

Metallomesogen Mixtures as Potential Materials for Application in Liquid Crystal Devices

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Abstract

In this work, we present a new approach for development of metallomesogen (MOM) mixtures for potential applications in electrooptical devices. Through combination of molecular engineering and physical mixing technique, we propose to overcome the major drawbacks of MOMs, including their inaccessible transition temperature and low solubility in liquid crystal hosts. In the present study, we report on the miscibility of bi-ligand Cu, Ni and Pd complex salicylal-diaminates metallomesogens as model structures. Accordingly, we studied the phase diagrams of two binary MOM mixtures with different metals and ligands. The preliminary results indicate the complete mesogenic miscibility, distinct eutectic points and wide mesogenic range, which provide as model materials in electro-optical devices.

Keywords : metallomesogens, eutectic mixture, miscibility, ligand, commercial nematics, guest-host

Introduction

The metal-containing liquid crystals, known as “metallomesogens” (MOMs) have been considered for sometimes as promising materials for electrooptical applications. However, until now a concrete evidence for the use of MOMs as commercial materials has not yet been realized. The past decades have witnessed an explosion of interest and activities on MOMs chemistry, demonstrating that the presence of metal complexation can add many physical and optical features not present in organic mesogenic systems. These features have been the main impetus for potential applications of MOMs in wide range electro-optical devices. These potential features of MOMs include additional selective absorptions, large electrical polarizability, refractive indices and birefringences, high order parameters, wide mesogenic temperatures, large dichroic ratios and stability.

Various studies of MOMs have suggested their potential applications in electroluminescent displays, smart sensors, encryption systems or fuel cells, and currently they constitute one of the most active fields of research (Serrano, 1996; Wang et al., 2015; Wang et al., 2016). In recent years, a great varieties of metallomesogens with photoluminescence (Krikorian et al., 2014; Geng et al., 2017), electroluminescence (Wang et al., 2016; Krikorian et al., 2014; Geng et al., 2017; Liu et al., 2011), Magnetic (Seredyuk et al., 2014; Fitzpatrick et al., 2016) and electric (Ionescu et al., 2012; Su et al., 2014; Su et al., 2016) properties have been reported. Also other scientific

works (Ginord-Godquin & Maitlis, 1991; Bruce, 1992; Blanca, 1996) and patent literature (Hakemi, (n.d.); Hakemi et al., (n.d.); Roviello et al., (n.d.); Hakemi et al., (n.d.); Hakemi et al., (n.d.)) have addressed calamitic and discotic MOMs for other potential applications as dichroic dyes, non-linear optics, thermal recording, thermochromism, passive optical filters, photo-sensing, laser addressing, optical and thermal recording, polarizing films, radiation absorbing films, ferroelectricity, ferromagneticity, electroconductivity, reaction catalysts, LC intermediates, ink jet and security printing, medicinal and agricultural components.

In spite of rapid development and many speculations on the application of MOMs, the scientific research have not yet been able to provide commercial materials, even in the simple guest-host systems. This has been mainly due to the lack of sufficient knowledge of structure-property relations for development of suitable materials. Many attempts have been made to synthesize and study the properties of MOMs, but these efforts have not been yet conclusive to provide proper commercial materials. One of the major problems in development of MOMs has been their inaccessible and high transition temperatures, risk of decompositions at higher temperatures, impractical mesophase range and chemical instability. Therefore, the key for application of MOMs is not only through the molecular engineering and synthesis of proper chemical structure, but also should be through miscibility of multi-component systems by physical or chemical mixing approach.

In this respect, the strategy of the present study is to report on the first attempt to provide new eutectic MOM mixtures for potential utilization in a wide-range electro-optical devices. In the following sections of this work, we describe our experimental approach on few synthesized bi-ligand calamitic nematic MOM model systems and through their binary phase diagrams developed eutectic mixtures with low melting temperature and wide nematic range. The present study is the first report of its kind, which is part of an extensive industrial research and development programs on application of MOM materials.

Materials and Methods

The utilized MOM compounds pertain to a common class of *salicylaldimines* metal complexes which corresponds to the general chemical formula presented in Figure-1.

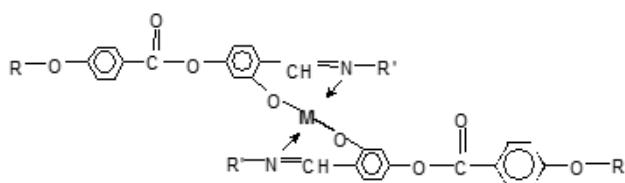
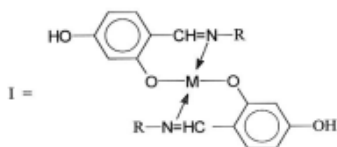


Figure 1: The general formula of the salicylaldimines MOMs.

The structural variations of the general formula in Figure-1 are obtained by changing the structure of the ligand's terminal groups R and R', which are different or the same having the same or different metal complex ion. While the details of general synthetic procedures of these class of MOMs chemistry as part of an extensive industrial development have been reported elsewhere (Caruso et al., 1990; Caruso et al., 1991; Caruso et al., 1991; Caruso et al., 1992; Sirigu & Roviello, (ca. 1994); Caruso et al., 1995; Sirigu & Roviello, (ca. 1995)), a brief synthetic routes of the four studied bis-ligand MOMs are mentioned in the following two categories:

Interfacial Synthesis: This procedure was carried out for the synthesis of 12-8N-Cu and AO-8N-Cu complexes. A carboxylic acid chloride was reacted with a previously prepared bis[N-[[2,4-dihydroxyphenyl] methylene+alkylamino] Cu(II) at the interface of two liquid phases in the presence of a phase transfer catalyst to prepare the following Complex (I):

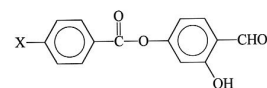


The Complex (I) was then synthesized by stepwise addition of appropriate n-alkylamine to equimolar amount of 2, 4-dihydroxybenzaldehyde and dissolved in absolute ethanol. In the presence of sodium acetate the stoichiometric amount of Cu (II) is added to this solution as acetate salt and dissolved in boiling ethanol. The Complex (I) was precipitated in crystalline form on cooling. The synthesis of 12-8N-Cu and AO-8N-Cu

complexes were carried out by dissolving 3.92g of previously synthesized R'COCl by standard methods in 80 ml anhydrous chloroform. A solution containing 3.33g of complex (I), 1.92g tetrabutylammonium hydrogen sulphate and 1.24g KOH in 150ml water was added under rapid stirring and the reaction was let go for around 10 minutes. The chloroformic phase was then repeatedly extracted with water, dried and finally concentrated to 30ml. The crystallization of final complexes was carried out by adding 150ml ethanol. With reference to the general formula mentioned in Figure-1, the chemical structures of the synthesized MOMs based on Cu(II) complexes and their ligands (R & R') are as follows:

- 12-8N-Cu: R= -O-(CH₂)₁₁-CH₃; R'= -(CH₂)₇-CH₃;
- A6O-8N-Cu: R= -(CH₂)₇-CH₃; R'= -O-(CH₂)₆-OOC-CH=CH₂;

Synthesis in Solution: This procedure was carried out for the synthesis of A11O-6ON-Ni and A11O-6ON-Pd complexes. It does not require neither preparation of Complex (I) nor the separation of imine RC=N-R' ligand. The preliminary step of the synthesis concerned the following aldehydes R-CHO intermediates:



These intermediates were prepared by standards sequential procedures toward the final esterification with 2, 4-dihydroxybenzaldehyde. At this step, a small fraction of esterification at the ortho position was produced. A purification was obtained via Cu (II) complex formation and successive HCl acid hydrolysis of recrystallized complex. The metal complex formation with various R' acrylate groups were then prepared by utilizing equimolar amounts of R-CHO and alkylamine to react in boiling ethanol solution in the presence of a large stoichiometric excess sodium acetate. The Stoichiometric amount of metal components Ni (ClO₄)₂·6H₂O (ethanol solution) or PDSO₄·3H₂O (concentrated water solution) were added. The purification by crystallization were then carried out from ethanol solution. With reference to the general formula mentioned in Figure-1, the nomenclature and chemical structures of synthesized MOMs based on Ni and Pd complexes and their ligands (R & R') are as follows:

- A11O-6ON-Ni: R= -(CH₂)₃-O-CH₂-CH₃; R'= -O-(CH₂)₁₁-OOC-CH=CH₂;
- A11O-6ON-Pd: R= -(CH₂)₃-O-CH₂-CH₃; R'= -O-(CH₂)₁₁-OOC-CH=CH₂.

In Table-1, we tabulate the nematic-crystal (TNC) and isotropic-nematic (TIN) transition temperatures of the studied MOM components obtained by DSC at 5 deg/min on cooling mode. All four synthesized MOM materials exhibit enantiotropic nematic phase with an overall mesogenic stability within 80 – 150 °C range.

MOM Compound	Transition Temperature (°C)	
	TIN	TNC
12-8N-Cu	129	103.5
A6O-N8-Cu	116	81.6
A11O-6ON-Ni	124	107
A11O-6ON-Pd	144	119

Table 1: Phase transitions of metallomesogen components.

The binary MOM mixtures 12-8N-Cu/A6O-8N-Cu and A11O-6ON-Ni/A11O-6ON-Pd were prepared by physical mixing method of binary MOM components. The phase diagrams of the mixtures with DSC were carried out by direct weighting of the components in DSC pan through repeated heating and cooling modes with scanning rates of 10° C/min and 5° C/min, respectively, until there was no change in their thermograms and mixings were completed. The phase diagrams of the binary MOM mixtures, their isotropic-nematic (TIN) and nematic-crystal (TNC) transition temperatures were determined by a Perkin Elmer DSC7 Differential Scanning Calorimeter (DSC) and Nikon Eclipse-50i polarizing optical microscope (OM) equipped with a temperature-controlled Mettler FP5 microscopic hot stage.

Results and Discussion

In Table-2 and Figure-2, we present the transition temperatures and phase diagrams of 12-8N-Cu / A6O-8N-Cu and A11O-6ON-Ni / A11O-6ON-Pd binary mixtures, respectively. It should be noticed that, the former mixture consists of the same Cu metal but different ligands (M-L1/M-L2), whereas the latter mixture contains the same ligand but different Ni & Pd metals (M1-L / M2-L).

12-8NCu (%wt)	TIN (°C)	TNC (°C)
0	116.0	81.6
25	117.7	71.2
50	122.0	80.8
75	124.4	90.8
100	129.0	103.5
A11O6ON-Ni (%wt)		
0	144	119
20.7	139	98
40.1	135	189
60.6	132	92
81.2	127	100
100	124	107

Table 2: Transition temperatures of 12-8N-Cu/A6O-8N-Cu and A11O-6ON-Ni/A11O-6ON-Pd mixtures.

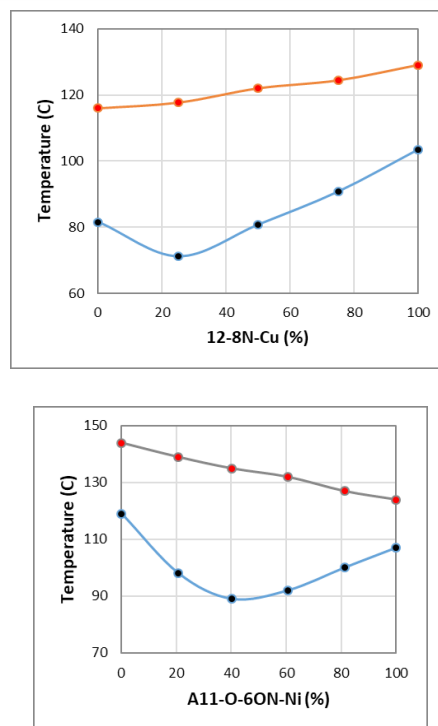


Figure 2: Phase diagrams of (left) 12-8N-Cu/A6O-8N-Cu and (right) A11O-6ON-Ni/A11O-6ON-Pd mixtures.

According to Figure-2, the structural differences between the two binary MOM mixtures is that, the 12-8N-Cu/A6O-8N-Cu mixture has the same metal-complex (Cu) and differed ligands, whereas the A11O-6ON-Ni/A11O-6ON-Pd mixture has the same ligand but different metal-complexes (Ni and Pd). The linear trends of isotropic-nematic (TIN) transitions within the whole composition range of both phase diagrams is the clear indication of complete mesogenic miscibility of the MOM components.

Also, both MOM mixtures exhibit strong eutectic points with the lowest nematic-crystal (TNC) transitions and largest nematic stability range. According to Table-2, the eutectic composition in 12-8N-Cu/A6O-8N-Cu mixture appears at around 12-8N-Cu=25 %wt, resulting to an expansion of nematic phase to around 46.5 °C. The eutectic point in A11O-6ON-Ni/A11O-6ON-Pd mixture occurs at around A6O-6ON-Ni=40 %wt with similar nematic phase extension of around 46.0 °C.

At the eutectic points, the phase diagrams in both MOM mixtures exhibit widest nematic range and lowest TCN transition temperatures than those of single MOM components. In addition, a comparison between the eutectic compositions of the two MOM mixtures indicate that, although both systems exhibit the same range of nematic expansion, the occurrence of eutectic composition in A11O-6ON-Ni/A11O-6ON-Pd mixture at 40% demonstrates the more crystalline structure similarities of its components with respect to 12-8N-Cu/A6O-8N-Cu mixture. This difference indicates that, the same ligand (different metal) in A11O-6ON-Ni/A11O-6ON-Pd mixture contributes more to similarity of their crystalline structure than

the same metal (different ligand) in 12-8N-Cu/A6O-8N-Cu mixture.

Conclusion

The main premise of the present work was to provide the mixing approach of few MOMs model system as a new strategy for qualifying them as commercial materials for application in electro-optical devices. Accordingly, as published recently on eutectic metallomesogens based on Alkyl / Alkoxy Azobenzene Pd-Complexes for application in guest-host electro-optical devices [27], here we studied the miscibility of binary mixtures of four salicylaldiaminate MOM structures with the different ligand and metal complexes. We found complete miscibility of MOM systems with significant eutectic points having lower melting temperatures and wider mesogenic range than the single components. Although the present studied MOMs and their mixtures not the ideal model materials, however the results clearly indicate that the MOM mixing approach is a valid and practical strategy to qualify and utilize these materials in liquid crystal hosts for commercial application.

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