of **CP22** is determined from the calculated voids being 9033.83 Å<sup>3</sup> (82.49%) per unit cell based upon the total volume of 10951.18 Å<sup>3</sup> and the filled space of 1917.35 Å<sup>3</sup> (17.51%).

The 1D CP [{Cu( $\mu_2$ -I)\_2Cu}{ $\mu$ -BzS(CH<sub>2</sub>)\_9SBz}<sub>2</sub>]<sub>n</sub> CP23 stems from reaction of L7 with CuI in a 1:1 metal-to-ligand ratio (Scheme 7). X-ray data reveal the presence of a ribbon architecture reminiscent to that of its BzS(CH<sub>2</sub>)<sub>8</sub>SBz analogue CP19 (Figure 25). Each planar and centrosymmetric Cu( $\mu_2$ -I)<sub>2</sub>Cu SBU is interconnected to the adjacent one through two bridging L7 ligands forming 26-membered stretched macrocycles. The Cu···Cu distance (2.7773(6) Å) is slightly shorter than that of CP19 built with BzS(CH<sub>2</sub>)<sub>8</sub>SBz (*d*Cu···Cu = 2.8479(5)) and closer to the intermetallic separation observed in the 1D CP1 built with BzSCH<sub>2</sub>SBz. These variations indicate that no correlation between the Cu···Cu separation and the methylene spacer length with this series of 1D ribbon-shaped CPs can be established. Because of the insertion of an additional CH<sub>2</sub> group into the alkane spacer, the distance between the midpoints of the Cu<sub>2</sub>I<sub>2</sub> rhomboids expectedly increases and now reaches ~15.3 Å. To the best of our knowledge, CP22 and CP23 are representatives of CuX-based materials featuring the longest flexible dithioether of type RS(CH<sub>2</sub>)<sub>n</sub>SR so far. Two 2D CPs,  $[(Cu_2I_2)(\mu$ -bis(ethylthiomethyl)biphenyl)<sub>2</sub>·MeCN·H<sub>2</sub>O]<sub>n</sub> and  $[(Cu_4I_4)(\mu$ -bis(ethylthiomethyl)biphenyl) 1.5·H<sub>2</sub>O]<sub>n</sub> assembled by the rigid ligand 4,40-bis(ethylthiomethyl)biphenyl, were reported, but this 10-carbon chain bears a biphenyl unit, rendering this ligand less flexible.<sup>26</sup> Other 10-atom dithioethers, 1,4-bis((methylthio)propanoyl)piperazine and 1,4-bis(2-methylthioethoxy)benzene, form extended 2D networks with CuI. These chains incorporate a piperazine heterocycle or a  $-O-C_6H_4-O-$  motif.<sup>27,28</sup>

Reactions of CuBr and CuCl with L7. Similar to the CuI salt, the self-assembly process of L7 with equimolar amounts of CuBr and CuCl produce the 1D [{Cu( $\mu_2$ -X)\_2Cu}{ $\mu$ -BzS-(CH<sub>2</sub>)<sub>9</sub>SBz}<sub>2</sub>]<sub>n</sub> CPs CP24 (X = Br) and CP25 (X = Cl) (Scheme 7, Figures 26 and 27). Like in the series CP19–CP21, [{Cu( $\mu_2$ -X)\_2Cu}{ $\mu$ -BzS(CH<sub>2</sub>)<sub>8</sub>SBz}<sub>2</sub>]<sub>n</sub>, CP23-CP25 are isostructural crystallizing in the triclinic space group  $P\overline{1}$ . Once again, no linear correlation is observable since the Cu···Cu



**Figure 24.** View of the distorted square segment of the 2D network of  $[\{Cu_4(\mu_3:I)_4\}\{\mu$ -BzS(CH<sub>2</sub>)<sub>9</sub>SBz $\}_2]_n$  (**CP22**). The H atoms and benzyl groups are omitted for clarity. Selected bond lengths [Å] at 173 K: Cu1–S1 2.321(7), Cu2–S2 2.314(8), Cu3–S3 2.296(8), Cu4–S4 2.304(7), Cu1–Cu2 2.862(4), Cu1–Cu3 2.639(5), Cu1–Cu4 2.722(4), Cu2–Cu3 2.730(5), Cu2–Cu4 2.805(5), Cu3–Cu4 2.717(4), Cu1–I1 2.676(4), Cu1–I2 2.724(4), Cu1–I4 4.413(4), Cu2–I1 2.727(3), Cu2–I2 2.660(3), Cu2–I3 4.489(4), Cu3–I2 2.678(4), Cu3–I3 2.653(4), Cu3–I4 2.709(3), Cu4–I1 2.673(4), Cu4–I3 2.670(4), Cu4–I4 2.707(3); symmetry transformations used to generate equivalent atoms: #1 2 – *x*, 2 – *y*, –*z*. #2 *x*, *y*, –1 + *z*. #3 1 – *x*, 2 – *y*, –*z*.

separations (173 K) vary as 2.8479(5) (X = I) to 2.9177(8) Å (X = Br), to 2.8884(11) Å for (X = Cl).

# THERMAL ANALYSIS

The thermal gravimetric analysis (TGA) of all compounds provides classical behavior for CPs constructed over CuX clusters with dithioethers ligands.<sup>36</sup> All compounds are stable below 200 °C. Table S6 (Supporting Information) provides the maxima in the first-derivative plot of the TGA trace, the experimental weight losses compared to the calculated ones, and proposed assignation based on the molecular formula deduced by crystallographic investigations. An attempt was made to establish a correlation between the nature of the cluster (Cu<sub>4</sub>I<sub>4</sub> vs Cu<sub>2</sub>X<sub>2</sub>) and the halide. A clear trend is observed for thermograms obtained for Cu<sub>4</sub>I<sub>4</sub> compounds (CP3, CP7, CP10, CP14, CP18, and CP22). These traces exhibit two well-



**Figure 25.** View of a segment of the 1D ribbon of  $[\{Cu(\mu_2-I)_2Cu\}\{\mu-BzS(CH_2)_9SBz\}_2]_n$  (**CP23**). Selected bond lengths [Å] and angles [°] at 173 K: Cu–S1 2.3482(6), Cu–S2 2.3274(6), Cu–I 2.6163(4), Cu–I # 2.6660(3), Cu–Cu# 2.7773(6); S1–Cu–S2 117.74(2), S1–Cu–I 105.183(18), S1–Cu–I# 104.895(14), S2–Cu–I 110.249(16), S2–Cu–I# 102.624(15), I–Cu–I# 116.567(11), Cu–I–Cu# 63.433(11). Symmetry transformations used to generate equivalent atoms: #1 1 + *x*, 1 + *y*, *z*. #2 -*x*, -1 - *y*, 1 - *z*.

separated plateaus (Figure 28a) most likely due to the decomposition of the ligands in the 200-400 °C range.

Above 600 °C, the weight losses may correspond to a blend of the remaining Cu metal and halides. The comparison of the TGA traces of **CP3**, **CP7**, **CP10**, **CP14**, **CP18**, and **CP22** (i.e., alkyl chain length increasing) indicates that the thermal stability increases with the chain length. For example, **CP22** (-(CH<sub>2</sub>)<sub>9</sub>-) is more stable by ~50 °C vs **CP4** (-(CH<sub>2</sub>)<sub>3</sub>-). However, **CP18** seems to be more stable than **CP22** by a few degrees. This general trend was previously noticed, and it was suggested that long chains have a better tendencies to dissipate the heat energy by low-frequency molecular motions.<sup>33</sup> The trend for the Cu<sub>2</sub>X<sub>2</sub> rhomboid-containing CPs (X = I, Br, Cl) is quite similar (Figure 28b-d), where the increase in the chain length tends to give more thermally stable CPs. However, in the Cu<sub>2</sub>Br<sub>2</sub>- and Cu<sub>2</sub>Cl<sub>2</sub>-containing CPs that second mass loss is less well-defined (Figure 28c,d).

#### PHOTOPHYSICAL PROPERTIES

The cubane motif Cu<sub>4</sub>I<sub>4</sub>L<sub>4</sub> (L = thioether) is also well-known for its luminescence properties.<sup>69–71</sup> Indeed, many groups reported the emission spectra of Cu<sub>4</sub>I<sub>4</sub>L<sub>4</sub>-containing 0D, 1D, 2D, and 3D species. These species exhibit generally intense and structureless bands spreading from 430 to 730 nm at room temperature.<sup>25,26,77–84,31,43,54,72–76</sup> The photophysical characterization of the thioether-containing cubanes and related species included





Article



**Figure 26.** View of two segments of the infinite ribbon of  $[{Cu(\mu_2-I)_2Cu}_{\mu-BzS(CH_2)_9SBz}_2]_n$  (**CP24**). Selected bond lengths [Å] and angles [°] at 173 K: Cu–S1 2.3088(9), Cu–S2 2.3274(9), Cu–Br 2.4944(5), Cu–Br# 2.5139(6), Cu–···Cu 2.9177(8); S1–Cu–S2 129.56(2), S1–Cu–Br 108.34(2), S1–Cu1–Br# 109.20(2), S2–Cu–Br 104.84(3), S2–Cu1–Br# 105.38(2), Cu–Br–Cu 71.262(17), Br–Cu–Br 108.737(17), Cu–S1–C1 103.17(10), Cu–S2–C12 107.55(12). Symmetry transformations used to generate equivalent atoms: #1 –1 + *x*, 1 + *y*, *z*. #2 1 + *x*, -1 + *y*, *z*. #3 1 – *x*, 1 – *y*, 1 – *z*.



**Figure 27.** View of a segment of the infinite 1D ribbon of  $[{Cu(\mu_2-Cl)_2Cu}_{\mu-BzS}(CH_2)_9SBz}_2]_n$  (**CP25**). Selected bond lengths [Å] and angles [°] at 173 K: Cu–S1 2.3105(12), Cu–S2 2.2829(11), Cu–Cl 2.3799(11), Cu–Cl# 2.3850(12), Cu-···Cu 2.8884(11); S1–Cu–S2 119.19(4), S1–Cu–Cl 104.11(4), S1–Cu–Cl# 106.38(4), S2–Cu–Cl 109.14(4), S2–Cu–Cl# 111.60(4), Cu–Cl–Cu 71.262(17), Cl–Cu–Cl 105.37(3), Cu–S1–C1 104.35(14), Cu–S2–C6 106.15(12). Symmetry transformations used to generate equivalent atoms: #1 1 + *x*, -1 + y, *z*. #2 -1 + x, 1 + y, *z*. #3 1 - x, -y, 1 - z.

in 0D–3D materials was extracted from more focused studies from the literature, and includes the emission lifetimes ( $\tau_e$ ) at 298 and 77 K, which generally range from 0.2 to 16  $\mu$ s. A table containing these reported photophysical data is provided in Table S7.<sup>32,34,61,85–90,35,36,42,44,46,48,53,59</sup> The cubane-containing CPs in this series make no exception (Figure 29) with the small difference that some bands expand beyond 700 nm (near-IR).

**CP4**, **CP8**, **CP11**, **CP15**, **CP19**, and **CP23** exhibit  $\tau_e$ 's values in the predicted range (Table 2;  $1.8 \le \tau_e \le 15 \,\mu s$ ). Similarly, the emission quantum yields ( $\Phi_e$ ) are large and the full-width at half-maximum (fwhm) notoriously shrinks upon cooling, which are again well-known characteristics associated with these materials. Attempts to find a correlation between the shortest and the mean Cu<sup>...</sup>Cu distances with any photophysical parameters (see some examples in Table 2, see also graphs in Figures S40) failed. A possible explanation for this observation is that, despite the similarity in cubane skeleton, the local environment for the molecular vibrations contributing to the nonradiative relaxation processes is different from one CP to the other. This intuitive statement stems from the unambiguous fact



Figure 28. TGA traces for the CPs. (a) For CPs containing  $Cu_4I_4$  core. (b) for CPs containing  $Cu_2I_2$  core. (c) for CPs containing  $Cu_2Br_2$  core. (d) For compounds containing  $Cu_2Cl_2$  core.

#### pubs.acs.org/IC

Article



Figure 29. Solid-state emission spectra of the Cu<sub>4</sub>I<sub>4</sub>-containing CPs at 298 (left) and 77 K (right).

Table 2. Photophysical Data of the $Cu_4I_4$ -Containing CPs at 29	8 and	.77	K
--	-------	-----	---

	$T(\mathbf{K})$	$\lambda_{\mathrm{ex}}\left(\mathrm{nm}\right)$	$\lambda_{\mathrm{em}}\left(\mathrm{nm} ight)$	fwhm $(cm^{-1})$	$\Delta_{\mathrm{fwhm}}{}^{a}\left(\mathrm{cm}^{-1} ight)$	$ au_{\rm e} (\mu { m s})$	$\chi^2$	Φ	$k_{\rm r}^{\ b} (10^5 {\rm s}^{-1})$	$k_{\rm nr}^{\ b} (10^5 {\rm s}^{-1})$
CP7	298	374	504	3700	1400	1.82	1.02	0.15	0.24	1.37
	77	356	505	2300		2.13	1.00			
CP10	298	364	601	3300	800	8.85	1.05	0.14	0.77	4.73
	77	338	646	2500		14.94	1.02			
CP14	298	367	613	3600	1400	9.26	1.02	0.18	0.20	0.93
	77	347	613	2200		8.12	1.03			
CP18	298	349	580	4700	2600	8.66	1.09	0.61	0.66	0.42
	77	330	517	2100		6.34	1.04			
CP22	298	360	606	4000	1100	6.29	1.03	0.36	0.42	0.74
	77	340	594	2900		8.57	1.05			
${}^{a}\Delta_{\text{fwhm}} = (\text{fwhm 298 K}) - (\text{fwhm 77 K}) {}^{b}k_{\text{r}} = \Phi/\tau_{e}; k_{\text{nr}} = (1-\Phi)/\tau_{e}.$										

	Table 3.	Comparison	between t	he Cu…	Cu Distances a	nd Selected	Photophysical	Parameters
--	----------	------------	-----------	--------	----------------	-------------	---------------	------------

	T(K)	shortest distance Cu…Cu(Å)	mean distance Cu…Cu (Å)	$\lambda_{\rm em}  (77 \ {\rm K}) ({\rm nm})$	$\lambda_{0-0}$ (77 K) (nm)	fwhm (77 K) $(cm^{-1})$	$ au_{\rm e}~(77~{\rm K})~(\mu{ m s})$
CP7	173	2.7013(5)	2.7897(6)	505	450	2300	2.13
CP10	100	2.7034(12)	2.7316(12)	646	530	2500	14.94
CP14	173	2.68(5)	2.6898(32)	613	535	2200	8.12
CP18	173	2.710(3)	2.723(11)	517	470	2100	6.34
CP22	100	2.717(5)	2.745(5)	594	507	2900	8.57

that the Cu…Cu distances vary (up to 0.1 Å in mean distances). Indeed, the void % varies (using Crystal Maker) as 83.2 (CP7), 84.6 (CP10), 84.5 (CP14), 85.0 (CP18), and 85.9% (CP22). So, the three most compact CPs are CP7, CP10, and CP14, which exhibit the largest nonradiative rate constants,  $k_{\rm nr}$ . This relationship is not linear but still suggests that the nonradiative processes may stem form frictions between the Cu<sub>4</sub>I<sub>4</sub> clusters with its surrounding ligands.

Noteworthy, **CP7** stands somewhat apart in this series (and those listed in Table S7). Indeed, this CP exhibits the most blueshifted emission ( $\lambda_{max} \approx 505$  nm). The likely reason for this difference is that the structural environment differs from the most frequently encountered Cu<sub>4</sub>I<sub>4</sub>L<sub>4</sub> motif (L = thioether), as one of the S-atoms is replaced by a  $\mu$ -I bridge (i.e., Cu<sub>4</sub>I<sub>5</sub>L<sub>3</sub>). Attempts to confirm this point with density functional theory (DFT) calculations proved inapplicable in this case. The resulting frontier MOs turned out to be localized invariably on the terminal atoms on the 1D [Cu<sub>4</sub>I<sub>4</sub>S<sub>3</sub>]<sub>n</sub> chain.

Moreover, the emission quantum yield for **CP18** (61%) is found interesting for lighting technologies.<sup>91</sup> Indeed, this value falls in the same range of those reported for a series of  $Cu_4I_4L_4$ cubane-containing 2D and 3D CPs (L = bidentate N-donor ligand), some of which have demonstrated potential applications in white light luminescence.<sup>74</sup> Finally, despite the stubborn fact that CPs constructed with CuCl and dithioethers are generally found to be not emissive (the two exceptions being a 2D-CP of formula [(CuCl)-(BzSCH<sub>2</sub>C $\equiv$ CCH<sub>2</sub>SBz)]<sub>n</sub> composed of polycyclic [Cu<sub>6</sub>Cl<sub>6</sub> $\equiv$ Cu<sub>6</sub>Cl<sub>6</sub> $\equiv$ ]<sub>n</sub> ribbons cross-linked by BzSCH<sub>2</sub>C $\equiv$ CCH<sub>2</sub>SBz ligands,<sup>35</sup> and the 3D CP of formula [Cu<sub>2</sub>Cl<sub>2</sub>(EtS-(CH<sub>2</sub>)<sub>4</sub>SEt)<sub>4</sub>]<sub>n</sub>.<sup>58</sup>), attempts were also made to observe emission from the species investigated in this work. Despite the use of a laser irradiation proved futile, and sometime quick decomposition was observed. This was the case for CP3, which showed no sign of thermal fragility in the TGA traces above.

# CONCLUSION

This exhaustive study on the complexation of flexible BzS- $(CH_2)_nSBz$  ligands with increasing chain lengths covering n = 1-9 toward CuX salts has demonstrated on the basis of 26 crystal structures that a multitude of different architectures with dimensionalities ranging from 0D to 3D can be obtained where the 1D and 2D dimensionalities are clearly the most frequent. Even unusual coexistences of different forms of 1D ribbons bearing  $Cu_2I_2$  rhomboids within the same crystal (**CP1**) and an unprecedented copresence of supramolecular isomers, namely, a 1D ribbon and a 2D sheet structure both bearing  $Cu_2Br_2$  rhomboids within the unit cell (**CP9**), are among the structural highlights of this contribution. Decisive factors for this structural

richness (keeping the nature of -SR constant) are the choice of the halide salt, the metal-to-ligand ratio, and the lengths of the CH<sub>2</sub> spacer unit. The metal-to-ligand ratio plays however a crucial role only in the case of CuI (Cu<sub>4</sub>I<sub>4</sub> cluster versus Cu<sub>2</sub>I<sub>2</sub> rhomboids), and all attempts to construct Cu<sub>4</sub>Br<sub>4</sub>S<sub>4</sub> clusters failed, albeit Cu<sub>4</sub>Br<sub>4</sub>N<sub>4</sub> and Cu<sub>4</sub>Br<sub>4</sub>P<sub>4</sub> are well-documented.<sup>92,93</sup> Although (CuI)<sub>n</sub> and (CuBr)<sub>n</sub> CPs assembled by acyclic dithioether ligands are nowadays quite common, this is definitively not the case with CuCl. This study has now filled the gap with seven novel CuCl·BzS(CH<sub>2</sub>)<sub>n</sub>SBz compounds, regardless of the spacer length varying from 1 to 9.

Noteworthy, no bonding of the sulfur atoms through the two lone pairs (i.e., a S-atom acting as a 4-electron donor) was observed, although such a Cu  $\leftarrow$  S  $\rightarrow$  Cu mode is conceivable since it has been reported before for 3D-[(Cu<sub>2</sub>X<sub>2</sub>){µ-EtS- $(CH_2)_4SEt$ ]<sub>n</sub> (X = Cl, Br).<sup>85</sup> Surprisingly, no solvent molecules are hosted within the cavities of the nanosized grid-shaped 2D sheets  $(for CH_2 = 6-9)^{37}$  nor placed between the 2D-layers, and no entanglement of the networks occurs despite the occurrences for other dithioether-CuX CPs.<sup>26,28,67,94–96</sup> Statistically, the size of the SBUs is dominated by the planar  $Cu(\mu_2-X)_2Cu$  rhomboid with Cu-Cu distances varying from 2.6867(6) to 3.092(4)Å (18 examples). No example featuring a butterfly-shaped  $S_2Cu(\mu_2-X)_2CuS_2$  motif has been encountered.<sup>73,75,97'</sup> In total, only five examples incorporating the closed-cubane Cu<sub>4</sub>I<sub>4</sub> cluster are observed. Finally, three CPs featuring -X-Cu-X-Cu-Xarrays with mononuclear copper centers complete the statistics. A statistical comparison of the dimensionality reveals the occurrence of 1 3D, 13 2D, and 12 1D CPs (including the two supramolecular isomeric forms of CP9), along with the sole example of 0D dinuclear [{ $Cu(\mu_2-Cl)_2Cu$ }( $\mu$ -L3)<sub>2</sub>] D1.

At first glance, this profusion of so many different architectures may appear confusing. Nevertheless, some trends are noticeable. Indeed, at first glance with  $BzS(CH_2)_{1-4}SBz$  as the assembling ligand, the outcome is almost unpredictable. However, the pattern of the architectures is more systematic starting with the longer-chain ligand  $BzS(CH_2)_6SBz$  L4. Reactions of 2 equiv of CuI with L4-L7 produce invariably nanosized 2D networks with Cu<sub>4</sub>I<sub>4</sub> clusters as SBUs, whereas independently of the nature of the halide, the reactions in a 1:1 ratio lead to the formation of isostructural CPs with Cu<sub>2</sub>X<sub>2</sub> rhomboids. These latter Cu<sub>2</sub>X<sub>2</sub>-containing networks are 2D sheets with L4 (3 examples) but constitute all 1D ribbons with L5–L7 (nine examples). However, despite the isomorphism of several 1D series  $[{Cu(\mu_2-X)_2Cu}{\mu-L}_2]_n$  no unambigous correlation between the nature of X and the Cu-Cu separation can be established. Although the occurrence of relativistic effects in Cu…Cu complexes is discussed in the literature, a possible contribution of such cuprophilic interactions remains speculative for our materials, since the short contacts in several compounds, notably, in the case of  $Cu_4I_4$ , are also certainly a consequence of the bridging bonding mode of the I atoms.  $^{98-105}$ 

Although the principal aim of this work is focused on structural aspects and basic understanding, and not on potential applications in catalysis and material sciences,  $^{28-30,67,106}$  we emphasize that these air-stable materials can be prepared in gram-scale. For all luminescent Cu<sub>4</sub>I<sub>4</sub> compounds, no aging was observed after several months. **CP14** was kept even for 1 week in a water-filled vial and did not lose its intense luminescence after air-drying, stressing its stability *vis-à-vis* hydrolysis and oxidation.

Noteworthy, only the cubane-containing materials are emissive. This outcome is somewhat quasi-predictable from the literature,  $^{69-71}$  but for applications purposes, this work

stresses the need for reliable synthetic methodologies to prepare these emissive  $Cu_4I_4S_4$ -containing species (or related clusters). Moreover, despite the enlarged list of reported cubanecontaining and related species, there is still no evidence for an obvious linear structure-luminescence property relationship. This task still seems illusive.

Future work will focus in a systematic investigation of CPs built upon aryl-S- $(CH_2)_m$ -S-aryl ligands and CuX with the hope that the lesser flexible arm aryl-S (compared to a more flexible aryl-CH<sub>2</sub>-S arm) induces a more demanding steric challenge around the S-atom. Alternatively, the use of ligand RS- $(CH_2)_m$ -SR with sterically less demanding substituents at the S-atom such as SMe or SEt, combined with long spacer units (m = 6-9)will certainly also impact the architecture and porosity of the networks leading to MOF-like structures incorporating voids allowing guest molecules to be included. This hypothesis has been recently corroborated by the observation that complexation of CuBr and CuCl with EtS-(CH<sub>2</sub>)<sub>4</sub>-SEt yields 3D networks  $[Cu_2X_2(EtS(CH_2)_4SEt)_4]_n$  whose unusual  $Cu \leftarrow S \rightarrow$ Cu bonding mode allows abnormal triplet energy migration processes.<sup>58,85</sup> So one may expect that also longer-chain EtS- $(CH_2)_m$ -SEt derivatives (m = 6-9) may allow the crystallogenesis of more porous CuX networks, in which the S-atoms act as four-electron donors instead of the more common twoelectron donor bonding mode.

## ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b03275.

Experimental procedure for synthesis of ligands and CPs, summary of X-ray data collection, powder X-ray diffraction patterns, TGA curves, IR and Raman spectra, absorption, emission, and excitation and lifetimes at 298 and 77 K of emissive species (PDF)

#### Accession Codes

CCDC 1960061–1960087 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

# AUTHOR INFORMATION

#### **Corresponding Authors**

- Pierre D. Harvey D'epartement de Chimie, Université de Sherbrooke, Sherbrooke, Qu'ebec, Canada J1K 2R1;
  orcid.org/0000-0002-6809-1629; Email: Pierre.Harvey@ USherbrooke.ca
- Michael Knorr Institut UTINAM, UMR CNRS 6213, Université Bourgogne Franche-Comté, 25030 Besançon, France; orcid.org/0000-0002-5647-8084; Email: Michael.Knorr@ univ-fcomte.fr

## Authors

- Adrien Schlachter Département de Chimie, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1;
   orcid.org/0000-0001-5215-8908
- Antony Lapprand Département de Chimie, Universifé de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1; Institut UTINAM, UMR CNRS 6213, Universifé Bourgogne Franche-Comté, 25030 Besançon, France

Daniel Fortin – Département de Chimie, Universife de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1;
 orcid.org/0000-0002-0223-6362

**Carsten Strohmann** – Anorganische Chemie, Technische Universität Dortmund, 44227 Dortmund, Germany

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.9b03275

# Notes

The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Research Council of Canada, the Fonds de Recherche du Québec-Nature et Technologies, Compute Canada and Calcul Québec, the Centre Quebecois sur les Matériaux Fonctionnels, and the CNRS. Dr. A. Bonnot is thanked for some preliminary investigations, as well as Dr. L. Viau for recording the PXRD of **CP22**. M.K. and C.S. thank the CNRS and the DFG for financial support.

#### REFERENCES

(1) Clark, P. W. Dehydrogenation of 1,6-Bis(diphenylphosphino)hexane by Rhodium(I) and Iridium(I) Complexes; Rhodium(I) and Iridium(I) Complexes Containing the Ligands 1,6-Bis-(diphenylphosphino)hexane, 1,6-Bis(diphenylphosphino)-trans-hex-3-ene, 1,6-Bis(diphenylarsino)hexane. *J. Organomet. Chem.* **1977**, *137*, 235-255.

(2) Al-Salem, N. A.; Empsall, H. D.; Markham, R.; Shaw, B. L.; Weeks, B. Formation of Large Chelate Rings and Cyclometallated Products from Diphosphines of Type  $But_2P(CH_2)NPBut_2$  (n = 5–8) and  $Ph_2P(CH_2)_5PPh_2$  with Palladium and Platinum Chlorides: Factors Affecting the Stability and Conformation of Large Chelate Rings. *J. Chem. Soc., Dalton Trans.* **1979**, 1972–1982.

(3) McDonald, W. S. The 20-Membered Ring Binuclear Complex  $Bis[\mu-1,7-Heptanediylbis(di-tert-butylphosphine)]bis-(dichloropalladium). Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 1979, 35, 3051–3052.$ 

(4) Thewissen, D. H. M. W.; Timmer, K.; Noltes, J. G.; Marsman, J. W.; Laine, R. M. Synthesis of  $\alpha, \omega$ -Bis(diphenylphosphino)alkane and  $\alpha, \omega$ -Bis(diphenylphosphino)(poly)ether Ligands and Complexes of Rhodium(I). *Inorg. Chim. Acta* **1985**, *97*, 143–150.

(5) Sekabunga, E. J.; Smith, M. L.; Hill, W. E. A Variable Temperature 31P NMR Study of 9–30 Atom Macrocylic Rings of Silver(I) with Long Chain Diphosphines. *J. Coord. Chem.* **2005**, *58*, 1187–1198.

(6) Owen, G. R.; Stahl, J.; Hampel, F.; Gladysz, J. A. Coordination-Driven Self-Assembly, Structures, and Dynamic Properties of Diplatinum Hexatriynediyl and Butadiynediyl Complexes in Which the sp Carbon Chains Are Shielded by sp<sup>3</sup> Carbon Chains: Towards Endgroup-Endgroup Interactions. *Chem. - Eur. J.* **2008**, *14*, 73–87.

(7) Streitberger, M.; Schmied, A.; Hey-Hawkins, E. Selective Formation of Gold(I) Bis-Phospholane Macrocycles, Polymeric Chains, and Nanotubes. *Inorg. Chem.* **2014**, *53*, 6794–6804.

(8) Chen, J.; Zhang, Q. F.; Bonaccorso, T. A.; Williard, P. G.; Wang, L. S. Controlling Gold Nanoclusters by Diphospine Ligands. *J. Am. Chem. Soc.* **2014**, *136*, 92–95.

(9) Brown, D. A.; Fitzpatrick, N. J.; Glass, W. K.; Ahmed, H. A.; Cunningham, D.; McArdle, P. Reactions of Some Group 15 Ligands with  $[(\eta^{\text{S}}\text{-Indenyl})\text{Fe}(\text{CO})_3]\text{BF}_4$ . J. Organomet. Chem. **1993**, 455, 157–166.

(10) Ueng, C. H.; Luo, T. T. An Unusual Bimetallic Molybdenum Carbonyl Derivative Containing a 22-Membered Ring: The Synthesis and Crystal Structure of Cis- $[Mo_2(CO)_8{\mu-Ph_2P(CH_2)_8PPh_2}_2]$ . *Inorg. Chim. Acta* **1995**, 237, 199–201.

(11) Schwach, M.; Hausen, H. D.; Kaim, W. Pulled Molecular Strings and Stacked Molecular Decks: Chelate-Ring Formation vs. MetalMetal Bridging in Dicopper(I) Complexes of 2,2'-Bipyrimidine with Diphosphine Ligands of Variable Polymethylene Chain Length. *Chem. - Eur. J.* **1996**, *2*, 446–451.

(12) Van Calcar, P. M.; Olmstead, M. M.; Balch, A. L. Architecture of Crystalline Polymers Formed from the Binuclear Complexes XAuPh<sub>2</sub>P-(CH<sub>2</sub>)NPPh<sub>2</sub>AuX through Weak Au(I)…Au(I) Interactions. *Inorg. Chem.* **1997**, *36*, 5231–5238.

(13) Yang, X.; Isaac, I.; Persau, C.; Ahlrichs, R.; Fuhr, O.; Fenske, D. Reactions of Silver Thiolates with Bidentate Phosphanes. *Inorg. Chim. Acta* **2014**, *421*, 233–245.

(14) Ramaprabhu, S.; Amstutz, N.; Lucken, E. A. C.; Bernardinelli, G. Copper-63,65 Nuclear Quadrupole Resonance of Complexes of Copper(I) Halides with Phosphorus-Containing Ligands. *J. Chem. Soc., Dalton Trans.* **1993**, 871–875.

(15) Camus, A.; Nardin, G.; Randaccio, L. Structure Determination of the 2:1 Derivatives of Copper(I) Bromide and Iodide with Bis-(Diphenylphosphino)Methane. A Simple Structural Scheme for the Formation of  $(CuX)_nL_m$  Species. *Inorg. Chim. Acta* **1975**, *12*, 23–32.

(16) Marsich, N.; Nardin, G.; Randaccio, L. A Tetranuclear Copper(I) Complex. The Crystal and Molecular Structure of the 2:1 Derivative of Copper(I) Iodide and Bis(diphenylphosphino)methane. *J. Am. Chem. Soc.* **1973**, *95*, 4053–4054.

(17) Fan, L. Q. Crystal Structure of Bis( $\mu_3$ -Iodo)-( $\mu_3$ -Iodo)- Bis( $\mu_2$ -Bis(diphenylphosphine)ethane)Tricopper(I) - Dimethylformamide (1:1), Cu<sub>3</sub>I<sub>3</sub>(C<sub>26</sub>H<sub>24</sub>P<sub>2</sub>), · C<sub>3</sub>H<sub>7</sub>NO. *Z. Kristallogr. - New Cryst. Struct.* **2011**, 226, 391–393.

(18) Benito, Q.; Le Goff, X. F.; Nocton, G.; Fargues, A.; Garcia, A.; Berhault, A.; Kahlal, S.; Saillard, J. Y.; Martineau, C.; Trébosc, J.; Gacoin, T.; Boilot, J.-P.; Perruchas, S. Geometry Flexibility of Copper Iodide Clusters: Variability in Luminescence Thermochromism. *Inorg. Chem.* **2015**, *54*, 4483–4494.

(19) Lobana, T. S.; Sharma, R.; Sharma, R.; Mehra, S.; Castineiras, A.; Turner, P. Versatility of Heterocyclic Thioamidis in the Construction of a Trinuclear Cluster  $[Cu_3I_3(dppe)_3(SC_5H_4NH)]$  and CuI Linear Polymers. *Inorg. Chem.* **2005**, *44*, 1914–1921.

(20) Effendy; Di Nicola, C.; Fianchini, M.; Pettinari, C.; Skelton, B. W.; Somers, N.; White, A. H. The Structural Definition of Adducts of Stoichiometry MX:Dppx (1:1) M = Cu I, Ag I, X = Simple Anion, Dppx =  $Ph_2P(CH_2)XPPh_2$ , x = 3–6. *Inorg. Chim. Acta* 2005, 358, 763–795. (21) Hartley, F. R.; Murray, S. G.; Levason, W.; Soutter, H. E.; McAuliffe, C. A. Systematics of Palladium(II) and Platinum(II) Dithioether Complexes. The Effect of Ligand Structure upon the Structure and Spectra of the Complexes and upon Inversion at Coordinated Sulphur. *Inorg. Chim. Acta* 1979, 35, 265–277.

(22) McAuliffe, C. A.; Parish, R. V.; Randall, P. D. Gold(I) Complexes of Unidentate and Bidentate Phosphorus-, Arsenic-, Antimony-, and Sulphur-Donor Ligands. *J. Chem. Soc., Dalton Trans.* **1979**, 1730–1735.

(23) Abd-El-Aziz, A. S.; Lei, Y.; De Denus, C. R. Aliphatic Diols in the Synthesis of Bis(cyclopentadienyliron) Arene Complexes. *Polyhedron* **1995**, *14*, 1585–1591.

(24) Chen, C.-L.; Su, C.-Y.; Cai, Y.-P.; Zhang, H.-X.; Xu, A.-W.; Kang, B.-S. A Non-Interpenetrating 2D Coordination Polymer from a  $(CH_2)_8$  Spacer-Based Highly Flexible Linear Ligand and AgCF<sub>3</sub>CO<sub>2</sub>. *New J. Chem.* **2003**, *27*, 790–792.

(25) Kim, T. H.; Lee, K. Y.; Shin, Y. W.; Moon, S.-T.; Park, K.-M.; Kim, J. S.; Kang, Y.; Lee, S. S.; Kim, J. New Crystalline Framework Formed from a Podal Ligand with  $S_2O_2$  Donor and CuI: Non-Interpenetrating Square-Grid with Cubane-like Cu<sub>4</sub>I<sub>4</sub> Cluster Nodes. *Inorg. Chem. Commun.* **2005**, *8*, 27–30.

(26) Zhang, J.; Xue, Y.-S.; Li, Y.-Z.; Du, H.-B.; You, X.-Z. Cuprous Iodide Coordination Polymers  $(CuI)_x(L)_y \cdot z$ (Solvent) Built on Linear Thioether Linkers. *CrystEngComm* **2011**, *13*, 2578–2585.

(27) Kim, T. H.; Lee, S.; Jeon, Y.; Shin, Y. W.; Kim, J. Reversible Photoluminescence Switch: A Stair-Step  $Cu_4I_4$  coordination Polymer Based on a Dithioether Ligand. *Inorg. Chem. Commun.* **2013**, *33*, 114–117.

(28) Kim, T. H.; Yang, H.; Park, G.; Lee, K. Y.; Kim, J. γ-Cul Nanocrystals from Self-Assembled Coordination Polymers. *Chem.* - *Asian J.* **2010**, *5*, 252–255.

(29) Saha, S.; Biswas, K.; Basu, B. 1-D Copper(I) Coordination Polymer Based on Bidentate 1,3-Dithioether Ligand: Novel Catalyst for Azide-Alkyne-Cycloaddition (AAC) Reaction. *Tetrahedron Lett.* **2018**, *59*, 2541–2545.

(30) Saha, S.; Biswas, K.; Ghosh, P.; Basu, B. New 1,2-Dithioether Based 2D Copper(I) Coordination Polymer: From Synthesis to Catalytic Application in A<sup>3</sup>-Coupling Reaction. *J. Coord. Chem.* **2019**, 72, 1810–1819.

(31) Peindy, H. N.; Guyon, F.; Khatyr, A.; Knorr, M.; Strohmann, C. Construction of 1D and 2D Copper(I) Coordination Polymers Assembled by  $PhS(CH_2)_nSPh$  (n = 1, 2) Dithioether Ligands: Surprising Effect of the Spacer Length on the Dimensionality, Cluster Nuclearity and the Fluorescence Properties of the Metal-Organic Framework. *Eur. J. Inorg. Chem.* **2007**, 2007, 1823–1828.

(32) Knorr, M.; Guyon, F.; Khatyr, A.; Däschlein, C.; Strohmann, C.; Aly, S. M.; Abd-El-Aziz, A. S.; Fortin, D.; Harvey, P. D. Rigidity effect of the dithioether spacer on the size of the luminescent cluster  $(Cu_2I_2)_n$  (n = 2, 3) in their coordination polymers. *J. Chem. Soc., Dalton Trans.* **2009**, 948–955.

(33) Knorr, M.; Guyon, F.; Khatyr, A.; Strohmann, C.; Allain, M.; Aly, S. M.; Lapprand, A.; Fortin, D.; Harvey, P. D. Construction of  $(CuX)_{2n}$  Cluster-Containing (X = Br, I; n = 1, 2) Coordination Polymers Assembled by Dithioethers  $ArS(CH_2)_mSAr$  (Ar = Ph, *p*-Tol; m = 3, 5): Effect of the Spacer Length, Aryl Group, and Metal-to-Ligand Ratio on the Dimensionality, Cluster Nuclearity, and the Luminescence Properties of the Metal–Organic Frameworks. *Inorg. Chem.* **2012**, *51*, 9917–9934.

(34) Knorr, M.; Khatyr, A.; Dini Aleo, A.; El Yaagoubi, A.; Strohmann, C.; Kubicki, M. M.; Rousselin, Y.; Aly, S. M.; Fortin, D.; Lapprand, A.; Harvey, P. D. Copper(I) Halides (X = Br, I) Coordinated to Bis(Arylthio)Methane Ligands: Aryl Substitution and Halide Effects on the Dimensionality, Cluster Size, and Luminescence Properties of the Coordination Polymers. *Cryst. Growth Des.* **2014**, *14*, 5373–5387.

(35) Bonnot, A.; Knorr, M.; Strohmann, C.; Golz, C.; Fortin, D.; Harvey, P. D. CuX (X = Cl, Br, I) Containing Coordination Polymers Built Upon Isomeric RSCH<sub>2</sub>C $\equiv$ CCH<sub>2</sub>SR (R = p-Tolyl, Benzyl) Dithioether Ligands: First Example of a Luminescent (CuCl)<sub>n</sub>/ Dithioether Network. J. Inorg. Organomet. Polym. Mater. **2015**, 25, 480–494.

(36) Bonnot, A.; Juvenal, F.; Lapprand, A.; Fortin, D.; Knorr, M.; Harvey, P. D. Can a Highly Flexible Copper(I) Cluster-Containing 1D and 2D Coordination Polymers Exhibit MOF-like Properties? *Dalton Trans.* **2016**, *45*, 11413–11421.

(37) Yang, H.; Kim, T. H.; Moon, S.-H.; Kim, J. Bis(benzylsulfanyl)methane. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2010**, *66*, o1519– o1519.

(38) Kuhn, N.; Schumann, H. Zur Koordination Mehrfunktioneller Thioether in Cyclopentadienyleisen-Komplexen. *J. Organomet. Chem.* **1986**, 315, 93–103.

(39) Fuchita, Y.; Maruyama, H.; Kawatani, M.; Hiraki, K. Synthesis and Characterization of Palladium Complexes with Bis(benzylthio)-methane. *Polyhedron* **1991**, *10*, 561–566.

(40) Li, J.-R.; Bu, X.-H.; Jiao, J.; Du, W.-P.; Xu, X.-H.; Zhang, R.-H. Novel Dithioether–Silver(I) Coordination Architectures: Structural Diversities by Varying the Spacers and Terminal Groups of Ligands. *Dalton Trans.* **2005**, 464–474.

(41) Martínez-Alanis, P. R.; Ugalde-Saldívar, V. M.; Castillo, I. Electrochemical and Structural Characterization of Tri- and Dithioether Copper Complexes. *Eur. J. Inorg. Chem.* **2011**, 2011, 212–220.

(42) Bonnot, A.; Strohmann, C.; Knorr, M.; Harvey, P. D. Metal-to-Ligand Ratio Effect on the Size of Copper Iodide and Copper Bromide Clusters in 1,4-Bis(cyclohexylthio)butane-spanned Coordination Polymers. J. Cluster Sci. 2014, 25, 261–275.

(43) Tae, H. K.; Park, G.; Yong, W. S.; Park, K. M.; Myong, Y. C.; Kim, J. Self-Assembled Copper(I) Complexes of Symmetric Dithioether Ligands. *Bull. Korean Chem. Soc.* **2008**, *29*, 499–502.

(44) Schlachter, A.; Viau, L.; Fortin, D.; Knauer, L.; Strohmann, C.; Knorr, M.; Harvey, P. D. Control of Structures and Emission Properties of (CuI)<sub>n</sub> 2-Methyldithiane Coordination Polymers. *Inorg. Chem.* **2018**, *57*, 13564–13576.

(45) Maelger, H.; Olbrich, F.; Kopf, J.; Abeln, D.; Weiss, E. Synthese Und Struktur Der Basenaddukte von Kupfer(I)-Halogeniden Mit Dimethylsulfid Und Tetrahydrothiophen/Synthesis and Crystal Structure of Lewis Base Adducts of Copper(I)-Halides with Dimethylsulfide and Tetrahydrothiophene. Z. Naturforsch., B: J. Chem. Sci. 1992, 47, 1276-1280.

(46) Bonnot, A.; Knorr, M.; Guyon, F.; Kubicki, M. M.; Rousselin, Y.; Strohmann, C.; Fortin, D.; Harvey, P. D. 1,4-Bis(Arylthio)but-2-enes as Assembling Ligands for  $(Cu_2X_2)_n$  (X = I, Br; n = 1, 2) Coordination Polymers: Aryl Substitution, Olefin Configuration, and Halide Effects on the Dimensionality, Cluster Size, and Luminescence Properties. *Cryst. Growth Des.* **2016**, *16*, 774–788.

(47) Toyota, S.; Matsuda, Y.; Nagaoka, S.; Oki, M.; Akashi, H. Reaction of 2-(Alkylthiomethyl)phenyllithium with Copper(I) Halides and Structure and Properties of One of the Products—Copper(I) Complexes of 2,2'-Bis(Alkylthiomethyl)Biphenyl. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 3115–3121.

(48) Knorr, M.; Guyon, F.; Khatyr, A.; Strohmann, C.; Allain, M.; Aly, S. M.; Lapprand, A.; Fortin, D.; Harvey, P. D. Construction of  $(CuX)_{2n}$  Cluster-Containing (X = Br, I; n = 1, 2) Coordination Polymers Assembled by Dithioethers  $ArS(CH_2)_mSAr$  (Ar = Ph, *p*-Tol; m = 3, 5): Effect of the Spacer Length, Aryl Group, and Metal-to-Ligand Ratio on the Dimensionality, Cluster Nuclearity, and the Luminescence Properties of the Metal–Organic Frameworks. *Inorg. Chem.* **2012**, *51*, 9917–9934.

(49) Raghuvanshi, A.; Dargallay, N. J.; Knorr, M.; Viau, L.; Knauer, L.; Strohmann, C. 1,3-Dithiolane and 1,3-Ferrocenyl-Dithiolane as Assembling Ligands for the Construction of Cu(I) Clusters and Coordination Polymers. J. Inorg. Organomet. Polym. Mater. **2017**, 27, 1501–1513.

(50) Baumgartner, M. R.; Schmalle, H.; Dubler, E. The Interaction of Transition Metals with the Coenzyme  $\alpha$ -Lipoic Acid: Synthesis, Structure and Characterization of Copper and Zinc Complexes. *Inorg. Chim. Acta* **1996**, *252*, 319–331.

(51) Gasparrini, F.; Giovannoli, M.; Misiti, D.; Natile, G.; Palmieri, G. Selective and Regiospecific Oxidation of Dithiaalkanes in a Gold(III) Catalyzed Phase-Transfer Process. *Tetrahedron* **1984**, *40*, 165–170.

(52) Li, J. R.; Zhang, R. H.; Bu, X. H. Synthesis and Crystal Structure of a 2D (6,3) Coordination Network,  ${[Ag(L)_{1.5}]NO_3}_n$  [L = 1,3-Bis(benzylthio)propane]. J. Chem. Crystallogr. 2004, 34, 501–505.

(53) Knorr, M.; Guyon, F.; Khatyr, A.; Allain, M.; Aly, S. M.; Lapprand, A.; Fortin, D.; Harvey, P. D. Unexpected Formation of a Doubly Bridged Cyclo-1,2-Dithian 1D Coordination  $Cu_2I_2$ -Containing Luminescent Polymer. J. Inorg. Organomet. Polym. Mater. **2010**, 20, 534–543.

(54) Xie, C.; Zhou, L.; Feng, W.; Wang, J.; Chen, W. Varying the Frameworks of Coordination Polymers with (CuI)<sub>4</sub> cubane Cluster by Altering Terminal Groups of Thioether Ligands. *J. Mol. Struct.* **2009**, *921*, 132–136.

(55) Chandrasekhar, V.; Azhakar, R.; Pandian, B. M.; Boomishankar, R.; Steiner, A. A Phosphorus-Supported Multisite Coordination Ligand Containing Three Imidazolyl Arms and Its Metalation Behaviour. An Unprecedented Co-Existence of Mononuclear and Macrocyclic Dinuclear Zn(II) Complexes in the Same Unit Cell of a Crystalline Lattice. *Dalton Trans.* **2008**, 5962–5969.

(56) Li, B.; Peng, Y.; Li, B.; Zhang, Y. Supramolecular Isomers in the Same Crystal: A New Type of Entanglement Involving Ribbons of Rings and 2D (4,4) Networks Polycatenated in a 3D Architecture. *Chem. Commun.* **2005**, 2333–2335.

(57) Lee, S. Y.; Park, S.; Lee, S. S. Copper(I), Silver(I), and Palladium(II) Complexes of a Thiaoxamacrocycle Displaying Unusual Topologies. *Inorg. Chem.* **2009**, *48*, 11335–11341.

(58) Schlachter, A.; Bonnot, A.; Fortin, D.; Karsenti, P.-L.; Knorr, M.; Harvey, P. D. Unusual Triplet—Triplet Annihilation in a 3D Copper(I) Chloride Coordination Polymer. *Phys. Chem. Chem. Phys.* **2019**, *21*, 16538–16548. (59) Aly, S. M.; Pam, A.; Khatyr, A.; Knorr, M.; Rousselin, Y.; Kubicki, M. M.; Bauer, J. O.; Strohmann, C.; Harvey, P. D. Cluster-Containing Coordination Polymers Built Upon  $(Cu_2I_2S_2)_m$  Units (m = 2, 3) and ArSCH<sub>2</sub>C≡CCH<sub>2</sub>SAr Ligands: Is the Cluster Size Dependent Upon Steric Hindrance or Ligand Rigidity? *J. Inorg. Organomet. Polym. Mater.* **2014**, 24, 190–200.

(60) Li, J. R.; Du, M.; Bu, X. H.; Zhang, R. H. Extended Chains via Hydrogen Bond Linkages of Dinuclear Copper(II) and Cadmium(II) Complexes with a New Flexible Disulfoxide Ligand. *J. Solid State Chem.* **2003**, *173*, 20–26.

(61) Knorr, M.; Guyon, F.; Kubicki, M. M.; Rousselin, Y.; Aly, S. M.; Harvey, P. D. Effect of *t*-BuS *vs. n*-BuS on the topology, Cu···Cu distances and luminescence properties of 2D  $Cu_4I_4/RS(CH_2)_4SR$  metal-organic frameworks. *New J. Chem.* **2011**, 35, 1184–1188.

(62) Tan, S. F.; Ang, K. P. Copper, Gold, and Platinum Complexes of 1,3-Dithiane. J. Singapore Natl. Acad. Sci. **1987**, *16*, 111–114.

(63) Guy, J. T.; Cooper, J. C.; Gilardi, R. D.; Flippen-Anderson, J. L.; George, C. F. Transition-Metal-Promoted Oxidation of Organic Sulfides. Synthesis, Characterization, and Structure of ( $\mu_4$ -Oxo)hexakis( $\mu_2$ -Chloro)tetrakis(dialkyl sulfoxide)tetracopper(II). *Inorg. Chem.* **1988**, *27*, 635–638.

(64) Ainscough, E. W.; Brodie, A. M.; Husbands, J. M.; Gainsford, G. J.; Gabe, E. J.; Curtis, N. F. Sulphur Ligand–Metal Complexes. Part 16. Copper Complexes of Thioethers and the Single-Crystal X-Ray Structure of the Polymeric Mixed-Valence Complex, Penta-μ-Chloro-Tris-μ-Tetrahydrothiophene-Tetracopper(I,II). J. Chem. Soc., Dalton Trans. **1985**, 151–158.

(65) Park, K.-M.; Yoon, I.; Yoo, B. S.; Choi, J. B.; Lee, S. S.; Kim, B. G. Trans -Dichloro(1,12-Diphenyl-5,8-Dioxa-2,11-Dithiadodecane-S,S')-Palladium(II). *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* 2000, 56, 1191–1192.

(66) Seo, M. L.; Yoon, I.; Seo, J.; Baek, H.; Ha, K. S. Synthesis and Crystal Structure of  $Hg^{2+}$  Complex with an  $S_2O_2$  Donor Dipodal Ligand. A Search for New Voltammetric Sensor for  $Hg^{2+}$ . *Bull. Korean Chem. Soc.* **2005**, *26*, 1293–1296.

(67) Bai, S.-Q.; Wong, I. H. K.; Zhang, N.; Lin Ke, K.; Lin, M.; Young, D. J.; Hor, T. S. A. A New 3-D Coordination Polymer as a Precursor for CuI-Based Thermoelectric Composites. *Dalton Trans.* **2018**, 47, 16292–16298.

(68) Petersenn, A. V. Gold(I)-Komplexe mit Sulfan- und Chloro- oder Phosphanliganden. *Arch. Pharm.* **1991**, *324* (7), 411–415.

(69) Harvey, P. D.; Knorr, M. Designs of 3-Dimensional Networks and MOFs Using Mono- and Polymetallic Copper(I) Secondary Building Units and Mono- and Polythioethers: Materials Based on the Cu–S Coordination Bond. J. Inorg. Organomet. Polym. Mater. 2016, 26, 1174–1197.

(70) Harvey, P. D.; Knorr, M. Stabilization of  $(CuX)_n$  Clusters (X = Cl, Br, I; n = 2, 4, 5, 6, 8) in Mono- and Dithioether-Containing Layered Coordination Polymers. *J. Cluster Sci.* **2015**, *26*, 411–459.

(71) Harvey, P. D.; Knorr, M. Luminescent Coordination Polymers Built upon  $Cu_4X_4$  (X = Br,I) Clusters and Mono- and Dithioethers. *Macromol. Rapid Commun.* **2010**, *31*, 808–826.

(72) Lee, E.; Lee, S. G.; Park, I. H.; Kim, S.; Ju, H.; Jung, J. H.; Ikeda, M.; Habata, Y.; Lee, S. S. Endo- and Exocyclic Coordination of a 20-Membered  $N_2O_2S_2$ -Macrocycle and Cascade Complexation of a 40-Membered  $N_4O_4S_4$ -Macrocycle. *Inorg. Chem.* **2018**, *57*, 6289–6299.

(73) Raghuvanshi, A.; Strohmann, C.; Tissot, J. B.; Clément, S.; Mehdi, A.; Richeter, S.; Viau, L.; Knorr, M. Assembly of Coordination Polymers Using Thioether-Functionalized Octasilsesquioxanes: Occurrence of  $(CuX)_n$  Clusters (X = Br and I) within 3D-POSS Networks. *Chem. - Eur. J.* **2017**, *23*, 16479–16483.

(74) Fang, Y.; Liu, W.; Teat, S. J.; Dey, G.; Shen, Z.; An, L.; Yu, D.; Wang, L.; O'Carroll, D. M.; Li, J. A Systematic Approach to Achieving High Performance Hybrid Lighting Phosphors with Excellent Thermaland Photostability. *Adv. Funct. Mater.* **201**7, *27*, 1603444.

(75) Chaabéne, M.; Khatyr, A.; Knorr, M.; Askri, M.; Rousselin, Y.; Kubicki, M. M. Bis{(4-Methylthio)Phenylthio}methane as Assembling Ligand for the Construction of Cu(I) and Hg(II) Coordination Polymers. Crystal Structures and Topological (AIM) Analysis of the Bonding. *Inorg. Chim. Acta* **2016**, *451*, 177–186.

(76) Kim, S.; Siewe, A. D.; Lee, E.; Ju, H.; Park, I. H.; Park, K. M.; Ikeda, M.; Habata, Y.; Lee, S. S. Ligand-Induced Formation of Copper(I) Iodide Clusters: Exocyclic Coordination Polymers with Bis-Dithiamacrocycle Isomers. *Inorg. Chem.* **2016**, *55*, 2018–2022.

(77) Henline, K. M.; Wang, C.; Pike, R. D.; Ahern, J. C.; Sousa, B.; Patterson, H. H.; Kerr, A. T.; Cahill, C. L. Structure, Dynamics, and Photophysics in the Copper(I) Iodide- Tetrahydrothiophene System. *Cryst. Growth Des.* **2014**, *14*, 1449–1458.

(78) Park, I. H.; Kim, H. J.; Lee, S. S. Anion-Dependent Coordinative Networking of Macrocycle with Copper(I) Halides. *CrystEngComm* **2012**, *14*, 4589–4595.

(79) Park, I. H.; Lee, S. S. Networking of Macrocycles: 1D and 2D Coordination Polymers of Dithia-18-Crown-6 with Copper(II) and Copper(I). *CrystEngComm* **2011**, *13*, 6520–6525.

(80) Jin, Y.; Kim, H. J.; Lee, J. Y.; Lee, S. S. S. Y.; Shim, W. J.; Hong, S. H.; Lee, S. S. S. Y. Hard/Soft Heterometallic Network Complex of a Macrocycle with Endo/Exocyclic Coordination. *Inorg. Chem.* **2010**, *49*, 10241–10243.

(81) Kang, E. J.; Lee, S. Y.; Lee, H.; Lee, S. S. Sulfur-Containing Mixed-Donor Tribenzo-Macrocycles and Their Endo-and Exocyclic Supramolecular Silver(I) and Copper(I) Complexes. *Inorg. Chem.* **2010**, *49*, 7510–7520.

(82) Lee, J. Y.; Lee, S. Y.; Sim, W.; Park, K.-M.; Kim, J.; Lee, S. S. Temperature-Dependent 3-D CuI Coordination Polymers of Calix[4]-Bis-Dithiacrown: Crystal-to-Crystal Transformation and Photoluminescence Change on Coordinated Solvent Removal. J. Am. Chem. Soc. 2008, 130, 6902–6903.

(83) Kim, T. H.; Shin, Y. W.; Jung, J. H.; Kim, J. S. J.; Kim, J. S. J. Crystal-to-Crystal Transformation between Three CuIcoordination Polymers and Structural Evidence for Luminescence Thermochromism. *Angew. Chem., Int. Ed.* **2008**, *47*, 685–688.

(84) Kim, T. H.; Shin, Y. W.; Lee, S. S.; Kim, J. Supramolecular Assembly of One-Dimensional Channels and Two-Dimensional Brick-Wall Networks from Asymmetric Dithioether Ligands and Copper(I) Iodide. *Inorg. Chem. Commun.* **2007**, *10*, 11–14.

(85) Bonnot, A.; Karsenti, P.-L.; Juvenal, F.; Golz, C.; Strohmann, C.; Fortin, D.; Knorr, M.; Harvey, P. D. The 3D  $[(Cu_2Br_2){\mu-EtS(CH_2)_4SEt}]_n$  Material: A Rare Example of a Coordination Polymer Exhibiting Triplet—Triplet Annihilation. *Phys. Chem. Chem. Phys.* **2016**, *18*, 24845–24849.

(86) Knorr, M.; Bonnot, A.; Lapprand, A.; Khatyr, A.; Strohmann, C.; Kubicki, M. M.; Rousselin, Y.; Harvey, P. D. Reactivity of CuI and CuBr toward Dialkyl Sulfides RSR: From Discrete Molecular  $Cu_4I_4S_4$  and  $Cu_8I_8S_6$  Clusters to Luminescent Copper(I) Coordination Polymers. *Inorg. Chem.* **2015**, *54*, 4076–4093.

(87) Harvey, P. D.; Bonnot, A.; Lapprand, A.; Strohmann, C.; Knorr, M. Coordination  $RC_6H_4S(CH_2)_8SC_6H_4R/(CuI)_n$  Polymers (R (n) = H (4); Me (8)): An Innocent Methyl Group That Makes the Difference. *Macromol. Rapid Commun.* **2015**, *36*, 654–659.

(88) Lapprand, A.; Bonnot, A.; Knorr, M.; Rousselin, Y.; Kubicki, M. M.; Fortin, D.; Harvey, P. D. Formation of an Unprecedented  $(CuBr)_S$  Cluster and a Zeolite-Type 2D-Coordination Polymer: A Surprising Halide Effect. *Chem. Commun.* **2013**, *49*, 8848–8850.

(89) Clément, S.; Goudreault, T.; Bellows, D.; Fortin, D.; Guyard, L.; Knorr, M.; Harvey, P. D. Probing Excited State Electronic Communications across Diethynyl-[2.2]Paracyclophane-Containing Conjugated Organometallic Polymers. *Chem. Commun.* **2012**, *48*, 8640–8642.

(90) Knorr, M.; Pam, A.; Khatyr, A.; Strohmann, C.; Kubicki, M. M.; Rousselin, Y.; Aly, S. M.; Fortin, D.; Harvey, P. D. Reactivity of CuI and CuBr toward  $Et_2S$ : A Reinvestigation on the Self-Assembly of Luminescent Copper(I) Coordination Polymers. *Inorg. Chem.* **2010**, *49*, 5834–5844.

(91) Liu, W.; Fang, Y.; Li, J. Copper Iodide Based Hybrid Phosphors for Energy-Efficient General Lighting Technologies. *Adv. Funct. Mater.* **2018**, *28*, 1705593. (92) Zhang, W.; Xiong, R.-G.; Huang, S. D. 3D Framework Containing  $Cu_4Br_4$  Cubane as Connecting Node with Strong Ferroelectricity. J. Am. Chem. Soc. **2008**, 130 (32), 10468–10469.

(93) Pike, R. D.; Starnes, W. H.; Carpenter, G. B. Cubane Tetrameric Complexes of Copper(I) Chloride and Bromide with Triphenyl Phosphite. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1999**, *55*, 162–165.

(94) Heller, M. A Novel Huge Diamond-like Three-Fold Interpenetrated Network of CuI and Crown Ether. Z. Anorg. Allg. Chem. 2006, 632, 441–444.

(95) Ovens, J. S.; Christensen, P. R.; Leznoff, D. B. Designing Tunable White-Light Emission from an Aurophilic  $Cu^{I}/Au^{I}$  Coordination Polymer with Thioether Ligands. *Chem. - Eur. J.* **2016**, *22*, 8234–8239.

(96) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Mitina, T. G.; Blatov, V. A. Entangled Two-Dimensional Coordination Networks: A General Survey. *Chem. Rev.* **2014**, *114*, 7557–7580.

(97) Su, C. Y.; Kang, B. S.; Sun, J.; Tong, Y. X.; Chen, Z. N. Transition Metal Complexes of Mixed Donor Acyclic Ligands Bearing Heterocyclic Moieties as Terminal Groups. Part 2. Synthesis, Crystal Structure and Properties of the Luminescent Copper(I) Complex  $[Cu_2I_2(Oesq)]$  (Oesq = 8,8'-[Oxybis(ethylenesulfanyl)]diquinoline). J. Chem. Res., Synop. 1997, 454–455.

(98) Siemeling, U.; Vorfeld, U.; Neumann, B.; Stammler, H.-G. Cuprophilicity? A Rare Example of a Ligand-Unsupported  $Cu^{I}-Cu^{I}$  Interaction. *Chem. Commun.* **1997**, 1723–1724.

(99) Poblet, J.-M.; Bénard, M. Cuprophilicity, a Still Elusive Concept: A Theoretical Analysis of the Ligand-Unsupported  $Cu^{I}-Cu^{I}$ Interaction in Two Recently Reported Complexes. *Chem. Commun.* **1998**, 1179–1180.

(100) Che, C.-M.; Mao, Z.; Miskowski, V. M.; Tse, M.-C.; Chan, C.-K.; Cheung, K.-K.; Phillips, D. L.; Leung, K.-H. Cuprophilicity: Spectroscopic and Structural Evidence for Cu–Cu Bonding Interactions in Luminescent Dinuclear Copper(I) Complexes with Bridging Diphosphane Ligands. *Angew. Chem.* **2000**, *112*, 4250–4254.

(101) Zheng, S.-L.; Messerschmidt, M.; Coppens, P. An Unstable Ligand-Unsupported CuI Dimer Stabilized in a Supramolecular Framework. *Angew. Chem., Int. Ed.* **2005**, *44*, 4614–4617.

(102) Pyykkö, P.; Mendizabal, F. Theory of d<sup>10</sup>-d<sup>10</sup> Closed-Shell Attraction. *Inorg. Chem.* **1998**, *37*, 3018-3025.

(103) Hermann, H. L.; Boche, G.; Schwerdtfeger, P. Metallophilic Interactions in Closed-Shell Copper(I) Compounds - A Theoretical Study. *Chem. - Eur. J.* **2001**, *7*, 5333–5342.

(104) Carvajal, M. A.; Alvarez, S.; Novoa, J. J. The Nature of Intermolecular  $Cu^{I}\cdots Cu^{I}$  Interactions: A Combined Theoretical and Structural Database Analysis. *Chem. - Eur. J.* **2004**, *10*, 2117–2132.

(105) Harisomayajula, N. V. S.; Makovetskyi, S.; Tsai, Y. Cuprophilic Interactions in and between Molecular Entities. *Chem. - Eur. J.* **2019**, *25*, 8936–8954.

(106) Zhang, J.; Li, M.; Cheng, L.; Li, T. Multifunctional Polymers Built on Copper–Thioether Coordination. *Polym. Chem.* **2017**, *8*, 6527–6533.