

Review

Perspectives on the Structural Design and Luminescent Behavior of Liquid Crystalline Materials Based on Copper(I) Complexes

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Abstract: This paper provides insight into the various studies that have been carried out to date on liquid crystalline materials based on copper(I) complexes. Although the study of copper(I) complexes with respect to their liquid crystalline property is quite limited, metallomesogens prepared with different structural components and ligands from groups such as azamacrocycles, alkythiolates, ethers, isocyanides, phenanthroline, Schiff bases, pyrazolates, phosphines, biquinolines, and benzoylthioureas are reported and summarized in this review. A special section is dedicated to the discussion of emission properties of copper(I) metallomesogens.

Keywords: copper(I); metallomesogens; luminescence; complex; ligand

1. Introduction

Liquid crystals are generally referred to as substances that blend the structure and properties of solid and liquid states; they share with liquids the ability to flow but also exhibit some structural arrangement similarities with solids. This intriguing combination of the properties of both liquid and solid states gives liquid crystals the ability to induce certain properties that enable useful applications in the displays of devices such as wristwatches, calculators, portable computers, and flat-screen televisions, as well as in sensors, smart windows, optical switches, etc. [1].

With so many compounds synthesized, liquid crystals containing metals, also known as metallomesogens, have become a major subject of study [2]. The incorporation of metal into organic matrices enhances and induces unique magnetic, spectroscopic, and redox properties of the resulting materials [3–9]. At least one liquid crystalline complex has been reported in the literature for most metals. However, issues often encountered with these complexes include those relating to the high transition temperatures (usually $>100\text{ }^{\circ}\text{C}$) and the low thermal stability associated with metallomesogens at elevated temperatures, which are major drawbacks that hinder the study of the physical properties of these materials. The performance parameters in electro-optical applications should be enhanced by luminescent liquid crystals, which offer anisotropic long-range order and consequently polarized emission [10,11]. Therefore, the preceding challenges make it difficult to observe light emission (luminescence) at elevated temperatures due to strong tendencies of the excited states to undergo deactivation through non-radiative transitions. Therefore, luminescence studies on metallomesogens in many cases were performed with samples in the solid state or dissolved in organic solvents [12].

Copper(I) complexes have not been studied to a great extent as luminescent materials in the liquid crystalline state, but they do possess luminescence properties with great potentials [13–22]. Copper, which is somewhat abundant and affordable, is a suitable alternative to noble metal complexes [23,24]. The ratio of triplet to singlet excitons is 3:1; consequently, for luminescent materials to be used in OLEDs, they should essentially be



Citation: Alkali, M.; Cîrcu, V. Perspectives on the Structural Design and Luminescent Behavior of Liquid Crystalline Materials Based on Copper(I) Complexes. *Chemistry* **2023**, *5*, 646–661. <https://doi.org/10.3390/chemistry5010046>

Academic Editor: Matthias Weil

Received: 17 February 2023

Revised: 10 March 2023

Accepted: 14 March 2023

Published: 15 March 2023



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able to harvest all the excitons. Because copper(I) complexes exhibit various metal-to-ligand charge-transfer (MLCT) behaviors, they can induce spin orbital coupling of the triplet and singlet states, leading to small energy separations between the energy levels [25]. This allows for reverse intersystem crossing (RISC), i.e., singlet harvesting, resulting in thermally activated delayed fluorescence (TADF) [26]. Therefore, liquid crystals based on copper(I) complexes have considerable promise for producing effective luminescent materials for a wide range of optical or electro-optical applications due to the large diversity of possible structures, including mononuclear or polynuclear complexes, and the great potential of emission behavior. In addition, the range of coordination geometries (such as linear, plan-trigonal, or tetrahedral) combined with the ligands' structural design provide a significant benefit for controlling the LC properties, including their enhanced thermal stability and mesophase type related to both calamitic and discotic materials.

A number of reviews have provided an overview of the luminescent properties of copper(I) complexes and their use in various applications [27–31]; however, a systematic review specific to copper (I) metallomesogens has not been reported. Liquid crystalline materials obtained from metal complexes of copper(I) exist in a variety of forms and structural geometries. These complexes have been designed using a wide variety of ligands from various groups, including azamacrocycles, alkythiolates, ethers, isocyanides, phenanthrolines, Schiff bases, pyrazolates, phosphines, biquinolines, and benzoylthioureas. In this paper, we review studies relevant to our interest in research on liquid crystalline materials in the form of copper(I) complexes from 1994 to the present. Furthermore, the known luminescent properties of these copper(I) complexes in their mesophase are highlighted.

2. Copper(I) Metallomesogens with Sulfur-Containing Ligands

A series of cationic macrocyclic copper(I) complexes based on non-mesogenic bis[4-(n-alkyloxy) benzamide derivatives of 1,10-diaza-4,7,13,16-tetrathiacyclooctadecane was reported in 1994 by Ghedini et al. [32]. The studied complexes had transition temperatures from the solid to liquid crystalline states ranging from 93 to 123 °C. Complex **1e** (Figure 1) demonstrated the clearest mesomorphism among the series, with sufficient thermal stability, so the research group focused their X-ray analysis on it, and the study revealed an X-ray diffraction pattern consistent with a disordered layered structure associated with a smectic phase of A or C type.

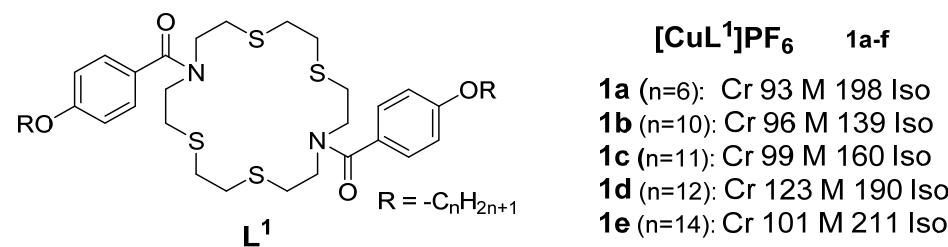


Figure 1. Copper(I) complexes from azamacrocycle derivatives. Transition temperatures are in °C [32].

Alkyl thiolates (R-SH) are strong ligands that can bind to metals via the donor S atom to obtain metal thiolates. In 1999, Espinet et al. [33] reported the preparation of a series of copper(I) thiolates, $[\text{CuSC}_n\text{H}_{2n+1}]$, where $n = 4, 6, 8, 10, 12, 14, 16$, and 18 . X-ray diffraction analysis of the polycrystalline sample revealed a layered structure in the solid state, contrary to previously reported work by Dance et al. (1991) [34]. However, the authors suggested that the discrepancies might have been due to the methodology used, indicating that the preparative method of the complex influences its stability towards oxidation. The textures of the complexes show a columnar mesophase based on stacking of cyclic $[\text{Cu}_4(\mu_2-\text{SC}_n\text{H}_{2n+1})_4]$ aggregates, with transition temperatures ranging from 56 to 210 °C.

A new class of copper(I) metallomesogens based on copper(I) halide complexes with thiourea-based ligands with long-chain alkoxy groups and a perfluoroctyl group were reported in 2018 by Ilis and Circu [35] (Figure 2). They found no liquid crystalline behavior

for the ligand but observed a hexagonal columnar phase for both complexes **2a** and **2b** at high temperatures above 100 °C via a combined study of POM, DSC, and XRD, while the thermal stability studied by TGA indicated a higher stability (180 °C) for the corresponding copper(I) complexes compared to that of the BTU (160 °C) ligand.

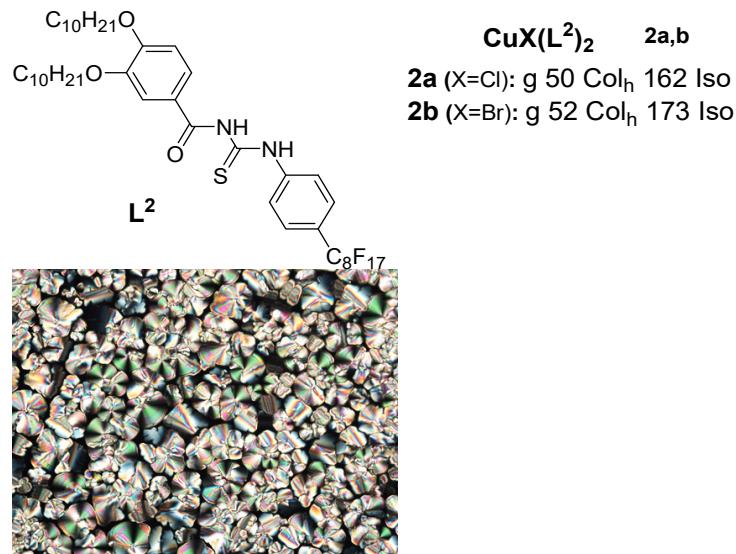


Figure 2. Copper(I) complexes with benzoylthiourea ligands. Transition temperatures are in °C. Inset: POM image of the Col_h phase of **2a** at 85 °C [35].

3. Copper(I) Metallomesogens with N-Donor Ligands

Many copper(I) complexes with N-donor ligands integrating pyrazole, 2,2'-bipyridine, 1,10-phenanthroline moieties, or Schiff bases have been described to date. Copper(I) metallomesogens with three-coordinate geometry were first reported by Lin et al. in 2001 [36]. The complexes were derived from bis[2-[3'-(3'',4''-dialkoxyphenyl)-5'-methyl-1'-pyrazolyl]ethyl] ethers and from bis[2-[3'-(3'',4',5'-trialkoxyphenyl)-5'-methyl-1'-pyrazolyl]ethyl] ethers. These novel complexes were obtained by complexing the ethers with [Cu(MeCN)₄]BF₄ (Figure 3). The reported copper(I) complexes with four or six alkoxy chains exhibited liquid crystalline behavior and are characteristic of columnar discotics. DSC analysis results indicated a higher enthalpy for the melting transitions at lower temperatures and a relatively lower enthalpy for the isotropization transitions at higher temperatures. The attachment of an additional alkoxy chain on the terminal benzene ring resulted in lower transition temperatures, while preserving the mesophase type (Col_{hd}).

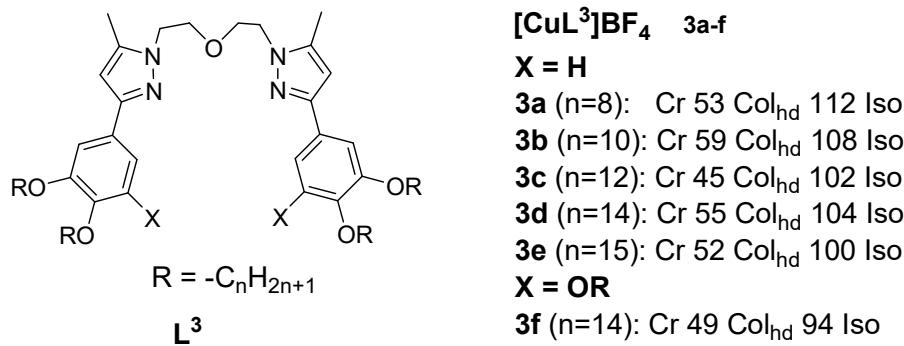


Figure 3. Copper(I) complexes with ether-type ligands. All temperatures are in °C [36].

Schiff bases are a diverse group of compounds formed by the nucleophilic substitution reaction of an aldehyde or ketone with an amine. These compounds are characterized by the presence of a double bond linking carbon and nitrogen atoms, the functionalities of which are

generated in many ways to combine a variety of alkyl or aryl substituents useful for the design of liquid crystalline materials, either organic or metallomesogens [37–42]. The lone pair of electrons on nitrogen provides a basis for making complexes with metals, including copper(I). Diverse liquid crystalline copper(I) complexes have been prepared with these ligands; the resulting complexes are indicated in Figure 4. Dinuclear copper(I) complexes (**4a** and **4b**) with Schiff bases based on the α,α' -imino-substituted 2,2'-bipyridine unit were developed by El-ghayoury et al. [43]. The two ligands adopt a rather unusual coordination mode in which the central unit bridges the two copper(I) centers. The tetrahedral surrounding is completed by the coordination of the two imino groups of each Schiff base ligand with the iminopyridine fragment chelated in a cis fashion to provide a symmetric structure. Complex **4a** is non-mesomorphic, owing to the unsuitable balance between the aliphatic chains and the aromatic core. The optical textures observed upon slow cooling of the isotropic melt of complex **4b** clearly indicate the existence of a viscous columnar phase at temperatures as low as 25 °C.

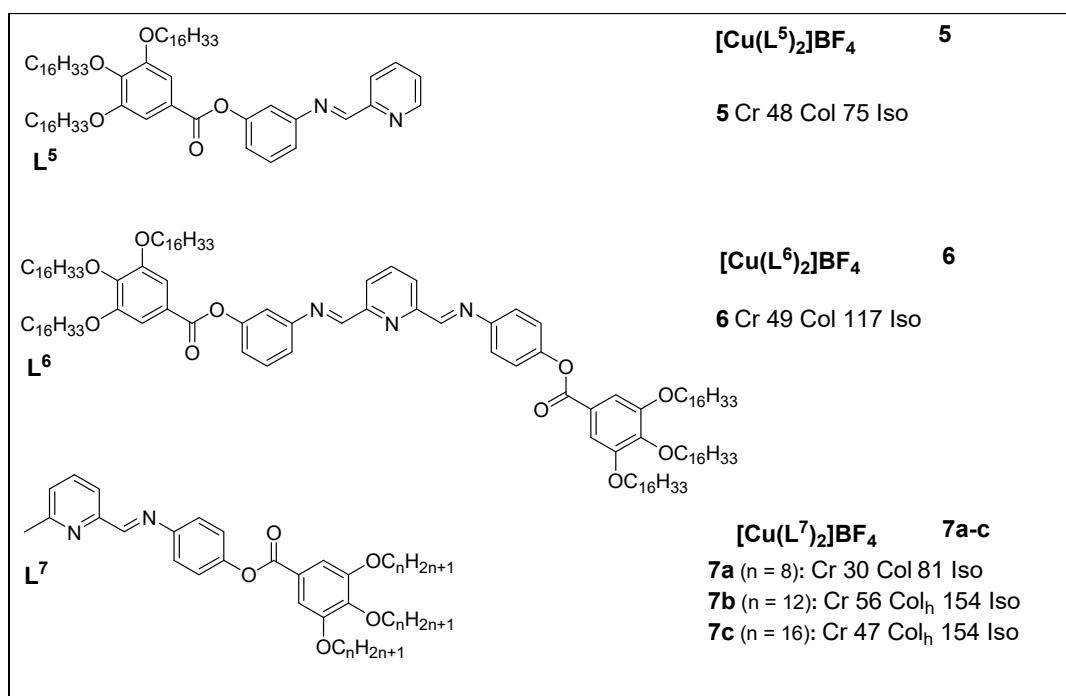
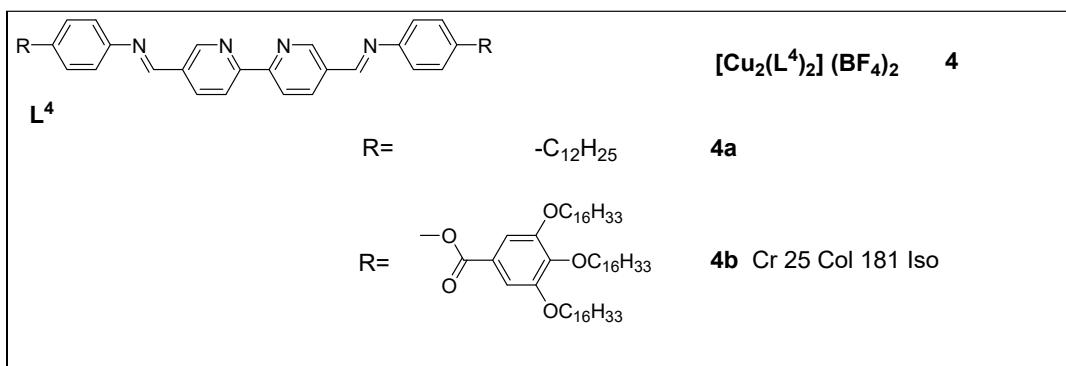


Figure 4. Copper(I) metallomesogens with Schiff bases. All transition temperatures are in °C (transition temperature for **4a** not reported) [43–45].

Although non-mesogenic, upon complexation with copper(I), free ligands **L⁵** and **L⁶** showed mesogenic character, as described by the DSC and POM experiments. The results

indicated that complex **6** showed high stability after several heating cycles relative to complex **5**, which was thought to be due to the lack of substituents at position 6. In addition, the optical textures observed for complex **6** during slow cooling from the isotropic melt are typical of a columnar phase (with pseudo-focal-conic textures [45]). Similarly, Douce and coworkers prepared new complexes (**7a–c**) by modifying the organic ligands to enable scrutiny of the nature of the packing in the liquid crystalline phase. In their work, the authors reported the preparation of new ligands with various chain lengths ($n = 8, 12$, and 16) bearing an additional methyl fragment in the α -position of the pyridine ring in order to protect the copper complex (**5**) against oxidation and decomplexation. The prepared complexes displayed hexagonal columnar mesophases with a transition temperature range of 30 to 56 $^{\circ}\text{C}$ [44].

A study by Ziessel et al. (2004) [46] presented mesomorphic materials based on copper(I) complexes with phenanthroline-based ligands (Figure 5). The authors aimed to engineer a structural framework with additional supramolecular binding factors (hydrogen bonding) so as to stabilize the mesophase both as a free ligand and within the complex. The thermotropic properties of the ligands and complexes of the phenanthroline derivatives were investigated via a combination of POM, DSC, and XRD methods. The ligand used for complexes **8b** and **8c** showed distinct cubic and disordered lamellar mesophases at different temperature regions in the reported XRD measurements. Neither the ligand with the shortest chain ($n = 8$) nor the corresponding copper(I) complex (**8a**) displayed any mesomorphic behavior in the investigated temperature region, but as expected, the related copper(I) complexes with longer chains (**8b** ($n = 12$) and **8c** ($n = 16$)) showed mesomorphic behaviors, displaying mesophases characteristic of an oblique columnar phase. In effect, the complexation of the metal center with the organic ligand resulted in a distinct change in the mesomorphic properties. It was observed that the mesophase stability was enhanced upon coordination with copper(I), as reflected by the large increase in the clearing temperature by nearly 50 $^{\circ}\text{C}$, whereas the melting temperature remained almost the same for the ligands, as well as for the corresponding complexes.

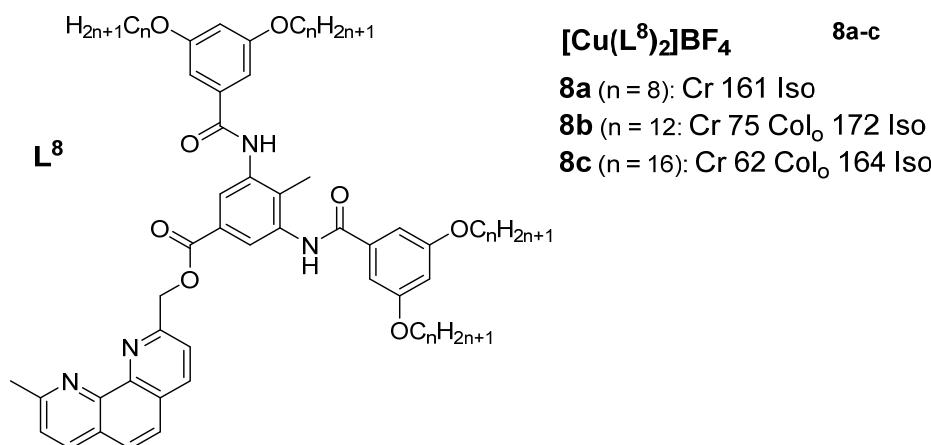
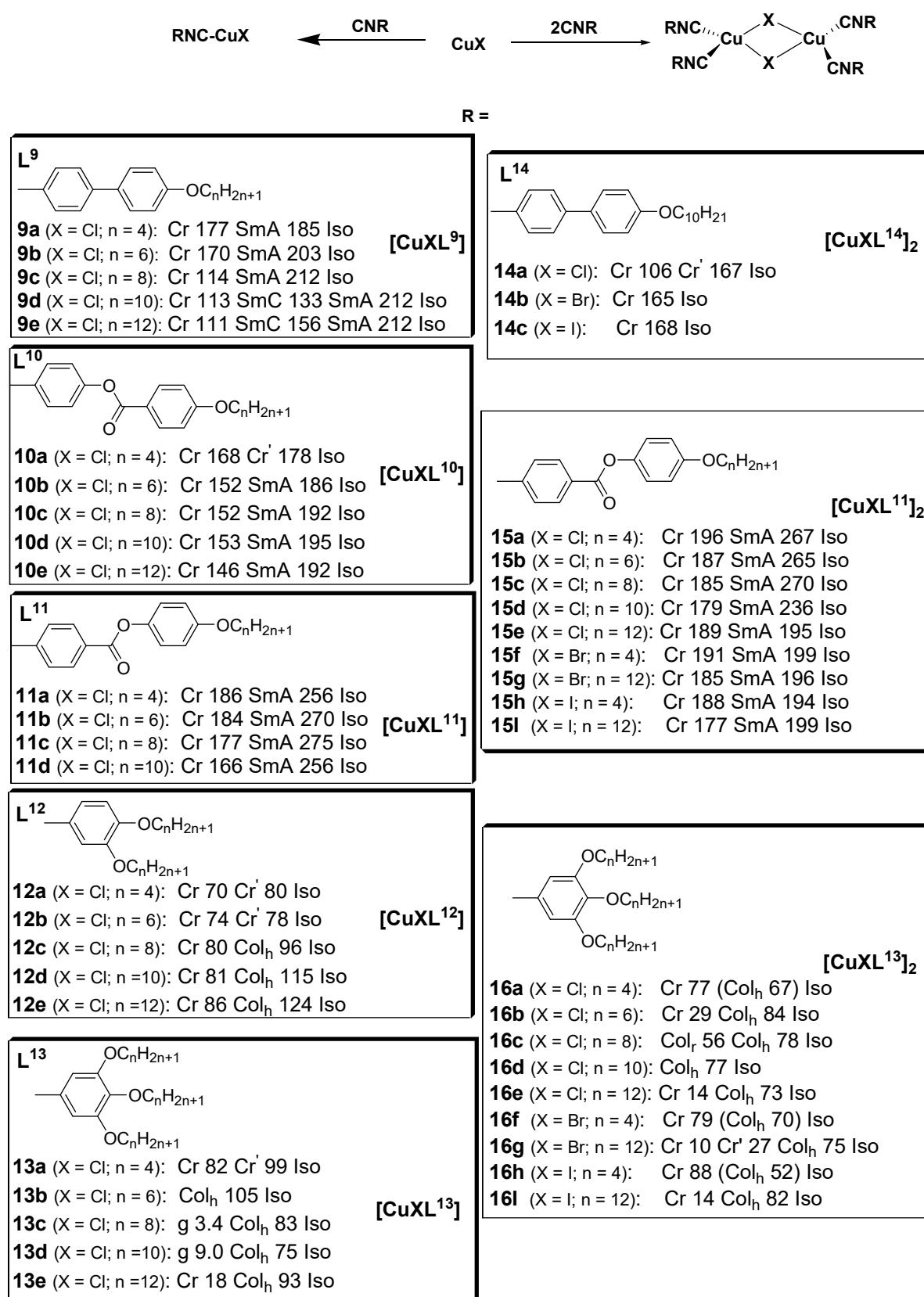
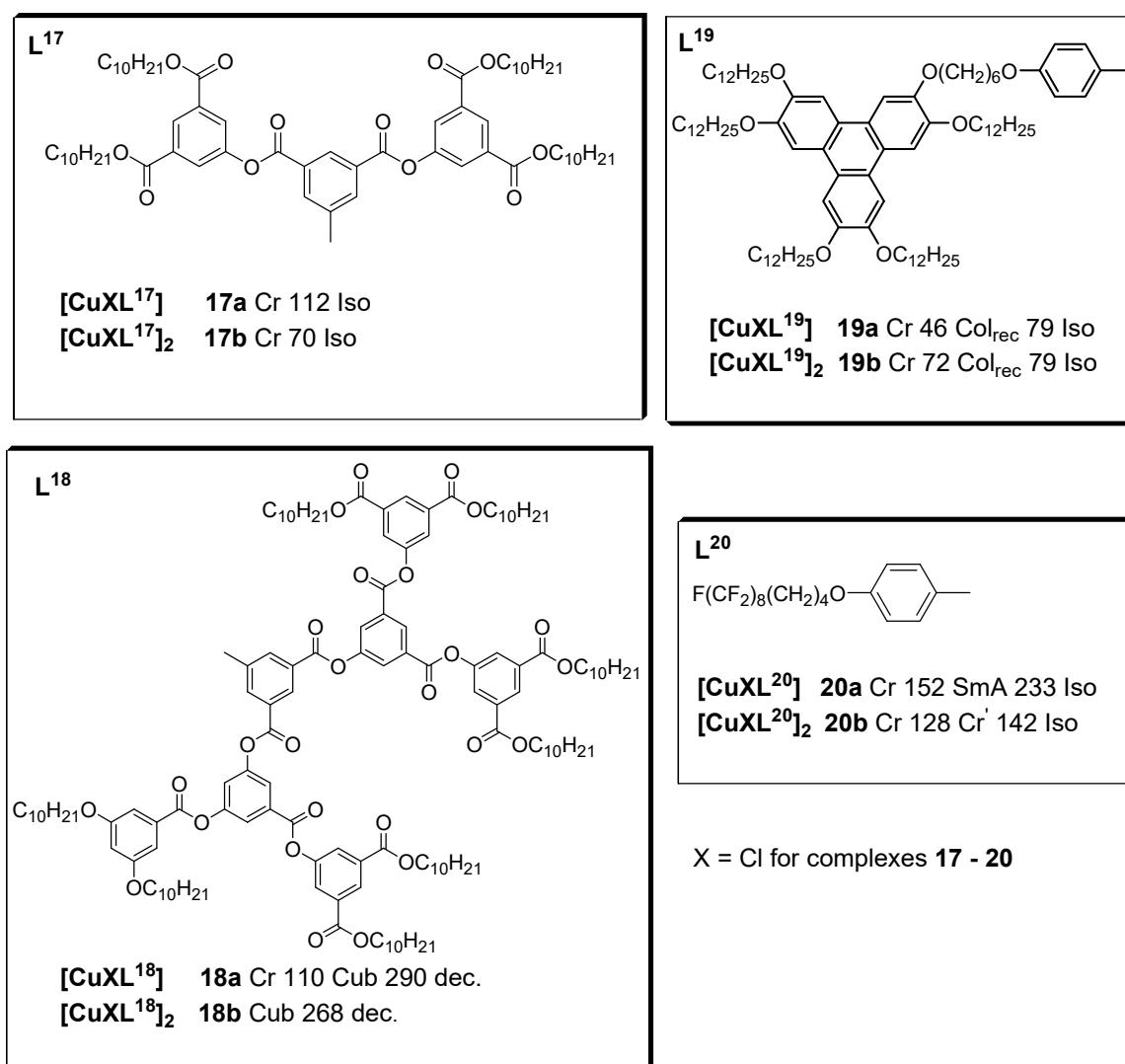


Figure 5. Copper(I) complexes with phenanthroline-based ligands. Temperatures are in ($^{\circ}\text{C}$) [46].

4. Copper(I) Metallomesogens with Isocyanide Ligands

Isocyanides are a class of organic compounds of the R-NC type, where R is a combination of groups obtained by the removal of a hydrogen atom from an organic compound and the carbon therein is triply bonded to nitrogen, the site of which is also capable of coordinating with metals. The isocyanides are isomers of the nitriles and are largely used in coordination chemistry [47]. These kinds of ligands have been used to design a large variety of transition metal complexes [48] and copper(I); metallomesogens are also well known for this. In general, the reaction of isocyanides with CuX (X is halide) resulted in a mononuclear complex; on the contrary, reaction of two equivalents of the isocyanide derivatives with CuX yielded binuclear copper(I) complexes, as depicted in Figure 6.

**Figure 6.** *Cont.*



X = Cl for complexes **17 - 20**

Figure 6. Mononuclear and dinuclear copper(I) isocyanide complexes. Transition temperatures are in °C [49–53].

The first set of liquid crystals based on copper(I) isocyanide complexes was reported in 2001 by Benouazzane et al. [52]. Some of the isocyanide ligands (L^{9-11}) were reported to display nematic and/or smectic A phases. The copper complexes (**9a–e**) showed SmA and SmC mesophases, while complexes **10b–e** and **11a–d** were found to display only SmA phases [52]. Further study indicated that the range of the SmC phase increases and that of the SmA phase decreases as the length of the chain increases. All the copper isocyanides reported in Figure 6 are mesogenic, except complexes **10a**, **12a**, **12b**, **13a**, **14a–c**, **20**, **17a,b**, and **20b**. The isocyanide ligands L^{12} and L^{13} , with a single aromatic ring, did not appear to be mesogenic, but upon complexation with copper(I), all the complexes (except **13a** with the shortest chain ($n = 4$)) showed liquid crystalline behavior.

After the successful preparation of stable linear copper(I) liquid crystals (complexes **9–13**) with isocyanide ligands reported in [52], in 2002, the same research group subsequently reported another series of binuclear copper(I) complexes (**14–16**) with mesogenic properties. The free isocyanide ligands were reported as promesogenic, with nematic and/or smectic A phases. Copper complexes **14a–c** lack mesogenic properties, whereas, copper complexes **15a–i** were found to be mesogenic. On the other hand, although the uncomplexed isocyanide ligands (L^{13}) are not liquid crystals, all their dinuclear copper isocyanide complexes (**16a–i**) had liquid crystalline properties, displaying columnar mesophases [53]. These liquid crystalline binuclear copper(I) complexes with isocyanide ligands reported by Benouazzane et al. were

the first examples of liquid crystals with a core formed by two tetrahedral structures sharing an edge. Dendrimers based on isocyanides were first reported by Coco et al. (2008) [51]. The authors found that whereas all the free, highly branched isocyanide ligands (**L¹⁷** and **L¹⁸**) and the metal complexes (**17a** and **17b**) were not liquid crystals, complexes **18a** and **18b** showed a cubic mesophase.

Chico et al. [50] reported two isocyano-triphenylene copper(I) complexes (**19a** and **19b**), both of which displayed good thermal stability in the range of study. The free isocyanide ligand appeared not to be mesomorphic, as observed by POM. The identification of the columnar mesophase for **19a** and **19b** was achieved by small-angle X-ray scattering on powder samples, which was measured as a function of temperature, consistent with the DSC and POM experiments. For these complexes, the columnar mesophases were stable in the temperature range of 46 to 79 °C.

The effect of incorporating a fluorinated chain in an isocyanide ligand with respect to its mesomorphic behavior when compared to its hydrocarbon derivative was studied by Dembinski and coworkers [49]. Previously, several studies [54–56] had investigated the fluorophobic effect of single aromatic ring-containing organic molecules containing a perfluoroalkyl chain; as such, a study was carried out on fluorinated analogs of hydrocarbon complexes in which mesomorphic behaviors had not been previously observed. The semi-perfluorinated isocyanide ligand (**L²⁰**), in contrast to its alkyl analog, exhibited liquid crystalline properties, showing a smectic A mesophase upon both heating and cooling. This was attributed to the fluorophobic effect, allowing for the mesogenicity of the isocyanide compound with a single benzene unit. The corresponding mononuclear copper complex retained the mesophase but with a high crystalline–mesophase transition temperature (152 °C), while the dinuclear analog did not show liquid crystalline properties [49].

5. Luminescent Metallomesogens Based on Copper(I) Complexes

A major drawback in the study of the physical properties of metallomesogens is associated with issues relating to their high transition temperature and stability at elevated temperatures. It becomes increasingly difficult to study the emissions at such high temperatures due to strong tendencies of the excited electrons to undergo deactivation via non-radiative transitions [12]. Few attempts have been made in this regard, and interesting findings have been reported. The luminescence data of the copper(I) complexes discussed in this section are summarized in Table 1.

Table 1. Summary of luminescence data for copper(I) metallomesogens reported in [57–60].

Complex	Phase (T/°C)	$\lambda_{\text{em}}^{\max}$ [λ _{exc}] (nm)	t (μs)	QY (%)
21a	Iso (80)	650 [280]	-	-
	Cr (20) [na]	640 [280]	11	-
	Cr (20) [a]	615 [280]	9	-
21b	Iso (80)	650 [280]	-	-
	Cr (20) [na]	650 [280]	15	-
	Cr (20) [a]	610 [280]	14	-
22	Cr (20) [na]	650 [280]	7	-
	Cr (20) [a]	640 [280]	-	-
23a	Col _h (25)	661 [290]	28	42
23b	Cr (25)	664 [290]	26	14
	Col _h (50)	664 [290]	22	-
23c	Cr (25)	663 [290]	21	24
24	SmA (25)	404, 519 [280], 519 [400]	-	-
	g (-196)	401, 487, 522 [280], 490, 522 [400]	-	9
24 [pg]	SmA (25)	385, 549 [280], 536 [400]	-	-
	g (-196)	397, 494, 529 [280], 496, 529 [400]	-	1

Table 1. Cont.

Complex	Phase (T/°C)	$\lambda_{\text{em}}^{\max}$ [λ _{exc}] (nm)	t (μs)	QY (%)
25a	Cr (25)	578 [570]	-	2.4
	L _{colg} (50)	-	-	0.7
	L _{col} (80)	-	-	0.2
	L _{col} (100)	-	-	0.06
25b	Cr (25)	578 [570]	-	2.2
	L _{colg} (50)	-	-	0.5
	L _{col} (80)	-	-	0.2
	L _{col} (100)	-	-	0.04
26a	Cr (25)	560 [570]	-	1.5
	Col _h (50)	-	-	0.4
	Col _h (80)	-	-	0.1
	Iso (100)	-	-	<0.01
26b	Cr (25)	560 [570]	-	1.1
	Col _h (50)	-	-	0.4
	Col _h (80)	-	-	0.2
	Iso (100)	-	-	<0.01

t = averaged lifetime; QY = absolute quantum yield; λ_{em} = wavelength of maximum emission; λ_{exc} = excitation wavelength; na = non-aged; a = aged; Pg = ground sample; SmA = smectic A phase; g = glassy state; Cr = crystalline phase; Iso = isotropic liquid; L_{col} = lamello-columnar phase; Col_h = columnar hexagonal phase; L_{colg} = frozen lamello-columnar phase.

Kishimura et al. were the first to describe the emission properties of copper(I) complexes in their liquid crystalline phase [57] in 2005. They reported a number of dendritic copper(I) pyrazolate complexes **21** and **22** (Figure 7), which were used to produce some thermally rewritable phosphorescent papers useful for security purposes.

The luminescence investigation of complexes from the pyrazolate ligands L²¹ [57] revealed dichroism at room temperature for the solid form of complex **21a**. Cooling of the hot melt (which emitted a red luminescence at λ_{max} 650 nm) naturally or by slow cooling led to blue-shift emission 640 and 610 nm. In essence, the red and yellow luminescence observed for **21a** could be thermally changed from one form to the other, depending on the manner and rate of cooling, which was also found to be the case for its liquid crystalline properties. Both the analyze complex (**21a**), both in aged and non-aged form, appeared to be phosphorescent, which is thought to a result of Cu(I) to Cu(I) interactions [57]. The photoluminescent data are summarized in Table 1.

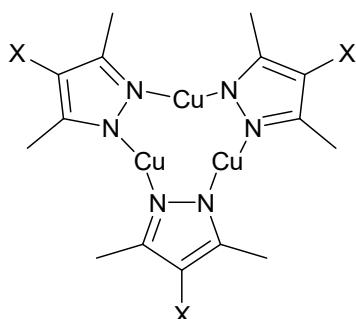
Furthermore, XRD analysis of the aged sample of complex **21a** showed diffraction patterns synonymous with a one-dimensional columnar phase, and the same complex (**21a**) viewed under a polarized optical microscope showed a fan-shaped texture characteristic of discotic liquid crystals; accordingly, it was concluded that the aged complex (**21a**) was composed of long-range discotic columnar assembly. The XRD pattern of the non-aged complex after natural cooling also indicated the presence of a columnar structure. DSC measurements carried out on the aged and non-aged complex (**21a**) revealed patterns based on which it was concluded that the discotic columnar assembly, which is believed to involve metallophilic interactions of Cu(I) to Cu(I) units with long alkyl chains, is formed in the aging process at about 40–50 °C. The stability of the dichroic luminescence was therefore found to be dependent on the pyrazolate ligand structure. Complex **21b** exhibited similar phosphorescent properties as complex **21b** upon rapid and slow cooling of its hot melt; however, the red luminescence turned yellow spontaneously, even at very low temperatures. For complex **22** (Figure 7), which has more dendritic units than the other studied complexes, did not show a clear luminescence dichroism, and aging of the complex **22** by slow cooling of its hot melt resulted in only a 10 nm red shift of the luminescence [57].

Building on the aforementioned work by Kishimura and coworkers, Gimenez et al. (2020) [58] recently reported a series of liquid crystals achieved with cyclic trinuclear copper(I) complexes (**23a** and **23b**) prepared using 3,5-dimethyl-4-(trialkoxyphenyl) pyrazolate ligands

(Figure 7). The compounds displayed well-organized hexagonal columnar mesophases, which were found to be stable at room temperature or near room temperature (Figure 8).

Both complexes **23a** and **23b** were reported to have orange-red-colored emissions at room temperature, and the photoluminescence exhibited a broad band centered around 661–664 nm (Figure 9). A landmark reported in this study [58] is the high quantum yield (QY) value of 42% measured in the liquid crystalline state, which is the highest recorded to date for any copper(I) metallomesogen. The QY obtained for **23a** in its liquid crystalline state was higher than that obtained in the crystalline states of complexes **23b** and **23c**. Thus, the work carried out by Giminez et al. [58] showed that low-temperature phosphorescent metallomesogens can be obtained from the more affordable and abundant copper metal.

Camerel et al. (2016) [59] reported a new class of copper(I) liquid crystals with a cubane core and based on phosphine ligands functionalized with promesogenic gallate-based moieties bearing either long alkyl chains of C8, C12, and C16 or cyanobiphenyl (CBP) fragments (Figure 10). Copper(I) cubanes are known for their ability to display both luminescence mechanochromism and thermochromism behavior [61–64].



Trinuclear Cu-Pyrazolate complex

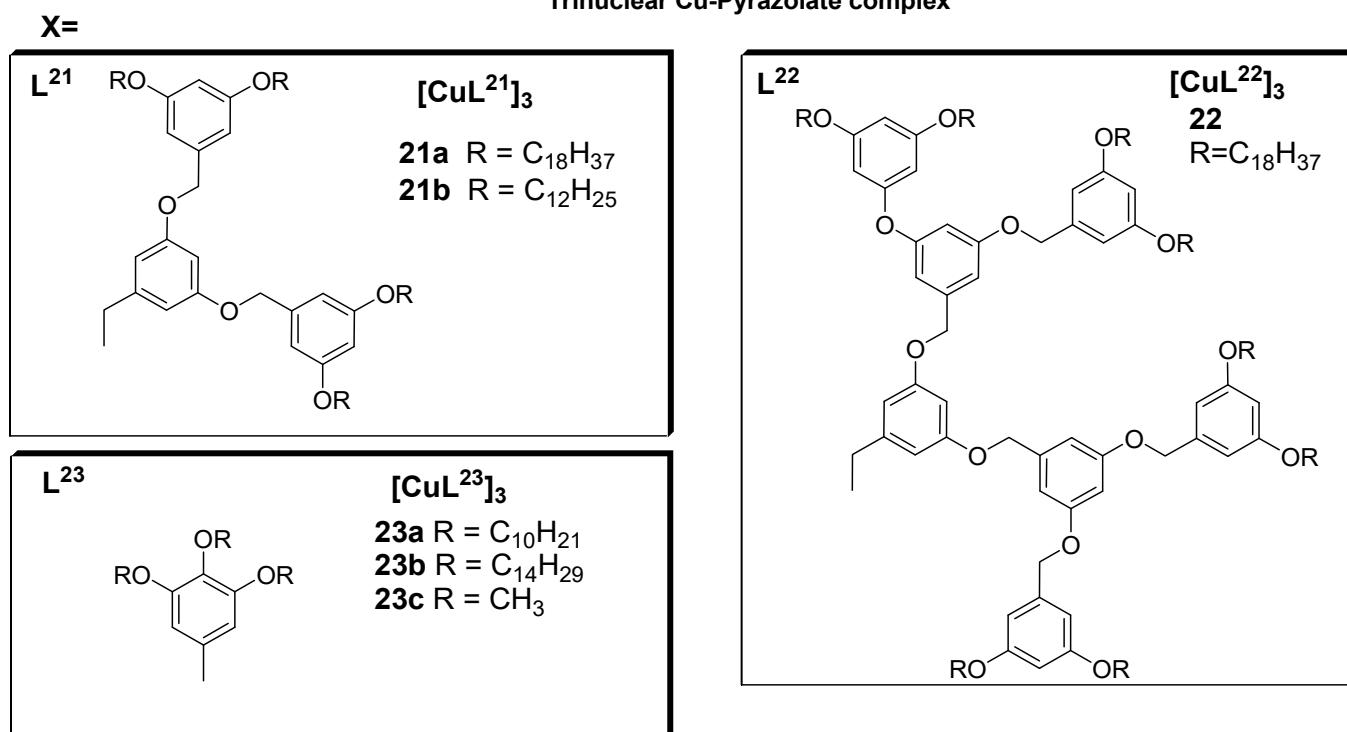


Figure 7. Ligands and representative structure of the copper pyrazolate complexes reported in [57,58].

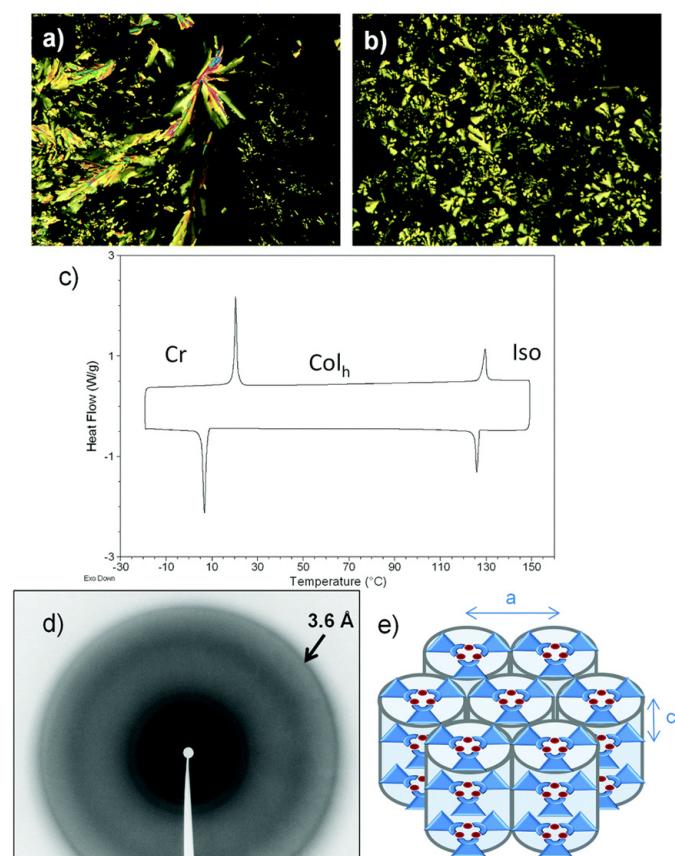


Figure 8. (a) Microphotograph of the region between crossed polarizers observed for the texture of the Col_h phase of **23a** upon cooling of the isotropic liquid at $126\text{ }^\circ\text{C}$. (b) Microphotograph of the region between crossed polarizers observed for the texture of the Col_h phase of **23b** upon cooling of the isotropic liquid at $98\text{ }^\circ\text{C}$. (c) DSC thermogram of **23a**. (d) XRD patterns of the Col_h phase of **23a**. The arrow indicates the halo corresponding to the stacking distance. (e) Self-assembly in the hexagonal columnar mesophase. (Reproduced from ref. [58] with permission from the Royal Society of Chemistry).

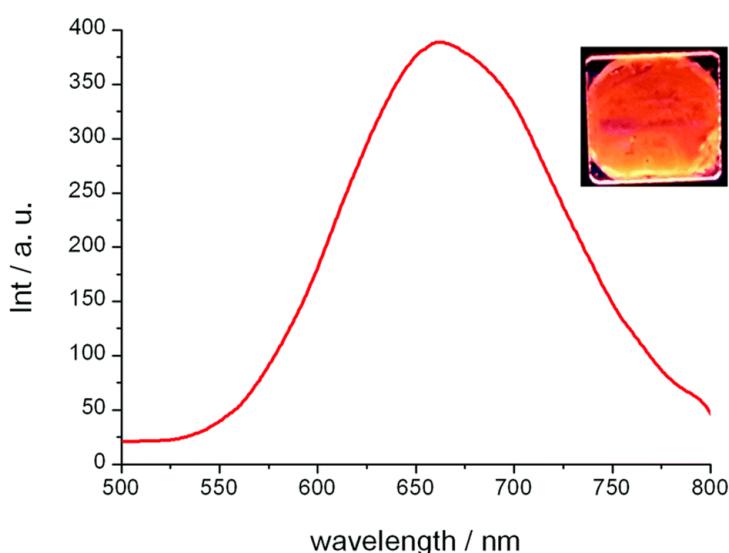


Figure 9. Photoluminescence spectrum in the columnar mesophase for **23a** at $25\text{ }^\circ\text{C}$ (excitation wavelength, 290 nm) and emission of the film observed under irradiation with a 254 nm handheld lamp (reproduced from ref. [58] with permission from the Royal Society of Chemistry).

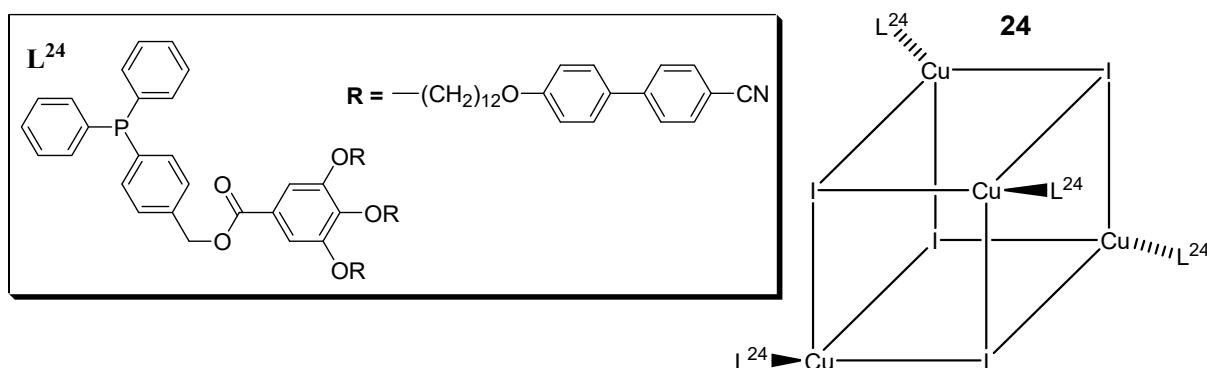


Figure 10. General structure of the functionalized $[\text{Cu}_4\text{I}_4(\text{L}^{24})_4]$ copper iodide clusters with phosphine ligands [59].

This study is an inventive example of integrating luminescence characteristics of copper iodide clusters $[\text{Cu}_4\text{I}_4(\text{L}^{24})_4]$ with the flexible self-assembly of liquid crystals. Only the compound functionalized with a cyanobiphenyl group (CBP), i.e., **24**, showed liquid crystalline behavior, displaying an SmA mesophase from room temperature to about 100 °C.

All the complexes reported in the work by Camerel et al. [59] revealed luminescence thermochromism for all the studied compounds; however, complex **24** displayed an unclassical behavior, which was attributed to the intrinsic luminescence properties of the cyanobiphenyl moiety itself, with a dual-emissive system that presented interesting emission properties. In addition to its liquid crystalline properties, compound **24** displayed luminescence mechanochromism with a modification of the emission wavelength in response to grinding (Figure 11).

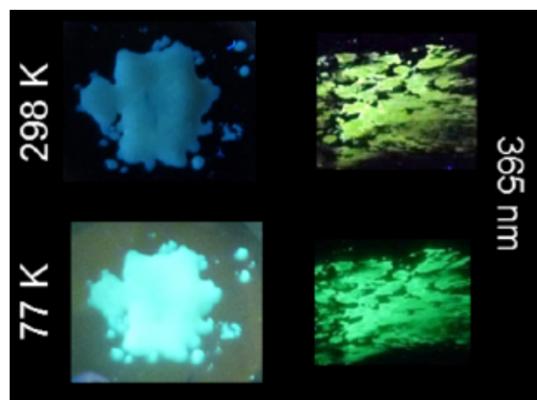


Figure 11. Photos of **24** under 365 nm (UV lamp) before and after grinding at 298 and 77 K. Reprinted (adapted) with permission from Chem. Mater. 2016, 28, 22, 8190–8200 (ref. [59]). Copyright 2016 American Chemical Society.

Cretu et al. (2018) [60] reported a new class of Cu(I) coordination complexes (**25a**, **25b**, **26a**, and **26b**) with 4,4'-bisubstituted-2,2'-biquinolines as depicted in Figure 12, which showed low-temperature lamello-columnar and columnar hexagonal thermotropic liquid crystalline phases. The highest deduction from the luminescence study is the presence of a medium-low-intensity band with a series of shoulders at 578 nm for **25a** and **25b** and at 560 nm for **26a** and **26b**, which is believed to be due to metal-to-ligand charge-transfer (MLCT) electronic transitions. When the solid samples were heated, they moved towards the liquid crystalline phases and retained the luminescence displayed in the solid state; however, with increased temperature, the intensity of the luminescence band decreased, and at temperatures over 120 °C, luminescence was completely quenched, although reversed with subsequent cooling of the samples. This behavior is attributed to the gain of the non-radiative kinetic constants when vibrational modes were enhanced by heating the samples [60].

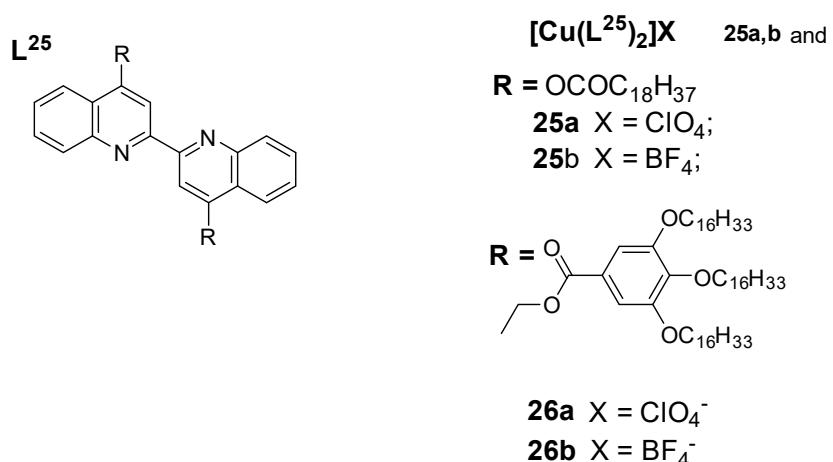


Figure 12. Copper(I) complexes with bisubstituted biquinoline ligands [60].

6. Conclusions

This review provides an overview of the different strategies imagined by chemists to control the LC properties of copper(I) complexes, focusing on their luminescent properties. Examples of copper(I) metallomesogens based on isocyanide ligands are, by far, the most prevalent. By utilizing suitable mesogenic groups, their LC characteristics can be simply modified. While a few other isocyanides produced hexagonal and rectangular columnar phases, as well as a cubic phase for the dendritic isocyanide supermolecules, the bulk of these complexes exhibit calamitic behavior with either SmA or SmC phases. The reported copper(I) complexes of Schiff-base-type ligands of bipyridine imine-, 2-iminopyridin-, and picoline-substituted imino ligands and those of alkyl thiolates all displayed varying columnar mesophases with different transition temperature ranges. Both the ether type and benzoyl thiourea ligands displayed characteristics of a hexagonal columnar mesophase for the corresponding metallomesogens, while the copper(I) complexes from phenanthroline ligands had an oblique columnar mesophase. Furthermore, interesting luminescent properties in liquid crystalline states were observed for copper(I) complexes from ligands with pyrazolate derivatives, phosphine ligands functionalized with copper iodide, and those of bisubstituted biquinoline ligands. The complex from the functionalized phosphine ligand displayed interesting mechanochromic luminescence characteristics. A high quantum yield of 42% in the liquid crystalline phase of the copper(I) metallomesogens from a pyrazolate ligand was reported. This work provides a basis for the design and preparation of many new multifunctional materials based on more copper(I) complexes with liquid crystalline behavior and improved luminescent properties.

Author Contributions: M.A.—literature search and original draft; V.C.—conceptualization, review, and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data sharing is not applicable to this article.

Acknowledgments: M.A. thanks the Romanian Ministry of Foreign Affairs and the University of Bucharest for funding and provision of other resources (project C1.2.PFE_CDI.2021-587/contract no.41PFE/30.12.2021).

Conflicts of Interest: There are no conflicting interest.

Abbreviations

LC—liquid crystal; DSC—differential scanning calorimetry; POM—polarizing optical microscopy; XRD—X-ray diffraction; TGA—thermogravimetric analysis; SmA/C—smectic A/C phase; Col_{rec}—rectangular columnar phase; Col_h—hexagonal columnar phase; Col_{hd}—disordered hexagonal columnar phase; Cub—cubic phase; dec.—decomposition; g—glassy phase; Iso—isotropic liquid phase; Cr, Cr'—crystalline phases.

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