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Carmen Cretu, Evelyn Popa, Giuseppe Di Maio, Angela Candreva, Ildiko Buta, et al.. Bimetallic liquid crystal blends based on structurally related 3d-metal coordination complexes. *Chemical Communications*, 2023, 59 (71), pp.10616-10619. 10.1039/d3cc02930a . hal-04282550

**HAL Id: hal-04282550**

**<https://hal.science/hal-04282550v1>**

Submitted on 15 Nov 2023

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# Bimetallic liquid crystal blends based on structurally related 3d-metal coordination complexes†

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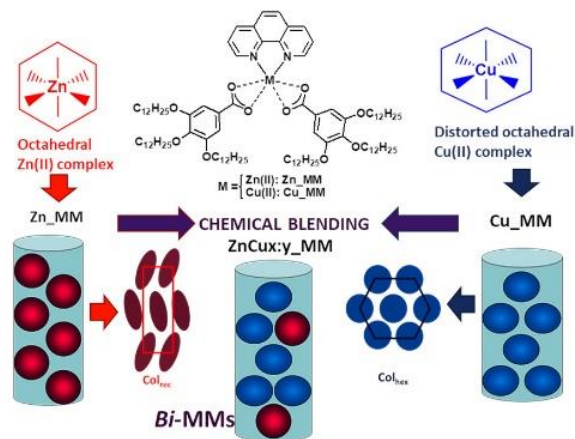
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Cite as : *Chem. Commun.*, **2023**, 59, 10616-10619. DOI: 10.1039/d3cc02930a

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d3cc02930a>

Received 19th June 2023; Accepted 31st July 2023; First published on 31<sup>st</sup> July 2023

Structurally related Zn(II) and Cu(II) metallomesogens based on phenanthroline and gallate chelating units by chemical blending self-organize into a single Col<sub>hex</sub> mesophase, forming hetero-bimetallic liquid crystalline materials.



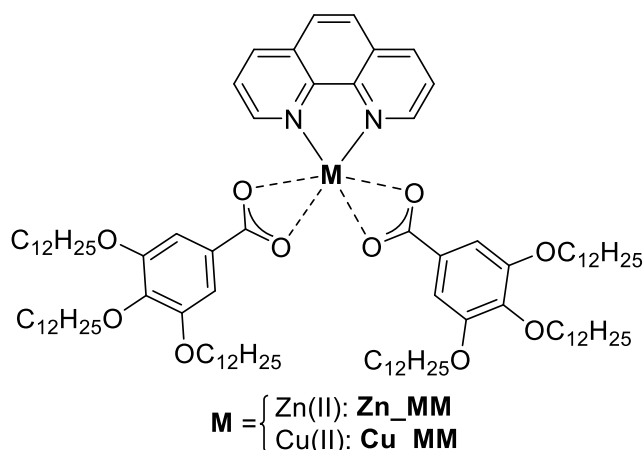
**Abstract** Hetero-bimetallic liquid crystalline materials, exhibiting a single Col<sub>hex</sub> mesophase, were obtained by simple chemical blending between two structurally-related Cu(II) and Zn(II) metallomesogens based on 1,10-phenanthroline and two chelating gallate ligands. Mesomorphous and optical properties were modified upon their relative respective proportions. This study highlights the numerous possibilities for the fabrication of new multifunctional polymetallic materials, with the possibility of tuning the properties and controlling supramolecular interactions between metal centres and corresponding synergistic effects.

Chemical blending is an industrial process that involves combining two or more dissimilar chemicals with the aim to create and fabricate new, versatile and homogeneous materials that have completely different or enhanced characteristics and functionalities than their pure constitutive components. Chemical blending is considered a key process in a wide range of industrial applications which, depending on the source products, is commonly used in the production of various chemical products and of human consumption goods. Obviously, to be effective, this process must be extremely precise so that the final product invariably meets exactly the same specifications, with the optimal properties also resulting from the selection of the appropriate proportions of the constituents. Blends are generally intended to remain homogeneous permanently as opposite to heterogeneous mixtures (i.e. emulsions, suspensions). Recently, chemical blending is investigated as cheap and green alternative to chemical synthesis for obtaining new advanced MOFs,<sup>1</sup> polymers<sup>2</sup> or biocomposites.<sup>3</sup>

Metallomesogens<sup>4</sup> are advanced functional materials with targeted applications in optoelectronics and display technologies, chemo-sensing and bio-related fields, catalysis, etc.<sup>5</sup> due to properties deriving from the metal-based coordination complex (photoluminescence, magnetic, catalytic, redox, etc.) and from liquid crystals (order, mobility, anisotropy, self-healing, etc.).<sup>6</sup>

Several, but not many, polymetallic liquid crystals i.e. bearing two and more metallic centers, have been reported thus far,<sup>4,6,7</sup> but in contrast, very few systems bearing different metallic ions,<sup>8</sup> probably due to synthetic challenges and disproportionation effects. Blending structurally related coordination complexes i.e. same ligands but differing by the nature of the metal ion, could, by complementary and/or synergic effects, represent a pertinent and effective alternative to difficult chemistry and lead quickly to versatile new mesogenic systems with enhanced properties, as it does for materials with improved biosensing,<sup>9</sup> catalytic,<sup>10</sup> and antimicrobial<sup>11</sup> activities, as well as bring important advantages in materials science (e.g. LC Display industry<sup>12</sup>) suggestive of novel applications.

Herein, we report a simple strategy to obtain “bimetallic metallomesogens” by the straightforward blending of structurally similar mesogenic coordination complexes with similar shapes but different metallic ions. Zn(II) and Cu(II) 1,10-phenanthroline (phen) based-complexes with two 3,4,5-tridodecyloxybenzoate coligands (**Zn\_MM** and **Cu\_MM**, Fig. 1, Fig. S1 and S2, ESI<sup>†</sup>) were synthesized and characterized.



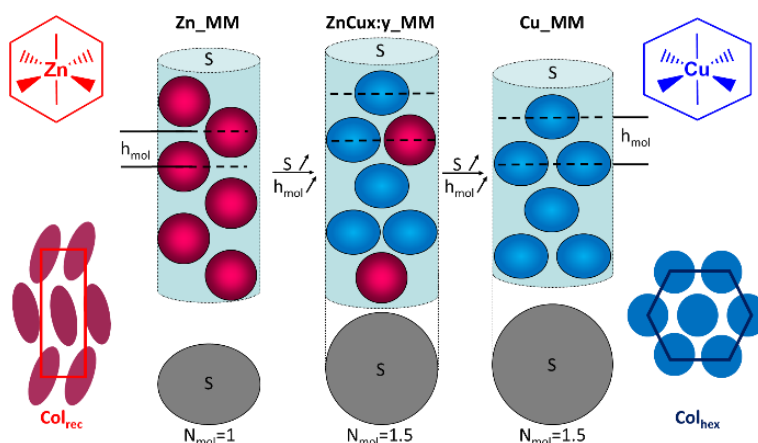
**Figure 1.** Chemical structure of coordination complexes **Zn\_MM** and **Cu\_MM**.

As found in literature, Cu(II) and Zn(II) complexes bearing N^N chelating ligands (i.e. phen) and benzoate as coligands, can coordinate in a variety of modes (unidentate, chelating, bridging, etc.), principally depending on the stoichiometry, reaction conditions or presence of competing coordinating solvents.<sup>13</sup> In similar reaction conditions, an octahedral environment around the metal center with a bidentate chelating mode for benzoate is preferentially obtained for Zn(II) complexes.<sup>14</sup> The bidentate mode of the benzoate is supported by the separation of  $\Delta = 179 \text{ cm}^{-1}$  of the C–O stretching frequencies ( $\nu_s$  and  $\nu_{as}$ ) in the FT-IR spectra (Fig. S1, ESI<sup>†</sup>).<sup>15</sup> Regarding **Cu\_MM**, literature indicates for the benzoate a preferential monodentate coordination resulting in distorted square planar geometry,<sup>16</sup> penta-coordination with the fifth position of the coordination sphere fulfilled by a coordinated water molecule,<sup>17</sup> or hexacoordination for benzoate derivatives with bridged monodentate<sup>18</sup> or bidentate chelating<sup>19</sup> modes. Similar FT-IR and  $\Delta$  values (Fig. S1, ESI<sup>†</sup>) indicate analogous

coordination around the metal center, therefore both complexes appear isostructural, having a hexacoordination around the metal centers fulfilled by one N<sup>^</sup>N and two O<sup>^</sup>O chelating ligands (Fig. 1).

Despite the a priori similar coordination environment around the metal centers and close ionic radii, the thermal stability, behavior, and supramolecular organizations of **Zn\_MM** and **Cu\_MM** are slightly different. As seen by TGA (in dynamic mode, Table S1 and Fig. S5, S6, ESI<sup>+</sup>), **Zn\_MM** ( $T_{\text{dec}5\%} = 320\text{ }^{\circ}\text{C}$ ) displays a higher thermal stability than **Cu\_MM** ( $T_{\text{dec}5\%} = 280\text{ }^{\circ}\text{C}$ ). Both complexes have different clearing temperatures well below decomposition (114.5  $^{\circ}\text{C}$  for **Zn\_MM** and 88.2  $^{\circ}\text{C}$  for **Cu\_MM**, respectively, Fig. 2). They both present enantiotropic columnar mesophases as showed by POM (focal conic and fan shaped textures, Fig. S3, ESI<sup>+</sup>), which remain on cooling down to room temperature, with no sign of crystallization. S/WAXS studies ultimately revealed that **Zn\_MM** self-organize into a  $\text{Col}_{\text{rec}}\text{-}p2gg$  and **Cu\_MM** into a  $\text{Col}_{\text{hex}}\text{-}p6mm$  mesophase (Fig. S7, S8 and Table S2, ESI<sup>+</sup>). The induction of columnar mesophases of different symmetries was truly unexpected, although this is not uncommon in octahedral metal complexes as already seen for instance in tris( $\beta$ -diketonato) coordination complexes of various metal ions.<sup>20</sup> Here, this difference could be a consequence of Jahn Teller distortion of the octahedral coordination geometry around the Cu(II) center, with a planar expansion and height reduction, that would somehow interrupt a regular stacking. The cylindrical columnar cross-section (*S*) of the  $\text{Col}_{\text{hex}}$  phase of the **Cu\_MM** complex is also about 50% larger than that of the  $\text{Col}_{\text{rec}}$  phase of the pure **Zn\_MM** complex (Table S2, ESI<sup>+</sup>), confirming that the complexes must be differently arranged within the columns, in agreement with the change of symmetry. More intimate details about the respective supramolecular organizations of the two subsets of columns within the lattices can be retrieved from the ratio between the molecular volume ( $V_{\text{mol}}$ ) and the lattice area (*A*, with  $Z_{\text{col}} = 2$ , for the rectangular symmetry, and  $Z_{\text{col}} = 1$  for hexagonal symmetry), scaled by the number of complexes,  $N_{\text{mol}}$ , along an arbitrary columnar repeat unit, the molecular thickness,  $h_{\text{mol}}$ , according to the formula,  $h_{\text{mol}} = V_{\text{mol}} \times N_{\text{mol}} / (A / Z_{\text{col}})$  (Table S2, ESI<sup>+</sup>). By trial and error on the  $h_{\text{mol}}/N_{\text{mol}}$  pair, calculations show that one Zn complex occupies every ca. 3.3  $\text{\AA}$  along the column, whereas for a similar height, 1.5 Cu complexes on average are needed to fill the available space (Table S2, volumes of the complexes and blends can be considered as quasi identical, ESI<sup>+</sup>). The proposed model would consist therefore of an alternated stacking of antiparallel Zn complex (likely through phen face-to-face interactions) within the columns, whereas the Cu complex would stack with an uneven distribution of complexes along the columns, i.e. with a 2 : 1 alternation every  $h_{\text{mol}}$  (Fig. 2).

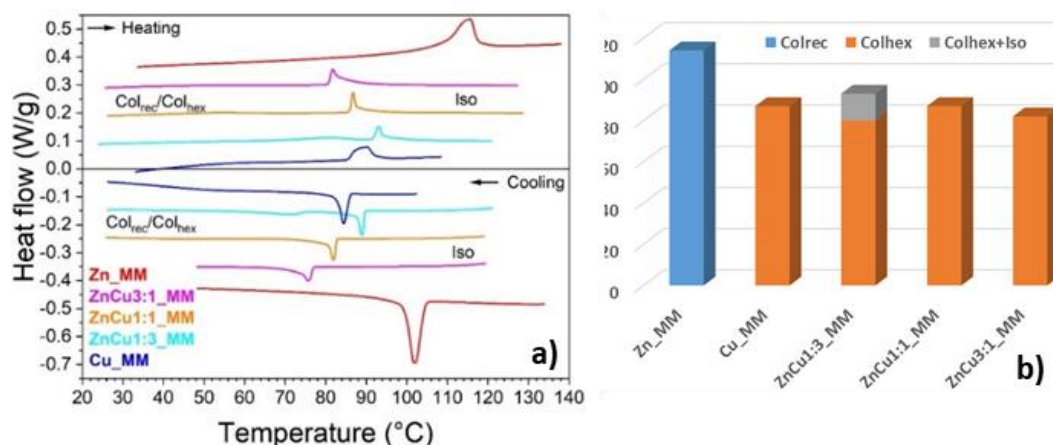
Despite mesophases of different symmetry, the high structural similarity between both coordination complexes nevertheless was compatible with the preparation of three blends with different weight ratio of the pristine complexes **Zn\_MM/Cu\_MM**, i.e. 1:3, 1:1 and 3:1 (labelled as **ZnCu1:3\_MM**, **ZnCu1:1\_MM** and **ZnCu3:1\_MM**, respectively), by simply dissolving the appropriate quantities in the minimum volume of  $\text{CH}_2\text{Cl}_2$  with stirring, followed by 20 min. sonication and then by slow solvent-evaporation at room temperature.



**Figure 2.** Schematic of the supramolecular organization proposed for **Zn\_MM**, **Cu\_MM** and their corresponding blends, in their respective mesophases (*S*,  $h_{\text{mol}}$ ,  $N_{\text{mol}}$  are defined in the text).

For the investigation of their thermal behaviors, the blends were first brought into the isotropic liquid, i.e. at around 100  $^{\circ}\text{C}$ , maintained in this state for a few minutes, and then cooled down. The reproducibility of the

thermal properties was checked by repeated cooling–heating cycles, with only small variation of transition temperatures and enthalpies (Table S1, ESI<sup>†</sup>). All 3 blends were found to self-organize into a single Col<sub>hex</sub> mesophase, as revealed by POM and S/WAXS (Fig. S4, S9–S11, ESI<sup>†</sup>), and with a small but visible effect of the ratio on the clearing temperatures, though all within the range of the pure Cu complex, but decreasing slightly as its content was reduced (Fig. 3). In all cases, the columnar cross sections are close to that of pure **Cu\_MM**, and increases smoothly with the copper content (Fig. 2 and Table S2, ESI<sup>†</sup>). This suggests that, as soon as **Cu\_MM** is added, the supramolecular organization within the column resembles that of the pure **Cu\_MM**, with an average of 1.5 molecule per repeat unit h<sub>mol</sub>. Note that the copper-rich blend, **ZnCu1:3\_MM**, behaves slightly differently than the other two, in that co-existence of a Col<sub>hex</sub> phase and isotropic liquid over almost 20 °C (broad transition) is observed below the isotropic liquid. Below 80 °C, the blend is homogeneous again as the other ones. The presence of low amounts of the **Cu\_MM** (at least 25 mol%) in the blend is sufficient to strongly destabilize the mesophase, and thus confirms a very low percolation threshold for these systems, as even in majority of **Zn\_MM**, the Col<sub>rec</sub> phase is completely lost. The ease of distortion of the coordination in **Cu\_MM** may indicate a less rigid structure, allowing an easier accommodation of the molecules inside the columns, in agreement with a low percolation threshold. The enhancement of the mesophase symmetry from rectangular to hexagonal is usually expected in blends, essentially due to some smoothing effects and the erasing of structural details.



**Figure 3.** DSC thermograms (a) and bar diagram (b) of metallomesogens **Zn\_MM** and **Cu\_MM** and of blends **ZnCu1:3\_MM**, **ZnCu1:1\_MM**, **ZnCu3:1\_MM** (2<sup>nd</sup> cycle).

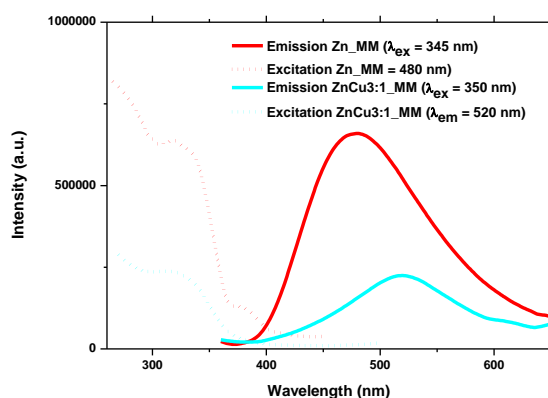
The photophysical properties of all the samples were investigated both in CH<sub>2</sub>Cl<sub>2</sub> dilute solutions ( $2.7 \times 10^{-6}$  M) and in condensed phase varying temperature (Fig. S12 and Table S3, ESI<sup>†</sup>). In solution, only the characterization of **Zn\_MM** and **Cu\_MM** is reported, because the blends are not formed in these conditions. The absorption spectra are quite similar, with only a lower grade of structuration for **Cu\_MM** than **Zn\_MM**, attributable to a lower rigidity of the Cu(II) than Zn(II) already discussed in the structural characterization, indicating ligand centred transitions. Absorption spectra are composed by an intense and sharp band centred at 272 nm with a shoulder at 295 nm (both due to  $\pi-\pi^*$  transition centred on the phen ligand) and a weak shoulder centred at 262 nm attributable to transitions on 3,4,5-tridodecyloxybenzoate ligands.<sup>21</sup> Furthermore, a very low band in the region between 300 and 350 nm is due to  $n-\pi^*$  transitions.<sup>21</sup>

The emission patterns of both complexes are superimposable (see Fig. S12, ESI<sup>†</sup>). An emission band centred at 345 nm was observed, generated by radiative deactivation of  $\pi-\pi^*$  electronic state on the phen. The excitation spectra collected on these emissions are very similar to the absorption spectra of the respective samples, confirming the origin of the detected emission. The emissions decays follow a mono-exponential kinetic, with an identical value of the lifetimes of 2.6 ns for all investigated concentrations. The emission quantum yields (EQY) at  $2.6 \times 10^{-6}$  M concentration, are 7.5% for **Cu\_MM** and 7.9% for **Zn\_MM**. Furthermore, all samples show a dependence of the emission quantum yield with concentration, the emission intensity decreases with increasing concentration (see Table S3, suggesting the presence of intermolecular interactions that quench the fluorescence intensity in solution).

In solid state, the photophysical behaviour is quite different respect to the solution. While **Zn\_MM** continues

to emit (albeit at longer wavelengths than in the solution), the luminescence of **Cu\_MM** is completely quenched. **Zn\_MM** shows an emission band centred at 480 nm (red line in Fig. 3), with an absolute quantum yield of 6.4% and a lifetime value of 4.2 ns.

The blend **ZnCu3:1\_MM** emission is centred at 520 nm (Fig. 4), while the lifetime is equal to 4.9 ns. Surprisingly, **ZnCu1:1\_MM** and **ZnCu1:3\_MM** do not emit. Emission failure of **Cu\_MM** in solid state is attributable to the  $Col_{hex}$  organization which, by distorting the coordination around the metallic centers, activates non-radiative deactivation paths. **Cu\_MM** acts as an emission quencher of **Zn\_MM** in **ZnCu1:1\_MM** and **ZnCu1:3\_MM** blends. The luminescent properties of **Zn\_MM** are retained only in the Zn rich blend (**ZnCu3:1\_MM**), which shows an emission band centered at 520 nm, identical to that of **Zn\_MM** (see discussion below) in LC phase (Table S1, ESI<sup>†</sup>).



**Figure 4.** Emission (continuous line) and excitation (dotted line) spectra of **Zn\_MM** and **ZnCu3:1\_MM** in the pristine solid state.

The emissive properties in the mesophase were investigated through three heating/cooling cycles, following the phase transition observed by DSC. After the first settling cycle, emission spectra and quantum yields were collected at different temperatures (Fig. S13, S14 and Tables S4, S5, ESI<sup>†</sup>).

For **Zn\_MM** after the first heating/cooling cycle the emission wavelength at room temperature (30 °C) suffers a red shift from 480 to 520 nm, while the initial EQY value of 6.4% is reduced at 3.8%. This is attributable to the transition from the crystalline phase to the mesophase. Until the isotropic liquid, only a reduction of the EQY with temperature, due to the increasing of the thermal non-radiative deactivation paths, was detected. At 120 °C a further red-shift of 10 nm of the emission maximum occurs, with a dramatic reduction of the EQY to 0.9%. During cooling the sample completely recovers the starting conditions. The photophysical properties during the 11<sup>nd</sup> heating/cooling cycle are unvaried.

The emission spectra of **ZnCu3:1\_MM**, unlike **Zn\_MM**, after the settling cycle, show a maximum at 520 nm, identical to that observed in the pristine solid state, while a shoulder is observed at about 445 nm (Fig. S14, ESI<sup>†</sup>). The emission intensity decreases with increasing temperature, due to the increasing of the thermal non-radiative deactivation paths (Table S5, ESI<sup>†</sup>). However, the emission intensity is not restored when, during the heating/cooling cycles, the system returns to the same temperature values, and this indicates kinetic paths in the phase transition process. Furthermore, the presence of the shoulder at 445 nm whose corresponding excitation spectrum is different from that collected on the maximum at 520 nm (Fig. S14, ESI<sup>†</sup>), suggests that the copper complex under these conditions shows a weak emission, which probably appears quenched as its concentration increases in the blend. Therefore, the photophysical properties of the blends are that of the single components, suggesting that the interaction between **Zn\_MM** and **Cu\_MM** are not strong enough to modify the electronic structures of these complexes. For **ZnCu1:1\_MM** and **ZnCu1:3\_MM**, the properties are determined by **Cu\_MM** that acts as a quencher towards **Zn\_MM**. For **ZnCu3:1\_MM** the emissive properties are identical to **Zn\_MM** in the LC phase and by varying the temperature, an additional signal attributed to a weak emission from **Cu\_MM** was registered.

The present communication opens up a new and simple strategy of obtaining hetero-bimetallic liquid

crystalline systems that may have great potential for various applicative fields. Structurally related complexes may be obtained with luminescent, redox, magnetic, catalytic properties, and preliminary demonstrate the possibility of chemical blending to obtain homogeneous new liquid crystals based on three metal centres with a plethora of combinations that can be realised.

### Acknowledgements

This work was supported by a grant of the Romanian Ministry of Education and Research, CNCS - UEFISCDI, project number PN-III-P4-ID-PCE-2020-1958, within PNCDI III. BD thank the CNRS and University of Strasbourg for support and Dr Benorît Heinrich for S/WAXS and DSC measurements.

**Conflicts of interest** There are no conflicts to declare.

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