

Review

LATEST PROGRESS ON LUMINESCENT HOMO- AND HETERO-POLYMETALLIC METALLOMESOGENS BASED ON *d*-BLOCK METAL COMPLEXES

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Abstract: Luminescent liquid crystalline metal complexes are attractive multifunctional materials due to their great potential of applicability in a wide range of domains from technological to medical fields. This review is focused on the luminescent homo- and hetero-polymetallic metallomesogens containing *d*-block metal ions and different mono and polydentate ligands published in the last ten years highlighting their ability to self-assembly in ordered lamellar or columnar phases according to their molecular structure. The luminescent properties in solution, solid and liquid crystalline states are also discussed.

Keywords: polymetallic metallomesogens, *d*-block metal complexes, luminescent properties.

INTRODUCTION

Liquid crystals are considered promising materials for different applicative fields due to their adaptive and controllable stimulus responsiveness characteristics with numerous applications beyond liquid crystal displays (LCDs) (Bisoyi et al. 2022). Despite the great potential in various technological, scientific and medical fields, there is a constant need to improve their properties to increase performance in the field of interest. Luminescent liquid crystals are considered novel materials in the production of energy-efficient display devices through their ability to enhance colour, brightness and view angle of display dispositive, eliminating dependency of LCDs by other expensive brightness sources (Kumar et al. 2023). The introduction of a metallic centre into liquid crystals, called “metallomesogens”, gives them unique and desirable properties compared to organic liquid crystals: electrical, redox, magnetic, optical, etc., properties induced by the metal ion (Giménez et al. 2002), being considered extremely promising materials for application in optoelectronics (Krikorian et al. 2014, Geng et al. 2017, Wang et al. 2016), energy (Ionescu et al. 2012, Su et al. 2016), medicine and even in agriculture (Hakemi et al. 2022). The presence of a second metal ion in the molecular architecture can tune the target properties of the

final homo or hetero-bimetallic complex. Moreover, hetero-bimetallic species (metal complexes containing two different metal centre) bring additionally physicochemical properties, metallic complementarity and/or synergism, increasing the capacity for novel application (Wenzel et al. 2014). In the literature, are known some examples of homo- (Cuerva et al. 2021) and hetero-polymetallic metallomesogens (Kadkin et al. 2008) obtained by direct metal-ligand synthesis without an accurate analysis of their functionality-related characteristics. To date, most of luminescent metallomesogens reported are monometallic, and their optical behaviour was studied in solid state or solution (Wang et al. 2012, Wu et al. 2018, Santoro et al. 2009). Due to their reduced stability and high transition temperatures, the optical measurements in the liquid crystalline states become problematic. However, through a proper and smart design of such materials, these drawbacks can be solved obtaining liquid crystals at relatively low to room temperature. Thus, only a limited example of liquid crystalline metal complexes based on zinc(II), copper(I), gold(I), silver(I) and lanthanide(III) ions have shown luminescent properties in liquid crystalline state (Szerb et al. 2022, Binnemans et al. 2009).

Herein, we present the recent progress over the last decade in development of luminescent

metallomesogens containing more than one *d*-block metal centre.

CLASIFICACION OF LUMINESCENT POLYMETALLIC METALLOMESOGENS

Homo-polymetallic metallomesogens

This kind of compounds are liquid crystalline metal complexes that contain two or more identical metal ions coordinated to mono/polydentate ligands forming metal oxide/halogen/fluorophenyl bridged complexes, metallacycles, metallacages, etc.

Chico et al. 2016 reported a homo-bimetallic linear Au(I) complex (**1**) based on a mesogenic isocyanide triphenylene ligand and a biphenyltetrafluoro-linker (Figure 1a). The complex displayed polymorphism when compared to its free ligand that showed only a columnar hexagonal mesophase (Colh) (Figure 1b) from 37 to 130 °C. Thus, complex **1** organized at high temperatures into nematic phase (N) between 122 and 172 °C and at lower temperatures exhibited columnar rectangular (Colr) from 102 to 122 °C.

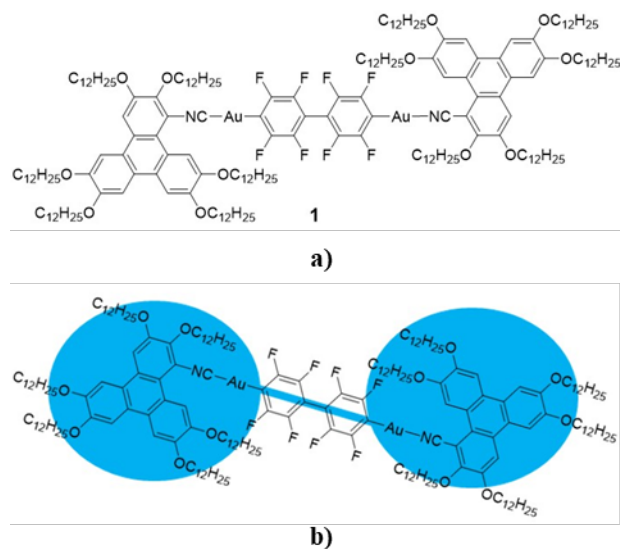


Figure 1. Chemical structure of **1** (a); The proposed molecular packing of **1** (b).

The Au(I) complex **1** showed a blue-violet emission ($\lambda_{\text{ex}} = 282 \text{ nm}$, $\lambda_{\text{em}} = 420 \text{ nm}$) in solution (CH_2Cl_2 , 10^{-5}M) at room temperature, similar with the free ligand. However, the emission quantum yield of the complex [$\Phi (\times 10^{-3}) = 0.0028$] was significantly reduced when compared to the ligand [$\Phi (\times 10^{-3}) = 0.2800$] due

to the increasing of the non-radiative deactivation process generated by the heavy metal effect (Ibrayev et al. 2024). The luminescence of **1** is quenched at higher concentration and also in the solid state and mesophase. Other linear type of bimetallic complexes reported (Al-Karawi et al. 2017) (**2–4**) (Figure 2a) contain hydrazine-based mesogenic ligands that exhibited nematic phases. Their Ag(I) complexes organized into smectic phases at relatively low temperatures (Table 1).

Table 1. DSC and emission data for Ag(I) complexes **2–4**

Comp.	Phase transitions $T_{\text{max}}^{\circ}\text{C}$ ($\Delta H/\text{KJ.mol}^{-1}$) first heating/cooling	Emission data on solid and mesomorphic state, $\lambda_{\text{em}}/\text{nm}$ ($\lambda_{\text{ex}} = 248 \text{ nm}$)
2	Cr ₁ –Cr ₂ 84.2 (20.21) Sm 125.1 (18.67) I / I 123.3 (–19.40) Sm 73.4 (–22.61) Cr ₂ –Cr ₁	494
3	Cr ₁ –Cr ₂ 79.5 (23.31) Sm 113.4 (19.44) I / I 108.2 (–20.94) Sm 65.9 (–24.82) Cr ₂ –Cr ₁	494
4	Cr ₁ –Cr ₂ 83.1 (21.24) Sm 115.3 (18.81) I / I 112.7 (–19.60) Sm 68.3 (–23.20) Cr ₂ –Cr ₁	493

Cr - crystalline solid, Sm - smectic mesophase, I - isotropic liquid

For these bimetallic silver(I) complexes, some interesting characteristics governed the liquid crystalline properties. In particular, similar bimetallic silver(I) complexes with shorter ($n < 6$) or longer chain lengths ($n > 8$) or with an asymmetric position of the azine group (not shown herein) were not mesomorphic. The liquid crystalline Ag(I) complexes (**2–4**) revealed intense blue emission at room temperature, both in solid and mesomorphic state (Table 1) attributed to a ligand-centred transition. However, in the isotropic phase, the luminescence was totally quenched but upon cooling it returns (Figure 2b).

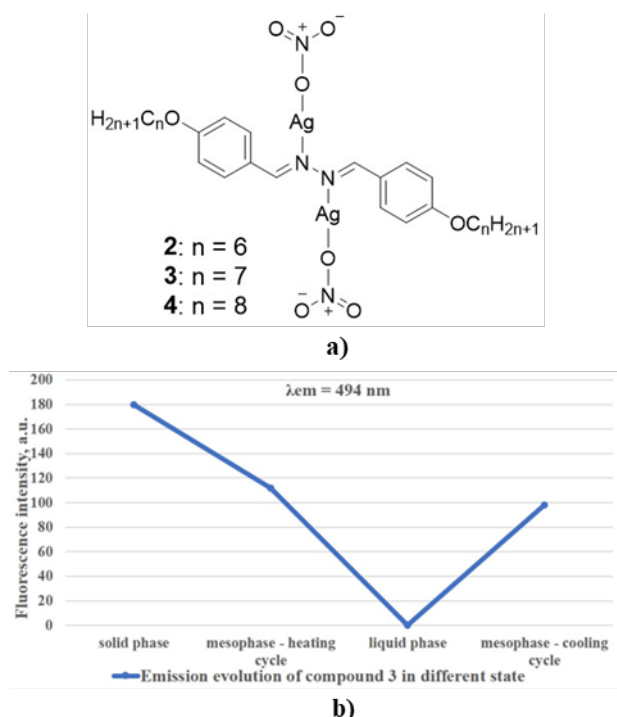


Figure 2. Chemical structure of Ag(I) metallomesogens (a); fluorescence evolution of complex **3** in solid, mesomorphic and liquid phase (b).

Micutz et al. 2014 obtained two homobimetallic Pd(II) complexes (**5** and **6** – Figure 3a) based on a Schiff base and an ancillary benzoyl-thiourea ligands showing mesomorphic properties at low temperatures. Their strategy to obtain room temperature metallomesogens was to vary the number of alkyl chains grafted on the ancillary ligands. Both complexes self-assembled into disordered columnar hexagonal phases that formed glassy mesophases at room temperature. The organization inside the columns slightly differ in the case of the two metal complexes, in the number of molecules filling the disks, from approximatively two molecules for **5** to one molecule for **6** (Figure 3b).

The complexes were emissive in solid state, solution and in the mesophase at room temperature showing a red emission attributed to an intra-ligand transition (Table 2).

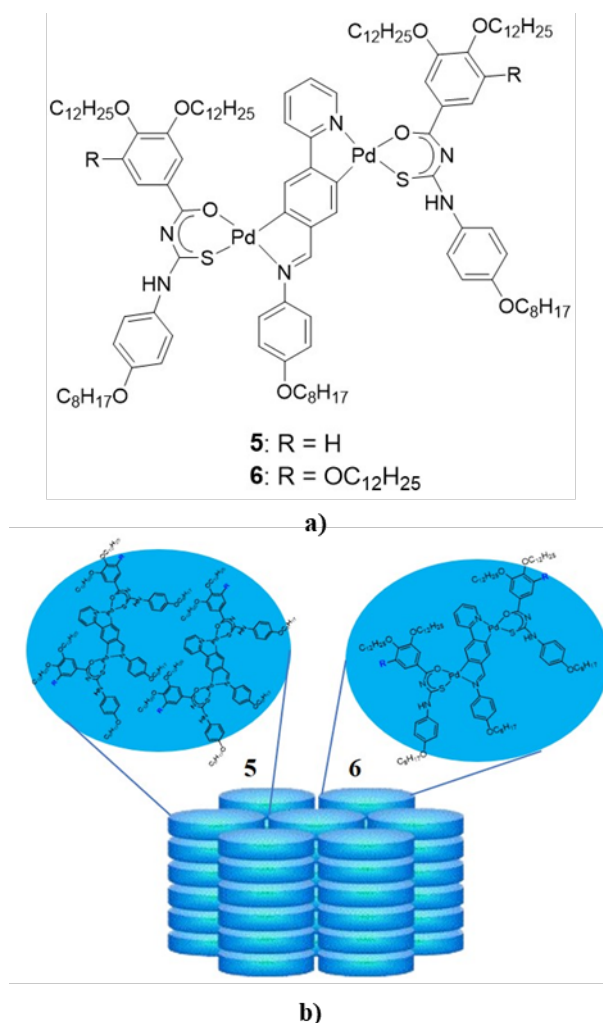


Figure 3. Chemical structure of metallomesogens **5** and **6** (a); the number of molecules that form columnar hexagonal unit (b).

Table 2. Emission data of binuclear Pd(II) complexes **5** and **6**

Comp.	Emission, λ_{em}/nm ($\Phi/%$)		
	Solid state ($\lambda_{ex} = 480$ nm)	Solution (CH_2Cl_2), $C_M = 5 \times 10^{-4}$ ($\lambda_{ex} = 283$ nm)	Condensed state at room temperature
5	546, 676, 736, 819(sh)	365(0.55)	Similar to solid state
6	556, 683, 744, 823(sh)	360(0.39)	Similar to solid state

Pastor et al. 2018 published a series of metal complexes based on derivatives of pyridyl- β -diketone ligands differently substituted with alkyl chains where the position of N-pyridine atom dictated the type of complexes obtained and the liquid crystalline properties in the resulting compounds. Hence, the bimetallic complexes (dimers) **7–10** were obtained with the ligands containing the pyridyl nitrogen atom placed in *ortho* position, where the zinc(II) atoms were linked by two bridging chlorine

atoms (Figure 4a), while the ligands with *para* position of the nitrogen atom have led to mononuclear Zn(II) complexes. These complexes showed SmA phases at high temperatures (over 180 °C) in a very short range of temperature (3 to 6 °C) followed by a re-entrant crystal phase on heating cycle until the clearing temperature (Figure 4b). On cooling cycle, the complexes froze in SmA phase.

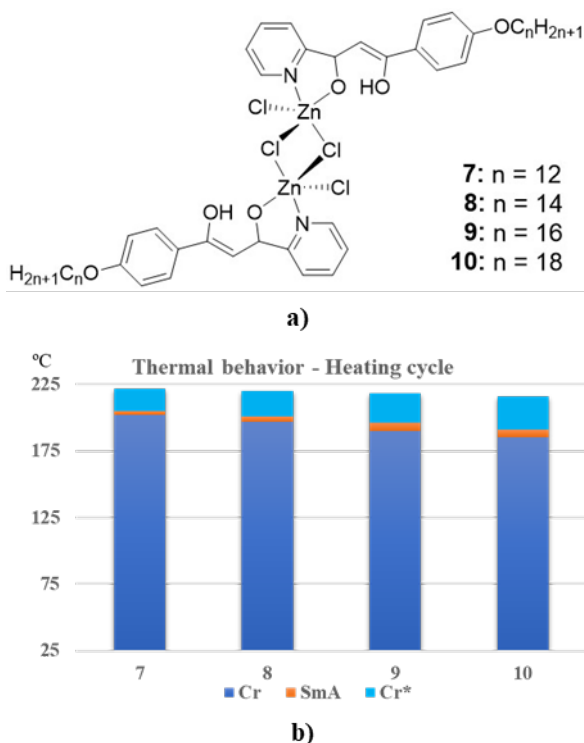


Figure 4. Chemical structure of metallomesogens 7–10 (a); thermal behaviour of the complexes (b) on heating cycle.

Nevertheless, these dimeric complexes had solubility problems that did not allowed the study of the luminescent properties in solution. However, the photophysical behaviour in solid state of only compound 7 was reported as representative of this class showing a blue emission ($\lambda_{em} = 495$ nm).

Pyridine-pyrazolate derivative ligands seem to have an interesting influence on the organization pattern of their Ag(I) complexes depending on the solvent polarity (Soria et al. 2016). Thus, in polar media, 1D oligomers are formed and in apolar solvents cyclic trimers are isolated, the last arrangement being predominantly encountered (Titov et al. 2019, Fujisawa et al. 2021). Therefore, three luminescent homo-polymetallic Ag(I) metallomesogens (11–13)

based on pyridine-pyrazolate type ligands, with cyclic structure and different alkyl chain length were reported by Soria et al. 2016 (Figure 5a). The complexes presented a trimeric structure in solid state that become an open chain 1D oligomeric structure in mesomorphic state and in solution, the Ag–N bond proving to be too weak to maintain the cyclic structure. These 1D oligomeric forms allowed them to self-assembly in smectic A phases at relatively high temperature, over 100 °C, and for compounds 12 and 13 the isotropization point (over 170 °C) was accompanied by decomposition.

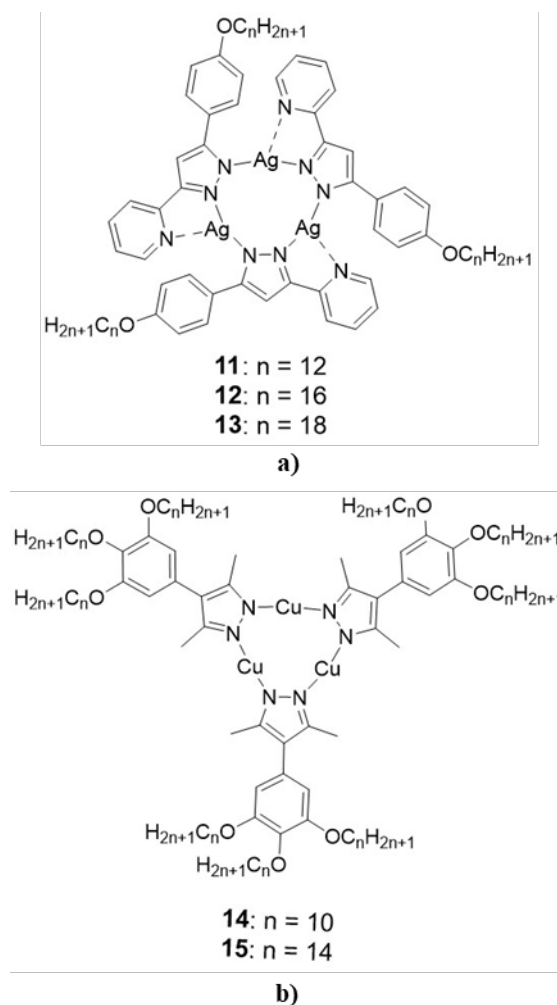


Figure 5. Chemical structure of metallomesogens 11–13 (a) and 14 and 15 (b).

All the Ag(I) complexes (11–13) emit in solution ($\lambda_{em} = 386$ nm, $\Phi = 0.07$ for 11) in their oligomeric form and become non-emissive in the cyclic form. Other cyclic homo-trimetallic Cu(I) metallomesogens (14 and 15) (Figure 5b) derived from phenyl-pyrazolinic ligands with phosphorescent properties were lately reported by Gimenez et al. 2020. Unlike the Ag(I)

metallomesogens **11–13**, the Cu(I) complexes displayed stable 2D columnar hexagonal (Colh) phases over a large temperatures range (108 °C and 57 °C, respectively) and lower clearing temperatures. On cooling cycle, both complexes froze in the mesophase at room temperature. The emissive properties were recorded on neat thin films at room temperature in Colh phase for **14** and in the crystalline phase and mesomorphic state, respectively (50 °C) for **15**. In all cases, an orange–red light emission (661–664 nm) was observed due to the metal-centred triplet state (^3MM) excimer transition with an impressive quantum yield value of 42% for **14**. By increasing temperature from room temperature to 50 °C for **15** a reducing of emission intensity and a minor decrease of lifetime (from 26 to 22 microseconds) were reported. In diluted THF solution, the complexes had a different behaviour showing a violet light emission similar with mesogenic phenyl-pyrazoles type ligands (Blanco et al. 2016). Huitorel et al. 2016 obtained an interesting dual emissive Cu(I) metallomesogen (**16**) based on a $[\text{Cu}_4\text{I}_4]$ cubane cluster and phosphine-based ligands containing cyanobiphenyl (CBP) as mesogenic moieties (Figure 6a). The Cu(I) cluster (**16**) exhibited a smectic A mesophase over a wide range of temperature from 25 °C to 100 °C where the organic moieties (ligand) alternate with the inorganic ones ($[\text{Cu}_4\text{I}_4]$ core) (Figure 6b).

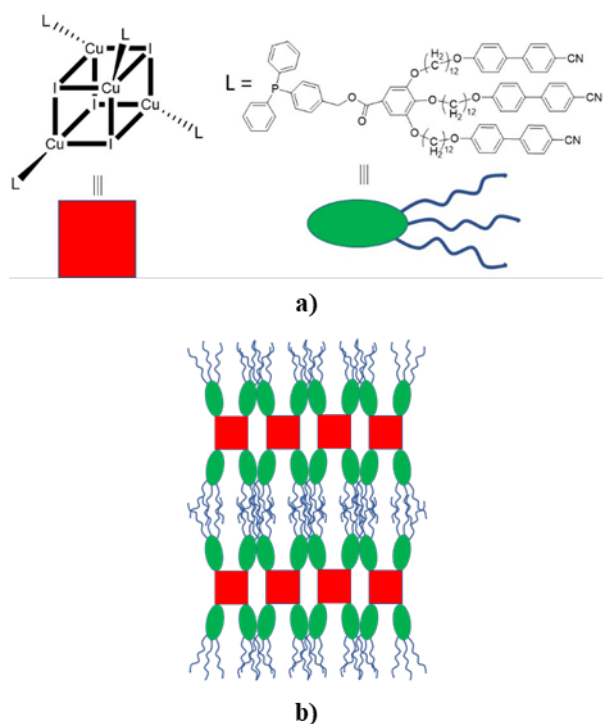


Figure 6. Chemical structure of metallomesogen **16** (a); schematic representation of proposed self-assembly of **16** into smectic A phase (b).

Under the UV light, the complex **16** showed a blue emission at room temperature that become greener by decreasing temperature to -196 °C. This temperature-luminescence dependency is known as thermochromism. Moreover, the luminescence was also influenced by mechanical stimuli as grinding/crushing that generated changes at molecular level by shortening the metallophilic copper-copper bonds and altering the ligands organization. Thus, considerable changes in the colour emission from blue to green-yellow were observed. Chen et al. 2020 reported a luminescent rhomboidal metallacycle (**17**) with both thermotropic and lyotropic properties, formed through a donor-acceptor interaction between an organic donor such as tetraphenylethene moiety and a bimetallic Pt(II) complex bearing hydrophilic chains as acceptor unit (Figure 7).

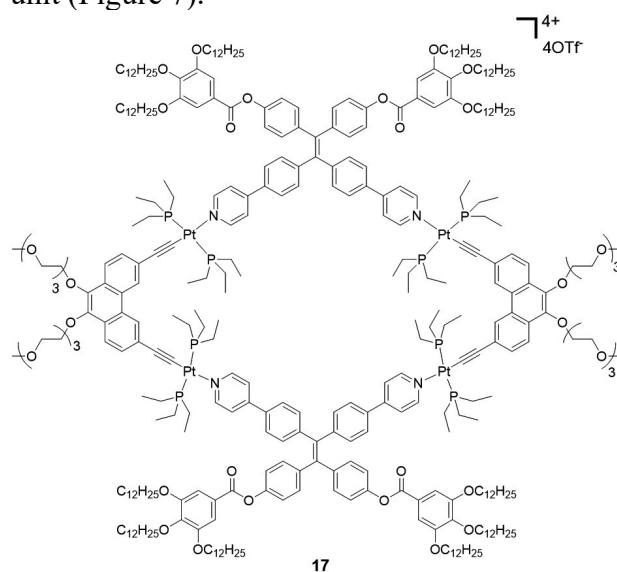


Figure 7. Chemical structure of metallomesogen **17**

The metallacycle **17** self-assembled into a 2D Colr phase at room temperature, stable up to 110 °C, while in DMF solution organizes into Colh mesophase. Through irradiation with UV light ($\lambda_{\text{ex}} = 365 \text{ nm}$) in solution of dichloromethane, the complex **17** emitted green light (544 nm). In dichloromethane/hexane mixture, a progressively increased emission intensity was observed when hexane was gradually added. The increase of the luminescence was attributed

to aggregate formation. The intensity of emission become significant when the hexane volume fraction exceeds 60% recording an increase of the quantum yield value from 1.12% to 8.37%. In the liquid crystalline state, the value of the quantum yield was higher (12.6%) compared to the solution at room temperature with increasing temperature. Furthermore, the influence of temperature on the emission of **17** in the liquid crystalline phase revealed the expected decreasing of the intensity emission due to increase of vibrational modes. So, all these evidences revealed the AIE characteristics of this homo-polymetallic metallacycle.

Hetero-polymetallic metallomesogens

The need of designing hetero-polymetallic metallomesogens with synergistic properties is imperative in the development of more sophisticated and smart devices. In the last few years, there has been a stagnation in the publication of luminescent metallomesogens that contain different metal ions since obtaining these compounds is a real challenge from a synthetic point of view. In this regard, our team reported two luminescent hetero-polymetallic (**18**) and (**19**) metallomesogens obtained from terpyridine derivative ligand and substituted gallate co-ligands bearing ferrocene units (Fc) (Andelescu et al. 2024) (Figure 8).

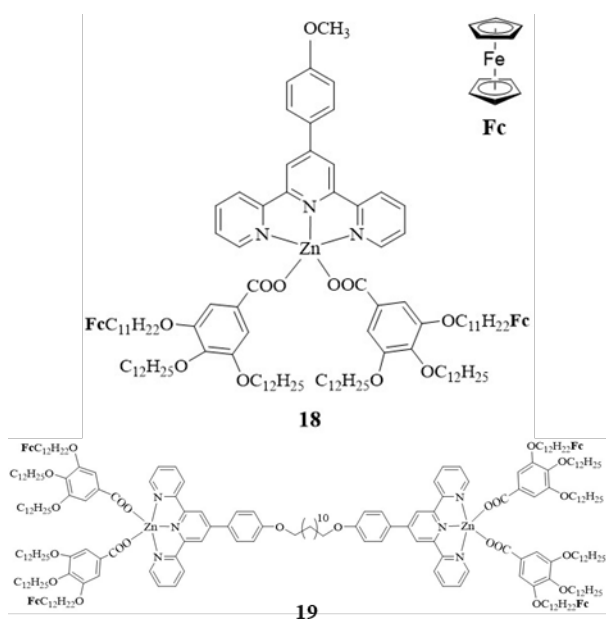


Figure 8. Chemical structure of metallomesogens **18** and **19**.

Both metal complexes exhibited 2D columnar hexagonal mesophases at room temperature for **18** and close to room temperature for **19** (70 °C) stable up to 188 °C and 156 °C, respectively. The presence of the aliphatic chain that linked the two Zn units (**19**) decreased the isotropization temperature to 156 °C for this complex. Moreover, the presence of the ferrocene fragment inserted into the aliphatic region of these metallomesogens led to a lower degree of the mesophase order, from 3D Mhex in the monometallic Zn(II) analogues (Popa et al. 2023) to 2D Colh in the polymetallic species (Popa et al. 2023). The photophysical properties of these metallomesogens were studied in solution and in the condensate states. Thus, in dichloromethane solution a violet emission (414 nm for **18** and 428 nm for **19**) was observed the red-shift of the emission maxima of complex **19** was attributed to vibrational motions caused by the bridging alkyl chain that link the two zinc containing units in case of **19**. The influence of the ferrocene unit in these hetero-polymetallic metallomesogens was also reflected through a red shift of the emission maxima in solution of both discussed compounds compared to their parent monometallic Zn(II) metallomesogen without ferrocene units (405 nm). Furthermore, by using different polarity solvents from polar (DMSO) to apolar ones (hexane) or increasing the polarity by gradually adding methanol to a dichloromethane solution containing the complex, significant changes in the photophysical properties were observed. Thus, by increasing the polarity of the media, an enhancement of the intensity and a red-shift of emission maxima was observed. Unfortunately, in the liquid crystalline state the emission was totally quenched when it was recorded at an excitation wavelength of 490 and 580 nm which correspond to the absorption of the molecule forming the Colh arrangement. However, a weak emission band centred at 430 nm was observed when excited at $\lambda_{\text{exc}} = 350$ nm emission attributed to the single non-aggregated molecules.

Other strategy to obtain hetero-bimetallic metallomesogens was by simply chemical blending of Cu(II) and Zn(II) metallomesogens that are structurally-related (Cretu et al. 2023). Both metal complexes are hexacoordinated with

an identical coordination sphere formed by the chelation of one 1,10-phenanthroline ligand and two functionalized gallate co-ligands (Figure 9a).

Even though the monometallic complexes (Zn_MM and Cu_MM) were structurally similar, the Zn(II) complex formed Colr mesophase while the Cu(II) complex self-organized into Colh mesophase, their isotropization temperature being around 100 °C. By mixing these two monometallic complexes in three different mass ratio (1:3, 1:1 and 3:1), three chemical blends (**20**: ZnCu = 1:3, **21**: ZnCu = 1:1 and **22**: ZnCu = 3:1) were obtained.

in case of blend **20** that contained a mixture of Colh and isotropic liquid before isotropization (Figure 9b). The photophysical properties of the blends were recorded in the condensed phases, and only the blend **20** was emissive in mesophase with an emission maximum centered at 520 nm ($\lambda_{\text{ex}} = 350$ nm) and a lifetime value of 4.9 ns. The emission of **20** was similar to that of monometallic Zn_MM precursor in the mesophase, while in case of **21** and **22**, the non-emissive behaviour was attributed to the quenching effect of Cu_MM. Moreover, a small shoulder having the maximum at 445 nm was observed in the emission spectra of blend **20**, assigned to Cu_MM precursor emission. Despite the quenching of the emission properties in this case, this strategy of obtaining bimetallic liquid crystalline systems by chemical blending may shows potential due to the straightforward synthesis compared to the classical ones.

CONCLUSIONS

In this short review, we outlined the homo- and hetero-polymetallic luminescent liquid crystals progress recorded in the last decade involving different mono and polydentate ligands and different metal centres such Ag(I), Au(I), Cu(I), Pd(II), Pt(II), Zn(II) and Cu(II). Thus, mesogenic or non-mesogenic ligands based on isocyanide, hydrazine, imine, thiourea, halo, phosphine, pyridyl, pyrazoles and carboxylate derivatives were used to synthesize polymetallic liquid crystalline metal complexes. Their mesomorphic properties are influenced by a series of factors as the length, number and position of alkyl chains, the position of the donor atoms involved in the metal ion coordination that controls the type of the resulting metal complex, the molecules' symmetry and shape, etc. To design luminescent metallomesogens, some additional aspects has to be considered starting from choosing appropriate metal ions that can induce emission in the resulting metal complex or using highly conjugated organic ligands with optical properties. The emission properties of these systems are highly influenced by the polarity of the solution or molecular environment and the aggregation phenomena. Additionally, metallophilic interactions can be formed with specific transition metal ions like Cu(I), Ag(I),

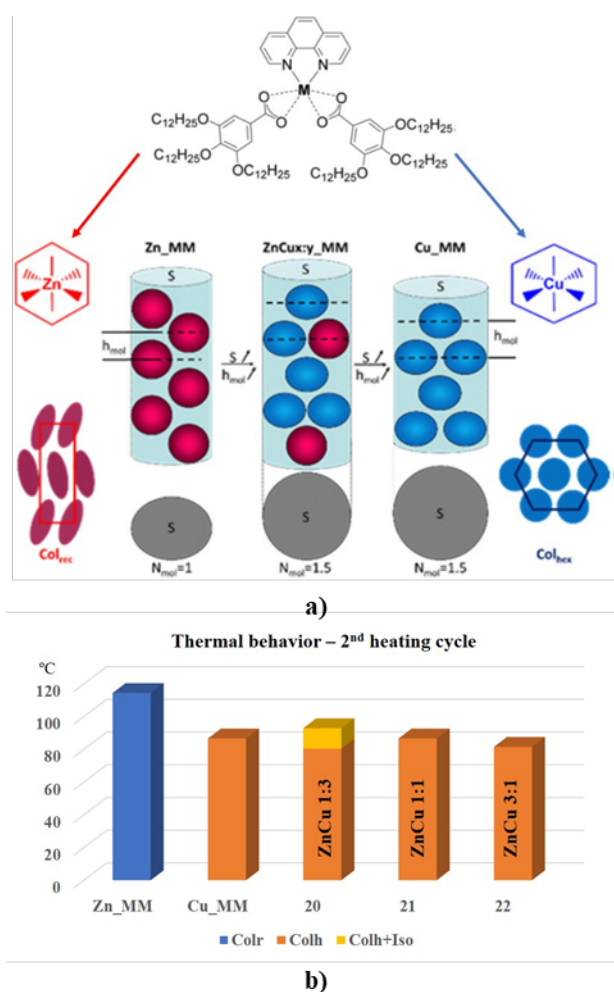


Figure 9. Schematic representation of the proposed self-assembly of the metallomesogenic precursors and the blends (a); thermal behavior of the blends **20–22** and their precursor (b)

From the mesomorphic point of view, all the blends self-assembled into Colh phases. The presence of the Cu(II) complex in these blends seem to stabilize the mesophase with higher symmetry (Colh). Small differences in the clearing temperature were observed, especially

Au(I) or Pt(II), playing an important role in tuning or altering the emission properties.

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REFERENCES

- Al-Karawi, A.J.M., 2017. From Mesogens To Metallomesogens. Synthesis, Characterisation, Liquid Crystal And Luminescent Properties. *Liq. Cryst.* 44(1), 1-15, <http://dx.doi.org/10.1080/02678292.2017.1371799>.
- Andelescu, A.A., Candrea, A., Popa, E., Visan, A., Cretu, C., La Deda, M., Szerb, E.I., 2024. Role of the Environment polarity on the Photophysical Properties of Mesogenic Hetero-Polymetallic Complexes. *Molecules* 29, 750, <https://doi.org/10.3390/molecules29040750>.
- Binnemans, K., 2009. Luminescence of metallomesogens in the liquid crystal state. *J. Mater. Chem.* 19, 448–453, <https://doi.org/10.1039/B811373D>.
- Bisoyi, H.K., Li, Q., 2022. Liquid Crystals: Versatile Self-Organized Smart Soft Materials. *Chem. Rev.* 122(5), 4887–4926, <https://doi.org/10.1021/acs.chemrev.1c00761>.
- Blanco, H., Iguarbe, V., Barberá, J., Serrano, J. L., Elduque, A., Giménez, R., 2016. Supramolecular Columnar Liquid Crystals with Tapered-Shape Simple Pyrazoles Obtained by Efficient Henry/Michael Reactions. *Chem.-Eur. J.* 22(14), 4924–4930, <https://doi.org/10.1002/chem.201504779>.
- Chen, L., Chen, C., Sun, Y., Lu, S., Huo, H., Tan, T., Li, A., Li, X., Ungar, G., Liu, F., Zhang, M., 2020. Luminescent Metallacycle-Cored Liquid Crystals Induced by Metal Coordination. *Angew. Chem. Int. Ed.* 59, 10143–10150, <https://doi.org/10.1002/anie.201915055>.
- Chico, R., Domínguez, C., Donnio, B., Heinrich, B., Coco, S., Espinet, P., 2016. Isocyano-Triphenylene Complexes of Gold, Copper, Silver, and Platinum. Coordination Features and Mesomorphic Behavior. *Cryst. Growth Des.* 16, 6984–6991, <https://doi.org/10.1021/acs.cgd.6b01206>.
- Cretu, C., Popa, E., Di Maio, G., Candrea, A., Buta, I., Visan, A., La Deda, M., Donnio, B., Szerb, E.I., 2023. Bimetallic liquid crystal blends based on structurally related 3d-metal coordination complexes. *Chem. Commun.* 59, 10616, <https://doi.org/10.1039/D3CC02930A>.
- Cuerva, C., Cano, M., Lodeiro, C., 2021. Advanced Functional Luminescent Metallomesogens: The Key Role of the Metal Center. *Chem. Rev.* 121, 12966, <https://doi.org/10.1021/acs.chemrev.1c00011>.
- Fujisawa, K., Saotome, M., Ishikawa, Y., Young, D.J., 2021. The influence of aryl substituents on the supramolecular structures and photoluminescence of cyclic trinuclear pyrazolato copper(I) complexes. *Nanomaterials* 11(11), 1-13, <https://doi.org/10.3390/nano11113101>.
- Geng, H., Luo, K., Cheng, H., Zhang, S., Ni, H., Wang, H., Yu, W., Li, Q., 2017. Novel columnar metallomesogens based on cationic platinum(II) complexes without long peripheral chains. *RSC Adv.* 7(9) 11389, <https://doi.org/10.1039/C6RA28767K>.
- Giménez, R., Lydon, D.P., Serrano, J.L., 2002. Metallomesogens: a promise or a fact?. *Curr. Opin. Solid State Mater. Sci.* 6(6), 527-535, [https://doi.org/10.1016/S1359-0286\(03\)00009-3](https://doi.org/10.1016/S1359-0286(03)00009-3).
- Giménez, R., Crespo, O., Diosdado, B., Elduque, A., 2020. Liquid crystalline copper(I) complexes with bright room temperature phosphorescence. *J. Mater. Chem. C* 8, 6552, <https://doi.org/10.1039/D0TC00642D>.
- Hakemi, H., 2022. Metallomesogen Mixtures as Potential Materials for Application in Liquid Crystal Devices. *J. Mater. Poly. Sci.* 2(4), 1-5, <https://doi.org/10.47485/2832-9384.1020>.
- Huitorel, B., Benito, Q., Fargues, A., Garcia, A., Gacoin, T., Boilot, J.-P., Perruchas, S., Camerel, F., 2016. Mechanochromic Luminescence and Liquid Crystallinity of Molecular Copper Clusters. *Chem. Mater.* 28, 8190–8200, <https://doi.org/10.1021/acs.chemmater.6b03002>.
- Ibrayev, N., Seliverstova, E., Valiev, R., Aymagambetova, A., Sundholm, D., 2024. The effect of heavy atoms on the deactivation of electronic excited states of dye molecules near the surface of metal nanoparticles. *Phys. Chem. Chem. Phys.* 26, 25986, <https://doi.org/10.1039/D4CP02621G>.
- Ionescu, A., Godbert, N., Crispini, A., Termine, R., Golemme, A., Ghedini, M., 2012. Photoconductive Nile red cyclopalladated

- metallomesogens. *J. Mater. Chem.* 22(44), 23617-23626,
<https://doi.org/10.1039/C2JM34946A>.
- Kadkin, O.N., An, J., Han, H., Galyametdinov, Y.G., 2008. A Novel Series of Heteropolynuclear Metallomesogens: Organopalladium Complexes with Ferrocenophane-Containing Ligands. *Eur. J. Inorg. Chem.* 1682–1688,
<https://doi.org/10.1002/ejic.200700750>.
- Krikorian, M., Liu, S., Swager, T.M., 2014. Columnar Liquid Crystallinity and Mechanochromism in Cationic Platinum(II) Complexes. *J. Am. Chem. Soc.* 136(8), 2952–2955, <https://doi.org/10.1021/ja4114352>.
- Kumar, A., Singh, G., 2023. Recent advances and future perspectives of photoluminescent liquid crystals and their nanocomposites for emissive displays and other tunable photonic devices. *J. Mol. Liq.* 386, 122607, <https://doi.org/10.1016/j.molliq.2023.122607>.
- Micutz, M., Iliş, M., Staicu, T., Dumitraşcu, F., Pasuk, I., Molard, Y., Roisnel, T., Cîrcu, V., 2014. Luminescent liquid crystalline materials based on palladium(II) imine derivatives containing the 2-phenylpyridine core. *Dalton Trans.* 43, 1151,
<https://doi.org/10.1039/C3DT52137K>.
- Pastor, M.J., Cuerva, C., Fernandez-Lodeiro, A., Lodeiro, C., Campo, J.A., Cano, M., 2018. Designing Zn(II) complexes as a support of bifunctional liquid crystal and luminescent materials. *Dyes Pigments* 149, 37-50, <https://doi.org/10.1016/j.dyepig.2017.09.039>.
- Popa, E., Andelescu, A.A., Ilies, S., Visan, A., Cretu, C., Scarpelli, F., Crispini, A., Manea, F., Szerb, E.I., 2023. Hetero-Bimetallic Ferrocene-Containing Zinc(II)-Terpyridyl-Based Metallomesogen: Structural and Electrochemical Characterization. *Materials* 16, 1946, <https://doi.org/10.3390/ma16051946>.
- Santoro, A., Whitwood, A.C., Gareth Williams, J.A., Kozhevnikov, V.N., Bruce, D.W., 2009. Synthesis, Mesomorphism, and Luminescent Properties of Calamitic 2-Phenylpyridines and Their Complexes with Platinum(II), *Chem. Mater.* 21, 3871–3882,
<https://doi.org/10.1021/cm9012156>.
- Soria, L., Cano, M., Campo, J.A., Rosario Torres, M., Lodeiro, C., 2016. Silver compounds based on N,N,N-tridentate pyridylpyrazolate ligands. An opportunity to build cyclic trimetallic and oligomeric luminescent liquid crystals. *Polyhedron* 125, 141-150,
<http://dx.doi.org/10.1016/j.poly.2016.10.049>.
- Szerb, E.I., Crispini, A., Aiello, I., La Deda, M., 2022. *Springer Handbook of Inorganic Photochemistry; Part XII: Inorganic Materials for Optoelectronics*, 62: Liquid Crystals, Section editor: Eli Zysman-Colman; Bahnmann, D.W., Patrocínio, A.O.T., Eds.; Springer Nature: Cham, Switzerland, pp. 1811–1848.
- Titov, A.A., Filippov, O.A., Smol'yakov, A.F., Godovikov, I.A., Shakirova, J.R., Tunik, S.P., Podkorytov, I.S., Shubin, E.S., 2019. Luminescent Complexes of the Trinuclear Silver(I) and Copper(I) Pyrazolates Supported with Bis(diphenylphosphino)methane. *Inorg. Chem.* 58, 8645–8656,
<https://doi.org/10.1021/acs.inorgchem.9b00991>
- Wang, Y., Fan, J., Shi, J., Qi, H., Baranoff, E., Xie, G., Li, Q., Tan, H., Liu, Y., Zhu, W., 2016. Influence of integrated alkyl-chain length on the mesogenic and photophysical properties of platinum-based metallomesogens and their application for polarized white OLEDs. *Dyes Pigments* 133, 238-247,
<https://doi.org/10.1016/j.dyepig.2016.05.024>.
- Wang, Y., Chen, Q., Li, Y., Liu, Y., Tan, H., Yu, J., Zhu, M., Wu, H., Zhu, W., Cao, Y., 2012. Highly Dichroic Metallomesogen of Dinuclear Platinum Complex: Synthesis and Liquid Crystal and Photophysical Properties. *J. Phys. Chem. C* 116, 5908–5914,
<https://doi.org/10.1021/jp211976x>.
- Wenzel, M., Bigaeva, E., Richard, P., Le Gendre, P., Picquet, M., Casini, A., Bodio, E., 2014. New heteronuclear gold(I)–platinum(II) complexes with cytotoxic properties: Are two metals better than one? *J. Inorg. Biochem.* 141, 10–16,
<https://doi.org/10.1016/j.jinorgbio.2014.07.011>
- Wu, X., Xie, G., Cabry, C.P., Xu, X., Cowling, S.J., Bruce, D.W., Zhu, W., Baranoff, E., Wang, Y., 2018. Linearly Polarized Electroluminescence from Ionic Iridium Complex-based Metallomesogens: The Effect of Aliphatic-Chain on Their Photophysical Properties. *J. Mater. Chem. C* 6, 3298–3309,
<https://doi.org/10.1039/C7TC05421A>.

Su, P.Y.S., Hsu, S.J., Tseng, J.C.W., Hsu, H.-F., Wang, W.-J., Lin, I.J.B., 2016. Polynuclear Silver(I) Triazole Complexes: Ion Conduction and Nanowire Formation in the Mesophase. *Chem. Eur. J.* 22(1), 323-330, <https://doi.org/10.1002/chem.201502823>.

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