

Eutectic Mixtures of Metallomesogens as Potential Materials for Electro-Optical Applications

H. Hakemi

Plastic Liquid Crystal Technology, Via Lambro 80, 20846 Macherio (MB), Italy

Correspondence authors*H. Hakemi**

Plastic Liquid Crystal Technology via Lambro 80
20846 Macherio (MB)
Italy

Submitted : 14 May 2022 ; Published : 13 June 2022

Citation: H. Hakemi, Eutectic Mixtures of Metallomesogens as Potential Materials for Electro-Optical Applications. *J mate poly sci*, 2022; 2(2):1 - 6.

Abstract

In this work, we present a new approach for utilization of eutectic mixtures of metallomesogens (MOM) as potential materials in electro optical devices. We studied the phase diagrams of blends of synthesized rod-like Palladium (Pd) alkyl/alkoxy-azobenzene complexes with their parent ligands and commercial nematic liquid crystal mixtures. The results indicate complete mesogenic miscibility and eutectic points of MOM-ligand mixtures. In addition, the MOM-ligand eutectic mixture also exhibited a complete nematic miscibility with three commercial liquid crystals TN10427, TNO623 and E43 that qualify them model materials in the guest-host electro-optical devices.

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

Introduction

The metal-containing liquid crystals, known as "metallomesogens" (MOMs) incorporating metal centres into selected organic structures have been studied for decades as potential and effective materials for technological applications (Serrano, 1996; Donnio & Bruce, 1999; Donnio et al., 2003; Date et al., 2003; Bruce et al., 2006; Porta et al., 2008). It has been demonstrated that the presence of metal complexation in liquid crystal chemical structures could add many physical and optical features not present in organic mesogenic systems. Such features have been the main driving forces for potential applications of MOMs in a wide range of electro optical applications including additional selective absorptions; large electrical polarizability, refractive indices and birefringences; high order parameters, mesogenic stability and dichroic ratios. In Short, MOMs offer the possibility of combining the supramolecular ordering of liquid crystal with other additional properties derived from the metal centre.

In the past few decades, in spite of development in chemical structures of MOMs, there has been only few reported studies on their applications in electro-optical and electroluminescent displays, smart sensors, encryption systems or fuel cells, which currently constitute one of the most active fields of research (Serrano, 1996; Wang et al., 2015; Wang et al., 2016). In recent years a great variety of MOM materials with photoluminescence and water-free proton conduction (Krikorian et al., 2014; Geng et al., 2017; Cristián Cuerva, 2018), electroluminescence (Wang et al., 2016; Liu et al., 2011), magnetic (Seredyuk et

al., 2014; Fitzpatrick et al., 2016) and electric (Ionescu et al., 2012; S. Su et al., 2014; S. Su et al., 2016) properties have been synthesised. Some scientific and patent literature are also reported on the potential applications of calamitic and discotic MOMs 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, ferromagnetism, electro conductivity, reaction catalysts, LC intermediates, ink jet and security printing, medicinal and agricultural components (Ginord-Godquin et al., 1991; Bruce, 1992; Blanca Ros, 1995; Hakemi, (n.d); Hakemi et al., (n.d); Roviello et al., (n.d); Hakemi et al., (n.d); Hakemi et al., (n.d); Binnemans, 2010; Gimenez et al., 2002).

In spite of all these developments in synthesis and characterization of MOMs but, the scientific works have not yet been able to provide proper materials for commercial applications, even in the simplest guest-host systems. Some of the major problems in development of MOMs has been due to their inaccessible and high transition temperatures, risk of decompositions at high temperatures, small mesophase range and low chemical stability. Therefore, the key to application of MOMs is not only through their molecular engineering, synthesis and chemical structure, but rather through blending and miscibility by physical and chemical mixing approach to overcome their above mentioned drawbacks.

In order to develop MOMs for application, one requires to make the “right” material for a systematic characterization to qualify for specific device applications. The real challenge to qualify MOMs for application is not necessarily in finding the properties found in organic mesogens or coordination chemistry, but also to discover new features that are not found in either materials.

The major problems of the current MOMs are their inaccessible and high transition temperatures, the risk of decompositions at higher temperatures, their impractical mesophase range and stabilities and, in general, the lack of scientific data on their physical properties. Consequently, any hope for development of commercial MOM materials, will be possible not only through molecular engineering and synthesis, but also by complementary mixing approach as has been done for commercial liquid crystal products. In this respect, we are reporting the study of this approach on the miscibility of rod-like bi-ligand MOM complexes based on salicylal-diaminates structures and we provided the phase diagrams of their binary mixtures with different metals and ligands by physical mixing method (Hakemi & Roviello, 2022). The preliminary results indicated that these MOMs mixtures exhibited complete mesogenic miscibility, distinct eutectic points and wide mesogenic range.

In the present study, we describe the experimental study on the physical mixing of mono-ligand rod-like MOMs based on alkyl/alkoxy-azobenzene Palladium metal-complex chemistry. Accordingly, we studied the phase diagrams, mesogenic miscibilities and eutectic points of binary MOM-ligand. We utilized the eutectic MOM-ligand mixture and studied its phase diagrams with two other MOMs and three commercial nematic mixtures TN10427, TNO623 and E43, in order to qualify them as potential materials in guest-host liquid crystal systems. The results of these studies are mentioned in the following sections.

Materials and Methods

The general chemical formula of synthesized ligands and mono-ligand MOMs based on a common class of Palladium (Pd) metal complex and alkyl/alkoxy-azobenzenes are presented in Figure-1.

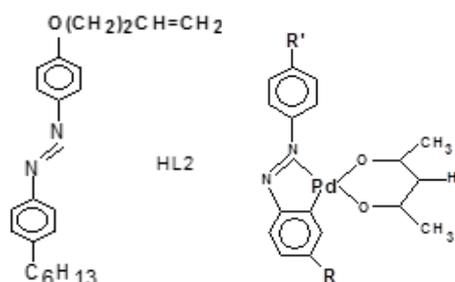


Figure 1: The general formula of ligand and MOM.

According to Figure-1, the chemical structures of MOMs are obtained by three different ligands incorporated in three Pd-alkyl/alkoxy-azobenzene complex chemical structures. With reference to the general formula of Figure-1, the nomenclature and chemical structures of utilized parent ligand and MOMs in

this study are as follows:

- **HL2:** R: C₆H₁₃; R': O(CH₂)₂CH=CH₂
- **Pd-L2:** R: C₆H₁₃; R': O(CH₂)₂CH=CH₂
- **Pd-L5:** R: OC₇H₁₅; R': O(CH₂)₃CH₂CH=C(CH₃)₂
- **Pd-L6:** R: OC₇H₁₅; R': O(CH₂)₂CH(CH₃)-(CH₂)₂CH=C(CH₃)₂

The structural variations are obtained by changing the structure of the ligand's terminal groups R and R', which may be also different in the same molecule, as well as variations of coordinated metal complex. The details of the synthetic procedures of this class of ligands and MOMs have been mentioned elsewhere (Ghedini et al., 1994; Ghedini et al., 1996a; Ghedini et al., 1996b; Hakemi et al., 2022). The utilized commercial liquid crystal mixtures include TN10427 and TNO623 (Hofmann LaRoche) and E43 (Merck). All materials were used as such. The phase diagrams of MOMs mixtures, as well as their mesogenic-crystal (TNC) and isotropic-mesogenic (TIN) 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. 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.

Results & Discussion

In Table-1, we tabulate the crystal-mesogenic and mesogenic-isotropic transition temperatures on heating (TCM & TMI) and cooling (TMC & TIM) modes, as well as the mesogenic phases of the ligand, MOMs and commercial nematic materials.

Compound	Transition Temperature (°C)		Mesophase
	T _{IM}	T _{MC}	
H-L2	48.1	14.8	Monotropic Nematic
Pd-L2	43.1	- 12	Monotropic Nematic
Pd-L5	39.1	23.8	Monotropic Nematic
Pd-L6	63.6	33.8	Enantiotropic Chiral Nematic
TN10427	114.5	- 40	Enantiotropic Nematic
TNO623	101.9	- 35	Enantiotropic Nematic
E43	77.8	- 4.5	Enantiotropic Nematic

Table 1: The transition temperatures of ligand, MOMs and commercial liquid crystal materials

According to data of Table-1, the studied ligand (HL2) and MOMs (Pd-L2, Pd-L5 and Pd-L6) exhibit low temperatures transitions. With respect to mesogenic type, the ligand HL2 exhibits an enantiotropic nematic phase, the MOM components Pd-HL2 and Pd-HL5 exhibit monotropic nematic phase, while Pd-HL6 shows an enantiotropic chiral nematic phase. All three commercial liquid crystals TN10427, TNO623 and E43 exhibit enantiotropic nematic phase.

The phase diagrams of MOMs, ligand and commercial liquid crystals were carried out through the following binary and ternary physical mixtures with the results mentioned in the subsequent sections:

- Binary MOM and parent ligand: Pd-L₂+HL₂
- Ternary eutectic MOM/ligand and MOMs with different ligands: Pd-L₂/HL₂ mixture with Pd-L₅ and Pd-L₆
- Ternary eutectic MOM/ligand and commercial liquid crystals: Pd-L₂/HL₂ mixtures with TN10427, TNO623 and E43.

Binary Mixtures of MOM and Parent Ligand:

In Table-2 we tabulated the transition temperatures and in Figure-2 we present the phase diagram of binary Pd-L2 MOM and H-L2 ligand mixtures at cooling modes, respectively.

Pd-L ₂ (%mole)	T _{IN} (°C)	T _{NC} (°C)
0	48.1	14.8
3.3	49.4	13.6
8.1	48.9	10.8
29.2	46.9	-10.7
62.5	45.9	-35
100	43.1	-12

Table 2: The transition temperatures of Pd-L2 / HL2 mixtures.

According to Table-2, both H-L2 ligand and Pd-L2 MOM exhibit similar isotropic-nematic (TIN) transitions whereas the presence of metal complex in PD-L2 shows a wider nematic range (52°C) and lower than that of H-L2 ligand (33°C), which is due to supper cooling of Pd-L2 and lowering of nematic-crystal (TNC) to -12°C. According to Figure-2, the Pd-L2/H-L2 phase diagram shows a complete linear trend of TIN transitions within the whole composition range, which is due to total nematic miscibility of the MOM and ligand. In addition, this mixture also exhibits a distinct eutectic point at the composition of around Pd-L 2= 62.5%wt. At the eutectic point the nematic range is expanded to 80°C with TNC = -35°C and TIN = 45.9°C, which makes this eutectic mixture as a potential candidate material for application in electro-optical devices.

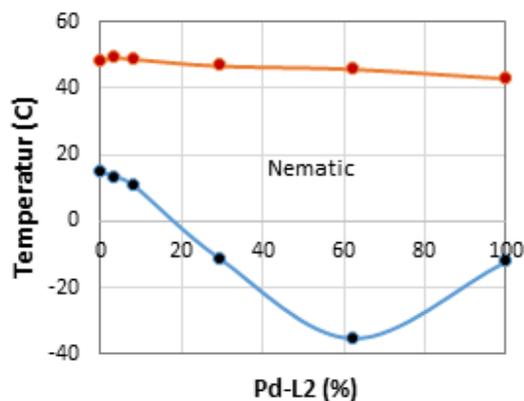


Figure 2: The phase diagram of Pd-L2 / HL2 mixtures

Pd-L5 (%mole)	T _{IN} (°C)	T _{NC} (°C)
0	45.7	-35
5	42.2	-35
20	40.8	-35
35	32.8	-35
50	35.2	-38
75	33.4	-10
90	33.7	10
100	39.1	23.8
Pd-L6 (%mole)	T _{IN} * (°C)	T _{NC} (°C)
0	45.9	-35
2	42	-35
5	41	-35
10	41.3	-38
20	44.2	-35
35	46.7	-15
100	63.6	33.8

Table 3: The phase diagrams of eutectic Pd-L₂/HL₂ with Pd-L₅ and Pd-L₆.

Ternary Mixtures of Eutectic MOM/Ligand and MOMs:

In Table-3 and Figure-3, we provide the transition temperatures and phase diagrams of ternary mixtures consisting of eutectic composition Pd-L2/L2 (62.5/37.5) with Pd-L5 and Pd-L6 MOMs with different ligands at the cooling modes.

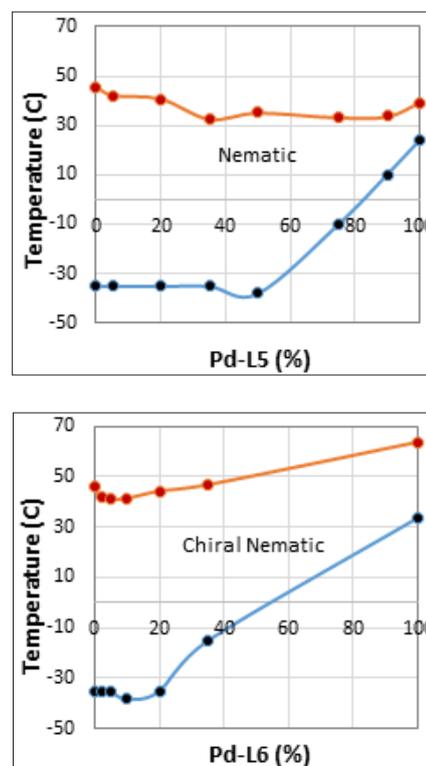


Figure 3: The ternary phase diagrams of eutectic Pd-L2/HL2 with Pd-L5 and Pd-L6 materials.

According to Figure-3, the Pd-L2/HL2 and Pd-L5 mixtures show nematic miscibility of the components due to predominantly linear trends of their T_{IN} transitions with a small eutectic point at around Pd-L5 = 50 %wt. with $T_{NC} = -38^{\circ}\text{C}$. The nematic stability at this eutectic composition is around 73°C . On the other hand, the phase diagram of eutectic mixture of Pd-L2/L2 with Pd-L6 exhibits a chiral nematic (cholesteric) phase within the total composition range and a chiral nematic miscibility as a result of a predominantly linear trend of their T_{IN}^* transition. This tertiary mixture also exhibits a small eutectic point at the composition of around Pd-L6 = 10 %wt. and a mesomorphic stability of around 79°C .

Although the addition of Pd-L5 and Pd-L6 to the eutectic Pd-L2/HL2 do not substantially improve the mesogenic stability in the studied model mixtures, but it indicates on the possibility of developing mixtures with more than one MOM component with different ligand and metal complex to provide the benefits of various MOMs in potential material for wide range of applications.

Ternary Mixtures of Eutectic MOM/Ligand and Commercial Nematics:

In Table-4 and Figure-4, we provide the transition temperatures and phase diagrams of ternary mixtures consisting of eutectic Pd-L2/L2 (62.5/37.5) and three commercial nematic mixtures TN10427, TNO623 and E43.

TN10427 (%wt.)	T_{IN} ($^{\circ}\text{C}$)	T_{NC} ($^{\circ}\text{C}$)
0	45.9	-35
25	59.2	-35
50	79.3	-35
75	95.3	-35
100	114.5	-40
TNO623 (%wt.)	T_{IN} ($^{\circ}\text{C}$)	T_{NC} ($^{\circ}\text{C}$)
0	45.9	-35
25	57.9	-35
50	72.9	-33
75	86.8	-35
100	101.9	-22
E43 (%wt.)	T_{IN} ($^{\circ}\text{C}$)	T_{NC} ($^{\circ}\text{C}$)
0	45.9	-35
25	57.4	-26
50	63.8	-15
75	74.0	-10.5
100	77.8	-4.5

Table 4: The ternary phase diagrams of eutectic Pd-L2/HL2 and commercial liquid crystals.

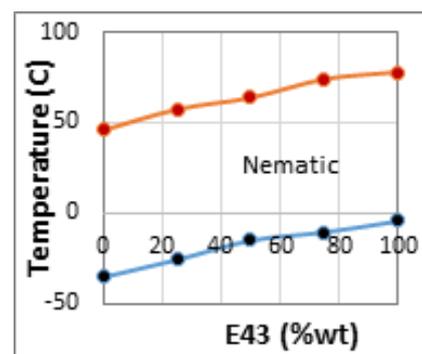
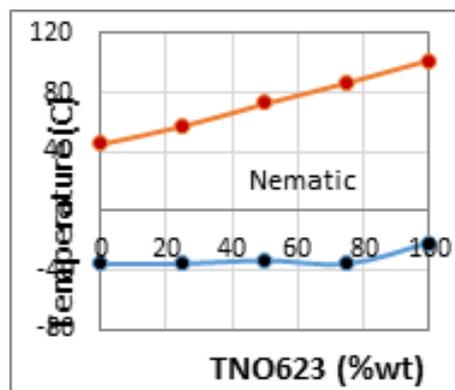
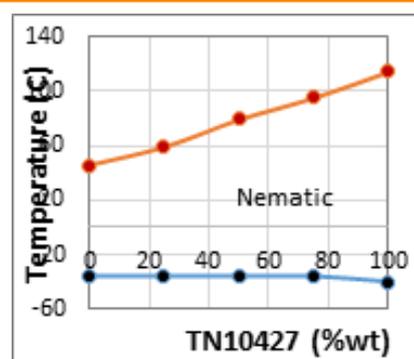


Figure 4: Phase diagrams of eutectic Pd-L2/H-L2 and commercial liquid crystals.

The phase diagrams of these ternary mixtures (Figure-4) indicates that due to linear trends of their T_{IN} transitions within the whole compositions of the mixtures, the eutectic Pd-L2/H-L2 is completely miscible in all three commercial nematic hosts. Also, the T_{NC} transitions of this mixtures exhibit the linear trends with no ulterior eutectic behavior. The nematic stability of these mixtures are relatively constant and dependent on T_{IN} transitions of the host commercial nematic materials. The complete mesogenic miscibility of this model eutectic MOM/ligand mixture in the commercial nematic materials suggests that MOMs can be utilized as guest materials in guest-host systems to exploit the unique properties of MOMs in the electro-optical devices.

Conclusion

In the present study, we showed that it is possible to introduce MOMs as alternative materials in electro-optical devices to not only utilize the unique properties of the presence of metal complexation in mesogenic materials but also to provide miscible mixtures to lower the melting temperatures, expand the mesogenic range and create eutectic mixtures for proper applications. Accordingly, we utilized few model MOM structures with low mesogenic transition temperatures and through physical mixing method and provided binary and ternary mixtures with eutectic behavior. Subsequently, a eutectic MOM/ligand mixture was utilized and mixed with other MOMs, as well as commercial liquid crystals to provide potential materials with the following criteria:

- The binary MOM/ligand mixtures showed complete nematic miscibility with a significant eutectic behavior and a wide nematic range of up to 80 °C.
- The ternary mixtures of eutectic MOM/ligand and MOMs with different ligands also exhibited good mesogenic miscibility, small eutectic points and mesogenic stability range of 73 -79°C.
- The ternary mixtures of eutectic MOM/ligand and three commercial nematic liquid crystals also exhibited mesophase miscibility without any ulterior eutectic points.

Ultimately, if the nematic range of eutectic MOM mixtures are large and comparable with those of commercial nematic hosts, the mixing MOMs approach as guest materials to combine with or totally substitute the commercial liquid crystal hosts will provide desired materials for a wide range of guest-host electro-optical devices.

Acknowledgment

The authors would like to acknowledge the Electro-Optical Film Group of Snia Riceche, Snia BPD (Fiat Group), Via Pomarico, Pisticci Scalo (MT), Italy, who sponsored and financed the research and development projects on Metallomesogens under collaboration contracts with Prof. M. Ghedini, University of Calabria, Rende (CA), Italy, during 1993-1996 period.

References

1. Serrano, J. L. (1996). *Metallomesogens: Synthesis, Properties and Applications*, Wiley VCH. Retrieved from: <https://onlinelibrary.wiley.com/doi/book/10.1002/9783527615094>
2. Donnio, B., & Bruce, D. W. (1999). *Liquid Crystals II Metallomesogens*. Mingos D M P, Berlin: Springer, 95. Retrieved from: https://link.springer.com/chapter/10.1007/3-540-68118-3_5
3. Donnio, B., Guillon, D., Deschenaux, R., & Bruce D. W. (2003). Metallomesogens, In J. A. McCleverty, & T. J. Meyer, (Eds.), *Comprehensive Coordination Chemistry II*. Oxford: Elsevier. Retrieved from: <https://www.elsevier.com/books/comprehensive-coordination-chemistry-ii/mccleverty/978-0-08-043748-4>
4. Date, R. W., Iglesias, E. F., Rowe, K. E., Elliott, J. M. & Duncan, W. Bruce. (2003). Metallomesogens by ligand design. *Dalton Trans*, 1914–1931. DOI: <https://doi.org/10.1039/B212610A>
5. Bruce, D. W., Deschenaux, R., Donnio, B., & Guillon, D.(2006). In *Comprehensive Organometallic Chemistry III*, Chapter 12.05. Elsevier, 195.
6. Porta, B., Khamsi, J., & Noveron, J. C. (2008). *Curr Org Chem*, 12, 1298.
7. Wang, Y., Shi, J., Chen, J., Zhu, W., & Baranoff, E. (2015). Recent progress in luminescent liquid crystal materials: design, properties and application for linearly polarised emission. *J. Mater. Chem. C*, 3(31), 7993. DOI: <https://doi.org/10.1039/C5TC01565K>
8. 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. DOI: <http://dx.doi.org/10.1016/j.dyepig.2016.05.024>
9. Krikorian, M., Liu, S., & Swager, T. M. (2014). Columnar Liquid Crystallinity and Mechanochromism in Cationic Platinum(II) Complexes. *J. Am. Chem. Soc.*, 136, 2952. Retrieved from: <https://pubs.acs.org/doi/pdf/10.1021/ja4114352>
10. 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(19), 11389. DOI: <https://doi.org/10.1039/C6RA28767K>
11. Cristián Cuerva de Alaíz. (2018). PhD thesis, Deptment of Inorganic Chemistry, University of Madrid.
12. Liu, S.-H., Lin, M.-S., Chen, L.-Y., Hong, Y.-H., Tsai, C.-H., Wu, C.-C., Poloek, A., Chi, Y., Chen, C.-A., Chen, S. H., & Hsu, H.-F. (2011). Polarized phosphorescent organic light-emitting devices adopting mesogenic host-guest systems. *Org. Electron.*, 12(1), 15- 12. DOI: <https://doi.org/10.1016/j.orgel.2010.09.020>
13. Seredyuk, M., Muñoz, M. C., Ksenofontov, V., Gütllich, P., Galyametdinov, Y., & Real, J. A. (2014). Spin Crossover Star-Shaped Metallomesogens of Iron(II). *Inorg. Chem.*, 53, 8442-8454. DOI: <https://doi.org/10.1021/ic5010159>
14. Fitzpatrick, A.J., Martinho, P. N., Gildea, B. J., Holbrey, J. D., & Morgan, G. G. (2016). Robust Room Temperature Hysteresis in an FeIII Spin Crossover Metallomesogen. *Eur. J. Inorg. Chem.*, 2016(13-14), 2025. DOI: <https://doi.org/10.1002/ejic.201501335>
15. Ionescu, A., Godbert, N., Crispini, A., Termine, R., Golemme, A., & Ghedini, M. (2012). Photoconductive Nile red cyclopalladated metallomesogens. *J. Mater. Chem.*, 22, 23617. DOI: <https://doi.org/10.1039/C2JM34946A>
16. Su, P. Y. S., Tseng, J. C. W., Lee, K.-M., Wang, J.-C. & Lin, I. J. B. (2014). Advanced molecular materials based on novel Pd(II) and Pt(II) metallomesogens for technological applications. *Inorg. Chem.*, 53, 5902. chrome-extension://efaidnbmnnnibpcajpcglclefindmkaj/<https://core.ac.uk/download/pdf/163093502.pdf>
17. 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. DOI: 10.1002/chem.201502823
18. Ginord-Godquin, M., & Maitlis, P. M. (1991). Metallomesogens: Metal Complexes in Organized Fluid Phases. *Angew Chem. Int. Engl.*, 30(4), 375-402. DOI: <https://doi.org/10.1002/anie.199103751>
 19. Bruce, D.W. (1992). Bruce, D.W., & Hare, D. O. (Eds.), *Inorganic Materials*, J. Wiley & Sons Ltd. DOI: <https://doi.org/10.1002/ange.19941060434>
 20. Blanca, Ros. M. (1996). Other Physical Properties and Possible Applications of Metallomesogens. In J. L. Serrano (Eds.), *Metallomesogens - Synthesis, Properties & Applications* (pp. 498). <https://vdoc.pub/documents/metallomesogens-synthesis-properties-and-applications-7lvccdep1g30>
 21. Hakemi, H. WO 95/01410.
 22. Hakemi, H., Caporusso, M., & Santangelo, M., EP 0747 461 A1.
 23. Roviello, R., Centore, B., Panunzi, & H. Hakemi, IT1394422.
 24. Hakemi, H., Lofer, A., & Peso, E. US62/065,805; PCT47459 WO2016/06327.
 25. Hakemi, H., Lofer, A., Peso, E., & Gal-Fuss, D.; US62/076,002. <chrome-extension://efaidnbmnnnibpcajpcglclefindmkaj/https://patentimages.storage.googleapis.com/64/f9/a2/d30800667d6b4e/WO2016071908A1.pdf>
 26. K. Binnemans. (2010). In D.W.Bruce, D. O'Hare & R.I.Watson(Eds.), *Inorganic Materials Series*. J.Wiley, 61-133. Retrieved from: <https://silobase.com/molecular-materials.html>
 27. Gimenez, R., Lydon, D.P.,& Serrano, J.L.(2002). Metallomesogens: a promise or a fact?. *Current Opinion in Solid State & Materials Science*, 6(6), 527-535. DOI: [https://doi.org/10.1016/S1359-0286\(03\)00009-3](https://doi.org/10.1016/S1359-0286(03)00009-3)
 28. Hakemi, H., & Roviello, A. (2022). *Jn*.
 28. Ghedini, M., Hakemi, H., Pucci, D., Aiello, I., & Pane, S. (1994). *SniaRicerche Internal Report*.
 29. Ghedini, M., Pucci, D., & Neve, F. (1996). Mesogenic cyclopentadienyl cyclopalladated azobenzene complexes. *Chem. Commun.*, 1996(2), 137. Retrieved from <https://pubs.rsc.org/en/content/articlelanding/1996/CC/CC9960000137>
 30. Ghedini, M., Morrone, S., Neve, F., & Pucci, D. (1996). Cyclopalladated azo- and azoxybenzene mononuclear complexes *Gazz. Chim. It.*, 126(8), 511-515. Retrieved from <https://chemport-n.cas.org/chemport-n/?APP=ftslink&action=reflink&origin=npg&version=1.0&coi=1%3ACAS%3A528%3ADyaK28Xms1amtro%3D&md5=fb3aaaa73bdea12ee4c0a06ff228f0b4>
 31. Hakemi, H., Roviello, A., Sirigu, A., Panunzi, B., & Ghedini, M. (2002). *Proceedings of 19th ILCC, Edinburgh, UK*.
 32. Hakemi, H., Roviello, A., Sirigu, A., Panunzi, B., & Ghedini, M. (2002). *Proceedings of 19th ILCC, Edinburgh, UK*.

Copyright: ©2022 H. Hakemi. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.