Advanced functional luminescent metallomesogens: the key role of the metal center

Cristián Cuerva,[†]* Mercedes Cano,[‡] Carlos Lodeiro[†§]*

[†] BIOSCOPE Research Group, LAQV@REQUIMTE Chemistry Department, NOVA School of Science and Technology, NOVA University Lisbon, 2829-516 Caparica, Portugal.

[‡] Department of Inorganic Chemistry, Complutense University of Madrid, Ciudad Universitaria, 28040 Madrid, Spain.

[§] PROTEOMASS Scientific Society, Rua dos Inventores, Madam Parque, Caparica Campus, 2829-516 Caparica, Portugal.

ABSTRACT: The use of liquid crystals for the fabrication of displays incorporated in technological devices (TVs, calculators, screens of eBook's, tablets, watches) demonstrates the relevance that these materials have had in our way of living. However, society evolves, and improved devices are looked for as we create a more efficient and safety technology. In this context, metallomesogens can behave as multifunctional materials because they can combine the fluidic state of the mesophases with properties such as photo and electroluminescence, which offers new exciting possibilities in the field of optoelectronics, energy, environment, and even biomedicine. Herein, it has been established the role of the molecular geometry induced by the metal center in metallomesogens to achieve the self-assembly required in the liquid-crystalline mesophase. Likewise, the effect of the coordination environment in metallomesogens has been further analyzed since its importance to induce mesomorphism. The structural analysis has been combined with an in-depth discussion of the properties of these materials, including their current and potential future applications. This review will provide a solid background to stimulate the development of novel and attractive metallomesogens that allow designing improved optoelectronic and microelectronic components. Additionally, nanoscience and nanotechnology could be used as a tool to approach the design of nanosystems based on luminescent metallomesogens for use in bio-imaging or drug delivery.

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1. Introduction

1.1. Liquid crystals: a look back

The discovery of liquid crystals dates back to 1888 when Reinitzer observed the phase changes that the benzoate of cholesteryl experimented by the effect of temperature,[1,2] later optically identified by Lehmann.[3] The intermediate phase between the solid and liquid phases was called mesophase or liquid crystal phase. These materials in which the mesophase is formed by temperature effect are known as thermotropic liquid crystals. The mesophase can be originated upon heating from the solid phase when the melting temperature is reached, and it will be stable until its transformation in the isotropic liquid at the clearing point. Upon cooling, a reversible phase behavior should be observed (enantiotropic behavior).[4] For example, cholesteryl benzoate, the first liquid crystal found by Reinitzer, melts to the mesophase at 145 ºC and it is stable until *ca*. 178 ºC when the isotropic liquid is formed.[1] However, in some cases, the mesophase does not appear upon heating and it is only originated after cooling back the compound from the isotropic liquid (monotropic behavior).[4] The supramolecular ordering in the mesophase can also change as a function of temperature, and mesophase transitions could occur. This phenomenon results of special interest to modulate additional anisotropic properties that present the material.

Since the discovery of liquid crystals, thousands of compounds with a great variety of molecular shapes, geometries and supramolecular stackings have been reported. In 1907, Vorländer established as a general rule that molecules should have an elongated shape to achieve the supramolecular organization required in the mesophase (calamitic liquid crystals),[5] and it was not until 1977 when Chandrasekhar and his co-workers described the first disc-like molecule that was able to induce mesomorphism (discotic liquid crystals).[6] At present, 133 years after their discovery, a great variety of molecular shapes have been described to be mesogenic, some of them rather surprising such as bent-, bowl- or roof-like shapes.[7,8,9,10,11,12,13,14,15] However, although the structural characteristics of these molecules can be very different, the self-assembly in the mesophase always responds to the same rules. On the one hand, calamitic liquid crystals can form nematic (N), smectic (Sm) and chiral mesophases (N* or Sm*) (Figure 1a).[16,17] In the particular case of smectic mesophases, it is also possible to distinguish several subtypes as a function of the preferred spatial direction of molecules in the layered packing (e.g.: smectic A (SmA) or smectic C (SmC) mesophases. On the other hand, the mesophases of discotic liquid crystals can be grouped similarly, but in this case, they are named as follows: nematic (N_D), columnar (Col_D) and chiral nematic (N^*_D) mesophases. At the same time, by considering the supramolecular arrangement in columnar mesophases, they can also be classified as hexagonal (Col_h), rectangular (Col_r), tetragonal (Col_t) and lamellar (Col_L) columnar mesophases (Figure 1b).[18]

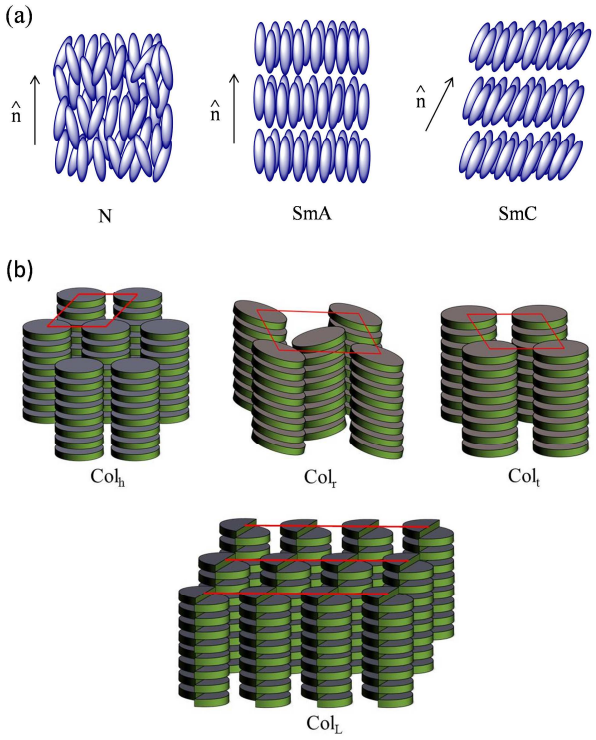


Figure 1. (a) Supramolecular organization in nematic, smectic A, and smectic C mesophases. (b) Several supramolecular packings that can be adopted by columnar liquid crystals. Adapted with permission from ref. 17 Copyright 2017 Cristián Cuerva de Alaíz.

Other important factor from the point of view of the potential applications of liquid crystals is the possibility to build aligned thin films. Columnar mesophases are not as easily to align as the nematic and smectic mesophases of calamitic liquid crystals, but it is possible.[19,20,21,22,23] Additionally, rather high stability ranges of up to 300 ºC have been found for some of these mesophases.[24,25,26] Uniaxial alignment of highly-stable columnar mesophases could give access to novel materials in which the liquid crystal state acts as a platform for enhancing certain properties, such as luminescence or conductivity.[27,28,29,30,31] Columnar arrangements could favor, for example, the establishment of metal-metal-to-ligand charge transfers (MMLCT) and/or aggregation induced emission enhancement (AIEE) behaviors. Likewise, the combination of the fluid nature of the liquid crystal state and the alignment of columnar mesophases offers the opportunity to boost the dielectric properties of conductive liquid crystal materials.

In the last decades, metallomesogens (metal coordination compounds that exhibit mesomorphic properties) have attracted a great interest due to the possibility of inducing additional properties derived from the metal center, such as luminescence, magnetism or conductivity, so increasing the applicability of these materials.[4,32,33,34,35,36] Since their high versatility, the properties and behavior of luminescent metallomesogens are

being studied in order to look for the implementation of these systems in technological devices, such electroluminescent displays,[37,38] smart sensors or encryption systems,[39] and even in biomedical applications, as contrast agents or drug carriers.[40] Moreover, the presence of a metal center offers the possibility of obtaining different coordination environments, which allows modulating both the mesomorphic and luminescence behavior.[4,41]

1.2. Lyotropic phases and amphiphilic metallomesogens

Lyotropic phases are obtained by molecular self-assembly when a mesogen with an amphiphilic nature is added over a solvent under certain conditions of concentration, temperature and pressure.[42] As thermotropic liquid crystals, different phases can be originated as a function of the mesogen´s molecular ordering. When a particular mesogen concentration, named critical micelle concentration (cmc), is achieved, mesogens are self-assembled into micellar phases, which can reorganize to form cubic, hexagonal and lamellar phases as concentration increases (Figure 2). Subconsequenlty, high concentrations give rise to reverse lyotropic phases from the lamellar one to reverse cubic, hexagonal and micellar phases.[43] It is noteworthy that not only purely organic mesogens can form lyotropic phases, amphiphilic metallomesogens can also be self-assembled to originate lyotropic phases in the presence of a solvent.[44]

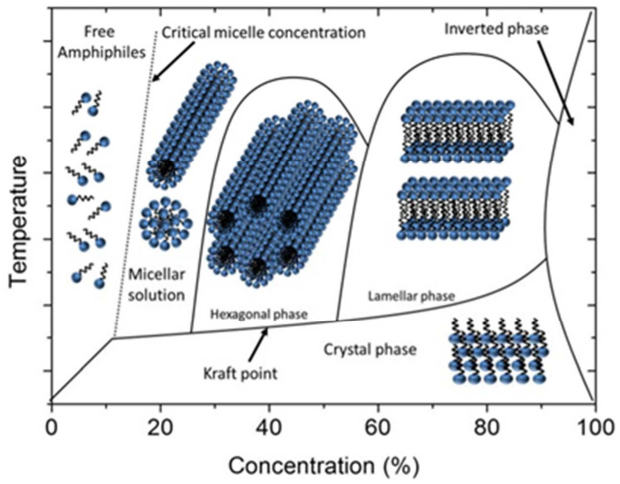


Figure 2. Schematic drawings showing the lyotropic phases of lyotropic liquid crystals as a function of the mesogen concentration and temperature. Reprinted with permission from ref. 43 Copyright 2017 Ingo Dierking

Materials exhibiting lyotropic phases are promising candidates for biological and biomedical applications.[45] They can used, for example, for the reconstruction of lipidic membranes and proteins, or for the encapsulation, transport, and controlled release of nucleid acids. It has been demonstrated also the usefulness of these materials as biosensors to detect antigens or patogens).[46] Moreover, the progress of nanoscience and nanothecnology have opened a new application field for them, because lyotropic phases can be used as template to synthesize nanoparticles, entrap hydrophobic drugs or prepare conductive nanofluids.[47,48,49,50]

1.3. Supramolecular interactions in metallomesogens: a tuning element in photophysical properties.

The development of new soft supramolecular materials with liquid crystal and luminescence properties is still a tremendous scientific challenge. More interestingly, when a metal ion coordinates to organic ligands give rise to a metallomesogenic system that enriches the field of "assembling-induced emission" materials. Due to the intrinsic electronic properties of the metal, among other physicochemical parameters induced or modulated by temperature, pressure, or viscosity, we can control and regulate the final emission and excitation wavelengths.

By contrast with purely organic materials, metallomesogens offers the possibility to generate new cooperative and dynamic intermolecular interactions as a consequence of the presence of the metal center.[51,52] The self-assembly presents in these kinds of materials allows at one point to achieve a thermodynamically stable structure, involving more cooperative interactions between the metal ions and the ligands, giving rise to functional materials whose properties can be modulated by controlling these interactions.

In many reported cases in this review using Zn(II), Ag(I), Au(I), Pt(II) and Ln(III) as the metal center, the electronic properties found in the liquid crystal state, accomplished by the beautiful self-organized structure induced by the presence of the metal center and an adequate ligand, allow to consider the coordination and organometallic compounds as good candidates for optoelectronic devices. All these complexes could have applications as advanced liquid crystal devices, sensors, photoelectronic materials, light-emitting diodes, phosphorescence-light emitting diodes, molecular and nanomolecular memory materials, advanced solar cells, molecular spintronics, among others.[53]

Different photophysical phenomena and mechanism can be explored with these systems from the most common photoinduced electron transfer (PeT) and photoinduced energy transfer (PET), to the most elaborate mechanism as intermolecular charge transfer (ITC), twisted charge transfer (TICT), excited-state intramolecular proton transfers (ESIPT), aggregation induce emission (AIE), aggregation induces quenching (AIQ), vibration-induced emission (VIT), and the Foster resonance energy transfer (FRET). All these well-known photophysical mechanisms have served as a brilliant source of inspiration in designing and creating new functional metallomesogens. The control of the non-permanent bonding interactions of these supramolecular entities provides a tool for modulating the photophysical behavior. These phenomena became a crucial factor in modulating the emission and excitation wavelength and, in consequence, the color of the material.

1.4. The role of the metal center in metallomesogens

The design of luminescent liquid crystal materials can be an important step to attaining the required improvements that are socially demanded for electro-optical device applications. Displays for image components or for data treatment represent most of the practical applications of the electro-optical devices. In this context, luminescent metallomesogens may be used as multifunctional materials since they combine the ordering of the fluid phases with luminescence properties.[54,55,56,57] This kind of compounds has received remarkable interests on the basis on the role that liquid crystals had in traditional liquid crystal displays (LCs), especially evident in cost-saving color liquid crystal digital displays.[58] Nevertheless, the problems of energy efficiency and low brightness represent most limitations of these devices. These limitations are mainly due to the use of polarizers and color filters, which transform a significant part of the incident light into thermal energy.[59] Thus, one of the best ways to overcome this disadvantage could be the use of luminescent mesogens.[60,61,62,63,64] Besides developing luminescent mesogenic materials, luminescent metallomesogens offer an exciting opportunity; these compounds can also combine the typical properties of the metal ions (dielectric properties, magnetism, carrier mobility, etc.) with the liquid crystal and luminescence properties induced by the supramolecular ordering of the mesophases.[65,66,67,68]

In order to get new luminescent metallomesogens for real applications (chemosensors, OLEDs, write-erase devices, stimuli-responsive materials), a suitable design can be obtained by introducing modifications in well-known chromophores. Although the main application of liquid crystal materials has been their incorporation in displays, it is well known that competition has been recently established between the LCDs (liquid crystal displays) and displays so-called OLEDs (organic light-emitting diodes), both commercially available.[69] They are basically two different technologies, emissive vs. non-emissive, but both with future and potential perspectives.[70] Liquid crystal materials do not emit light, so that an emitting unit (backlight) is required to illuminate the display panel. In this context, liquid crystals with linearly polarized light offer an interesting alternative as a source for LCD displays.[37]

Most of the luminescent metallomesogens involve Ag(I), Au(I) and Pt(II) metal centers, as well as lanthanides.[71,72,73] The first two offer a great variety of possibilities respect to the coordination modes, which gives access to different suitable geometries for inducing mesomorphism. The establishment of metallophilic Au-Au and Ag-Ag interactions is responsible of the luminescence properties of these materials.[74] Additionally, it allows obtaining supramolecular organizations such as helical or cyclic structures that hardly could be originated with other metal centers.[75,76] On the other hand, the efficient emission and the typical square-planar coordination of Pt(II) complexes make them promising candidates for the achievement of phosphorescent metallomesogens with polarized light emission at room temperature.[77] A substantial effort has been made in recent years to achieve Pt(II) metallomesogens that can be used in the fabrication of OLEDs. To date, a series of phosphorescent metallomesogens has been prepared based on the modification of known chromophores by introducing molecular anisotropy to achieve liquid crystal behaviour.[78,79] The first OLED prototype using a Pt(II) metallomesogen has been recently reported, so those great research efforts are still needed in this field.[38]

Ir(III) complexes exhibit similar luminescence properties than Pt(II) ones, achieving long lifetimes, high quantum yields and long-lasting phosphorescence at room temperature.[80,81,82] In fact, it has been proved that these materials, which can exhibit high phosphorescence quantum yields near to 100%, are excellent candidates for the development of devices.[83] However, the metal center adopts an octahedral coordination environment that hinders the consecution of mesomorphism, so that only some few Ir(III) metallomesogens with electroluminescence behavior have been reported to date.[73]

Another wide field of application for metallomesogens is the development of chromoactive materials, which currently have attracted high interest due to their potential usefulness in the fabrication of sensors, data recording devices and encryption systems, among others.[84,85,86,87] Luminescent emission in metallomesogens, in which lamellar or columnar molecular self-assemblies are favored, causes variations in the HOMO and LUMO orbitals, and therefore also in their photophysical behavior. Thus, modifications in the molecular structure, although they could be small, can modify or induce molecular interactions, originating changes in the luminescence emission or even responses to certain external stimuli. The influence of external stimuli on the luminescent emission of these materials, both in the solid state and in the mesophase, opens up new possibilities for their considering as chromoactive materials, and consequently, for their application as sensors to detect temperature and/or pressure changes, pollutant metal ions, acidic media of different strength, among others.[87,39] Chromoactive materials based on crystalline compounds, polymers and LC materials are known.[88,89,90,91,92] However, the impact of metallomesogens in this area is less developed although they are good candidates by combining the ordered and fluid states of the liquid crystal phases with the luminescent properties induced by the metal center.[87,86,89]

The research of mononuclear Ln(III)-metallomesogens has been carried out from ligands as Schiff bases, β-diketonate, bis(benzylimidazolyl)pyridine, pyridone or macrocycles.[93,94] These species show smectic and/or columnar mesophases with relatively high melting temperatures (190-240 °C). The emissive properties of the solids, which are maintained in the mesophase, are dependent on the Ln(III) ion. However, the development of lanthanide-based cluster species is low as compared to that of transition metals. Different cluster species with β-diketone ligands in which the Ln / ligand ratio implies 4, 5 or greater nuclearities are known.[95,96,97,98] The optical

and magnetic properties derived from f electrons allow them to consider as a platform of reinforcing agents for polymer properties. The introduction into these species of ad hoc elements on the ligands drives to achieve added functionalities that can additionally improve in polynuclear species.

Herein, we provide a comprehensive overview of the advancements, perspectives, and challenges of luminescent metallomesogens based on coordination compounds of Ag(I), Au(I), Pt(II), Zn(II), Ir(III) and Ln(III), also including BF_2 derivatives. It has also been established the role of both the coordination environment and the functionalization of the ligands to achieve the supramolecular organization required in the liquid-crystalline mesophase. We have combined a structural analysis with an in-depth review of the thermal and photoluminescence behaviors of these materials. The work presents the most recent advances in the design of AIEE-active metallomesogens with stimuli-responsive properties, including their current and future applications.

2. Boron difluoride complexes: in the frontier between liquid crystals and metallomesogens

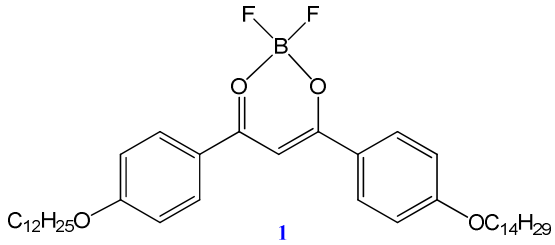
Boron difluoride complexes containing N^N, N^O or O^O coordinated ligands have been reported to be highly fluorescent materials. In particular, one of the best-known materials is the boron dipyrromethene derivatives (bodipys).[99,100,101] These compounds show large extinction coefficients, high fluorescent quantum yields in solution, tunable photophysical properties and good stability, so that they are widely used as dyes for imaging technologies (sensing materials, memory chips and security inks).[102,103,]

Other related well-known materials are those concerning with the family of boron β-diketonate compounds. The photophysical properties of this type of boron difluoride derivatives are originated as a consequence of the electron deficiency of the dioxaborine ring. This fact facilitates the existence of charge transfers from the ligands to this ring.[104] In this context, the presence of aryl groups at the 1,3-positions of the β-diketone core should be required to improve the luminescence properties because the luminescence in the solid state is favored by the presence of π-conjugation, which in turns favors a molecular π-stacking.[105,106,107] Additional intermolecular interactions, such as hydrogen bonds or dipole-dipole contacts, can also be responsible for the luminescence behavior in the solid state.[108] Therefore, changes in the molecular conformation or in the packing modes cause significant variations in the emission spectra of the boron difluoride complexes.

Luminescent boron difluoride β-diketonates and their synthetic procedures have been described for a long time.[109] These materials generate a great interest in the scientific community because of their photophysical and photochemical behaviors, which have been used for relevant applications.[110] Although the boron atom is a pseudo-metal and B(III) compounds cannot be considered as metallomesogens, boron difluoride β-diketonates behave as highly-emitting materials and additionally, they can adopt the required molecular shape to induce liquid crystal properties, which opens new opportunities to achieve bifunctional materials with capabilities for photonic devices.[111,112,113] Thus, the B(III) compounds can be considered as a boundary between organic liquid crystals and metallomesogens. We consider that the study of the molecular shape originated by coordination of the selected ligand to the BF_2 fragment, and the relationship that it has with the supramolecular organization in the liquid crystal state, could of great help for design luminescent metallomesogens with high fluorescence quantum yields close to the unity and stimuli-responsive behaviors.

By combining both luminescence and liquid crystal properties in the same material, it is possible to create defect-less optical nanomaterials with monoaxial oriented molecules exhibiting highly efficient luminescence. On this basis, Turanova et al. prepared and described the first boron difluoride β-diketonate compound possessing both properties.[114] This compound, namely boron difluoride 1-(4-dodecyloxyphenyl)-3-(4-tetradecyloxyphenyl)-propan-1,3-dionate **1** (Chart 1), forms a SmA mesophase at 92 ºC, remaining stable up to 129 ºC when it is transformed into the isotropic liquid. Likewise, the emission spectrum displays a band centered at 530 nm that reveal that the compound emits yellow light.

Chart 1

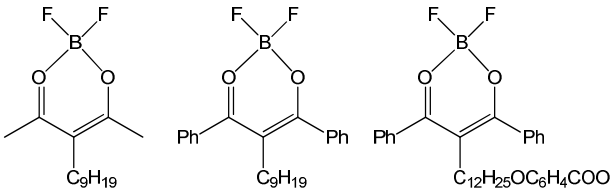


1

Following with this discovery and based on the increasing interest on the study of new light-emitting materials, the same authors reported the study of boron diketonate derivatives using α-substituted β-diketones as starting ligands.[115] Long alkyl chains as C_9H_{19} were introduced at the 2-position of the β-diketone, while CH_3 or C_6H_5 group were located at 1- and 3-positions (Chart 2), neither of the two cases (complexes **2** and **3**) were liquid crystal materials. By contrast, when the $C_{12}H_{25}OC_6H_4COO$ group was introduced at the mentioned 2-position (compound **4**), the resulting boron difluoride compounds exhibit nematic and smectic mesophases at 89 ºC and 102 ºC, respectively. The results were explained by the weakness of the molecular interactions in **2** (only supporting alkyl chains), and by the low geometric anisotropy in **3**. By contrast, the liquid crystal behavior of **4** was related to the increased anisotropy

polarizability determined by the great geometric anisotropy (length to wide molecular ratio).[116]

Chart 2



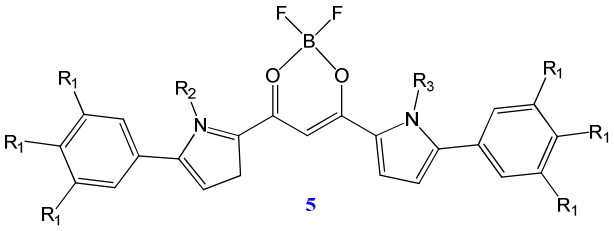
2 **3** **4**

All the three 2-substituted complexes **2**, **3** and **4** showed luminescent behaviour, so that the mentioned complex **4** can be again defined as bifunctional material, exhibiting luminescent properties and liquid crystal polymorphism.

Liquid crystals materials exhibit interesting properties that are related to their molecular anisotropy and mobility.[18] Thus, on building soft materials, planar and π-conjugated molecules are selected as sub-units due to the ability to achieve organized stacking assemblies. In general, these π-conjugated systems are crucial for forming organized structures, whose phases significantly depend on the geometries of these units.

In this context, Maeda and coworkers have investigated some dipyrrolyldiketone boron(III) complexes (Chart 3), which in previous studies were proved to present anion responsive behaviors.[117] The core of these anion receptors exhibits a "rod-like" shape; however they are able to form "disk-like" units consisting of several π-conjugated units. In fact, liquid crystal behavior was found for compounds **5a** ($R_1 = OC_{16}H_{33}$, $R_2 = R_3 = H$) and **5b** ($R_1 = OC_{20}H_{41}$, $R_2 = R_3 = H$) which show Col_h mesophases as a result of the self-assembly into dimeric species. Related compounds **5c** ($R_1 = OC_{16}H_{33}$, $R_2 = H$, $R_3 = CH_3$) and **5d** ($R_1 = OC_{16}H_{33}$, $R_2 = R_3 = CH_3$) containing one or two N-blocked positions also form Col_h or Col_r mesophases, respectively. The UV/visible absorption and fluorescence emission of all mentioned compounds give rise to notable variations which were related to the stacking structures.

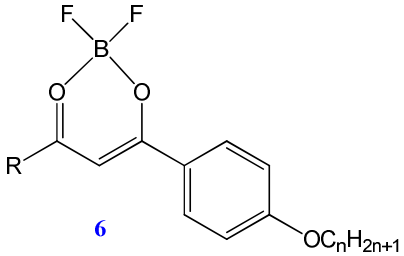
Chart 3



5

In 2010, Cano`s group investigated the photophysical properties of novel di(aryl) diketonate BF_2 dyes **6** (Chart 4), which behave as highly emissive fluoroforophores in the solid state and in solution.[118] There was demonstrated the low tendency to self-aggregation that these dyes have, so being potentially useful for applications such as OLEDs, fluorescent sensors, or solids laser dyes. In addition, they exhibit a strong Stokes shift, facilitating the separation between the excitation and the emission light. Moreover, emission lifetime is also enhanced. These parameters can be modulated in the solid state by modifying the geometry of the compounds, or by switching the fluorophore concentration in solution.

Chart 4

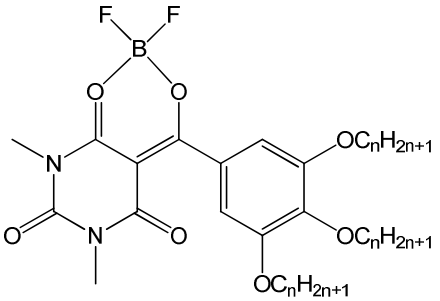


6

R = H or $C_6H_4OC_nH_{2n+1}$; n = 10-18

Taking into account the importance of molecular shape and size of the mesogenic structure, the research of liquid crystal materials has been directed to explore new type of mesogenic compounds. In this context, in addition to the established interest of boron difluoride β-diketonate complexes as liquid crystal materials that has been probed to exhibit high luminescence quantum yield in many cases,[111,114,115,119] new designs have been investigated in the last years.

Chart 5



7a-d n = 8, 10, 12, 14

In particular, Giziroglu et al. have reported a series of 1,3-dimethyl-5-(3,4,5-tris(alkoxy)benzoyl)barbituric acid derivatives containing chain length of 8, 10, 12 and 14 carbon atoms at the alkyl chain and their corresponding boron difluoride complexes **7a-d** (Chart 5).[120] Liquid crystal properties were only found in boron difluoride derivatives with longer alkyl chains **7c** and **7d**, which exhibit enantiotropic nematic mesophases with mosaic textures under polarized light (Figure 3). The phase transition temperatures are relatively low of around 50 ºC,

the existence ranges of the mesophases being of *ca*. 20 ºC. Despite these exciting features, no studies of its potential luminescent behavior appears to be performed.

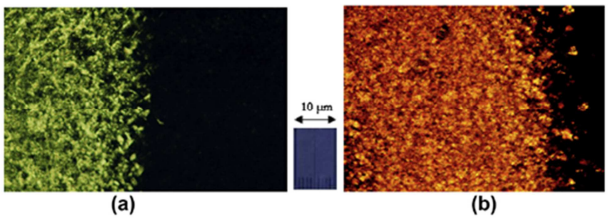
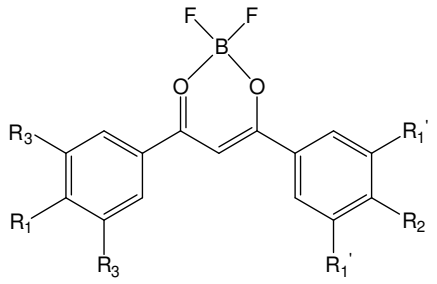


Figure 3. POM microphotographs showing the formation of the nematic mesophase from the isotropic liquid for compounds (a) **7c** and (b) **7d**. Reprinted with permission from ref. 120. Copyright 2013 Elsevier Ltd.

Chart 6



8 $R_1 = OC_nH_{2n+1}$; $R_1' = OC_mH_{2m+1}$; $R_2 = R_3 = H$
9 $R_1 = OC_nH_{2n+1}$; $R_1' = R_2 = OC_mH_{2m+1}$; $R_3 = H$
10 $R_1 = H$; $R_1' = R_2 = OC_mH_{2m+1}$; $R_3 = OC_nH_{2n+1}$

Considering the idea of employing molecular asymmetry as a successful tool to induce and modulate mesomorphism, Sanchez and coworkers prepared a series of β-diketone ligands decorated with different number and length of terminal alkyl chains.[121] Those were used to be coordinated to the BF_2 group, so generating the three families of compounds **8**-**10** shown in Chart 6. In comparison with the mesomorphic behaviour of boron difluoride derivatives containing alkyl-unsymmetrically monosubstituted diketonate ligands,[119] no liquid crystalline phases were found for complexes **8** and **9** decorated with 3 or 4 chains at the periphery. However, it was proved that the presence of five alkyl chains unsymmetrically distributed in complexes of type **10** induces columnar mesomorphism at near room temperature. The mesophases were identified as hexagonal columnar (Figure 4), this result being related to the space occupation by the five substituents. Thus, the hemidiscotic molecules formed are self-assembled to form discs (Figure 5), which are organized in a hexagonal columnar arrangement. All the compounds behave as fluorescent materials in solution as well in the solid state. In CH_2Cl_2 solution, the fluorescence spectra display a broad emission band at ca. 506 - 512 nm for compounds whit 3 or 4 alkyl chains, and at around 520 nm for derivatives bearing five alkyl chains. This effect is attributed to the enhanced electron-donating of the alkyl chains.

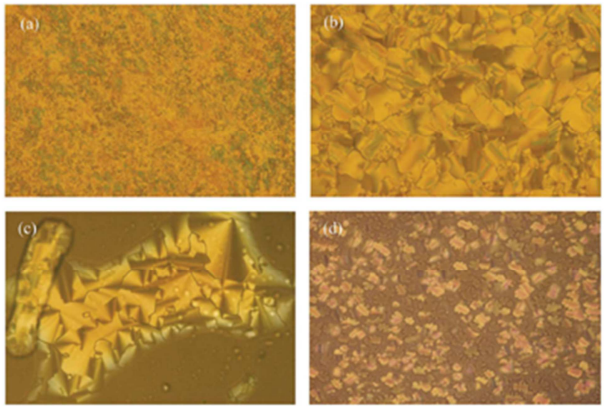


Figure 4. POM microphotographs showing the textures observed in the mesophase of **10** (n = m = 16) at (a) 60 ºC on heating, (b) 59 ºC on cooling, and (c) 57 ºC on cooling. (d) Microphotograph of the mesophase of **10** (n = 14, m = 12) taken at 36 ºC on cooling. [121] - Reproduced by permission of The Royal Society of Chemistry.

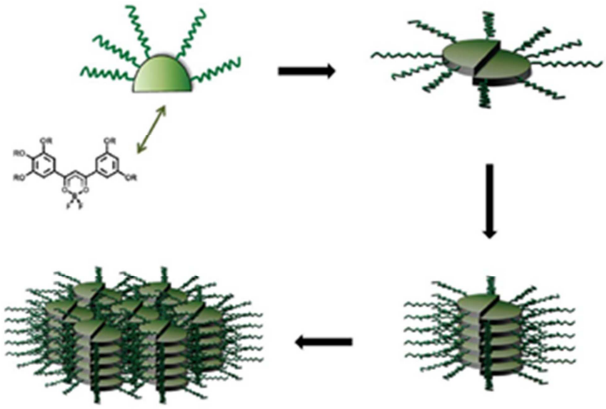
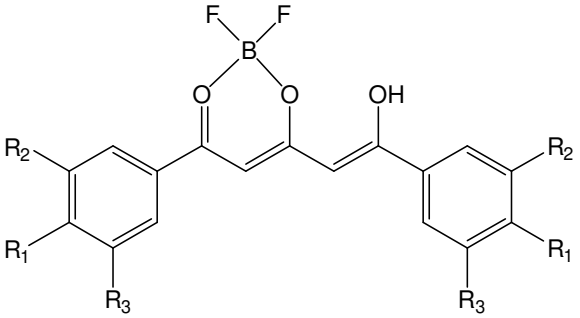


Figure 5. Schematic drawing of the proposed molecular arrangement in the Col_h mesophases. [121] - Reproduced by permission of The Royal Society of Chemistry.

Following the precedents above recovered, the same authors were involved in the preparation and study of several triketones as ligands towards the BF_2 group.[122] The goal was to consider that in those cases, the presence of a large molecular core, an increase of the molecular polarization, as well as an expansion of the π-conjugation should be critical factors to improve the liquid crystal properties on the boron difluoride complexes. Thus, four families of complexes established on the basis of the number and position of the alkyl chains on the alkyloxiphenyl substituents were prepared (Chart 7). All complexes of the families **11** – **14** with long-chain length exhibit enantiotropic mesomorphism. Families **11**

and **12** carrying one or two adjacent chains in each aromatic substituent gave rise to smectic mesophases, while if these two chains are not adjacent or in complexes with three chained in each aromatic ring, discotic mesophases are found. On the other hand, in all cases, results evidence the existence of luminescence both in solution and in the solid state, showing changes in the position of the absorption and emission bands when triketonate ligands are decorated with six alkyl chains. Moreover, complexes exhibit sensory abilities toward Cu^{2+} and Hg^{2+}.

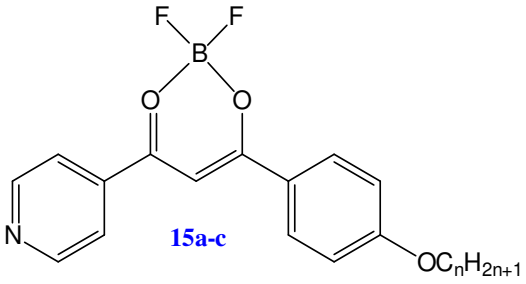
Chart 7



11 $R_1 = OC_nH_{2n+1}$ (n = 16, 18); $R_2 = R_3 = H$
12 $R_1 = R_2 = OC_nH_{2n+1}$ (n = 12, 14, 16, 18); $R_3 = H$
13 $R_1 = H$; $R_2' = R_3 = OC_nH_{2n+1}$ (n = 12, 14, 16, 18)
14 $R_1 = R_2' = R_3 = OC_nH_{2n+1}$ (n = 12, 14, 16, 18)

The aggregation-caused quenching (ACQ) is a crucial inconvenient when developing luminescent boron(III) materials. Taking into account this feature, new strategies are required to avoid this drawback. In this context, Cano et al. were interested in exploring the effect of the inclusion of a pyridine fragment carrying the nitrogen atom at the *para*-position in a new family of β-diketonate difluoride boron(III) compounds (Chart 8).[123] The compounds **15a-c** exhibit luminescence in the solid state and in solution (λ_{em} ~ 500-550 nm), with high quantum yields in $CHCl_3$ of around 0.5-0.7. Polymers thin films doped with these boron difluoride derivatives exhibit interesting reversible acidochromic and thermochromic behaviors, which increases the potential application of these materials (Figure 6). Unfortunately, none of these difluoride boron compounds bearing *p*-N-pyridyl β-diketonate ligands have shown mesomorphic properties, but this study opens new opportunities to design liquid crystals that exhibit high luminescence and chromic behaviors.

Chart 8



n = 12, 14, 16

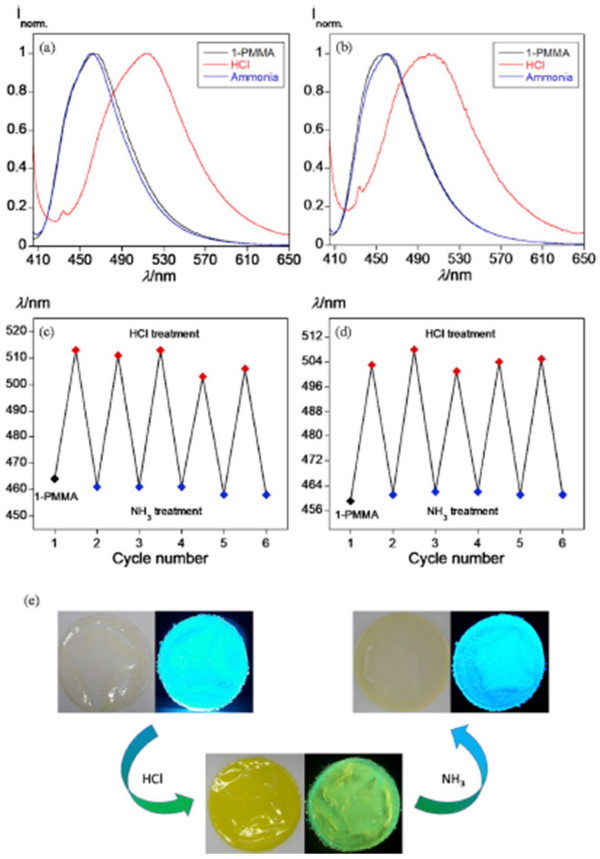


Figure 6. Acidochromic properties of a PMMA film doped with **15a** under treatment with (a) $HCl_{(aq)}$ (12 M) and (b) HCl vapors. (c,d) Reversibility is achieved by addition of NH_3 solution or treatment with their vapors during successive cycles. (e) Images of the PMMA film taken with the naked eye and under UV light, showing its acidochromic behavior. Reprinted with permission from ref. 123. Copyright 2020 Elsevier Ltd.

3. Light-emitting Ag(I) and Au(I) self-assembled materials

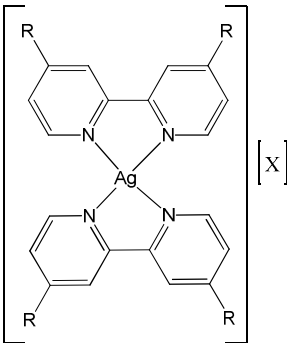
Silver and gold complexes frequently show luminescence properties as a result of the presence of metallophilic Au-Au and Ag-Ag interactions.[124] When designing lumines-

cent Ag(I) and Au(I) metallomesogens, it is important that the complexes emit light at room temperature, which opens a vast horizon of potential applications. In the last years, a common strategy to design luminescent silver and gold metallomesogens is taking advantage of the supramolecular ordering in the mesophase since it can contribute to overtake metal-metal interactions.

3.1. Luminescent Ag(I) metallomesogens

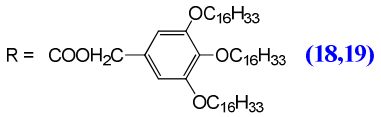
One of the first Ag(I) species reported to exhibit mesomorphism and luminescence properties was designed by coordination of chelate 4,4-disubstituted 2,2'-bipyridines to the silver center (Chart 9). This family of complexes (**16** – **19**) synthesized and studied by Pucci et al. in 2005 show hexagonal and rectangular columnar mesophases at temperatures below 100 ºC as a function of the counter-ion.[125] Although the stability range of the mesophases is relatively narrow (10 – 30 ºC), the low melting and clearing temperatures avoid thermal decomposition of the materials. Moreover, all the compounds emit light at room temperature both in solution (λ_{em} = 300 -350 nm) and in the solid state (λ_{em} = 280 -310 nm).

Chart 9

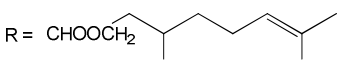


X = CF_3SO_3, DOS (dodecylsulfate)

R = $COOC_{16}H_{33}$ **(16,17)**



(18,19)

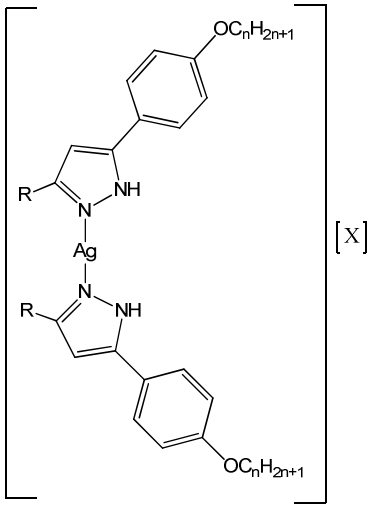


(20,21)

Following this research line, the same authors developed a series of bischelate ionic Ag(I) complexes bearing 2,2'-bipyridine type-ligands with BF_4^-, PF_6^-, $CF_3SO_3^-$ and dodecylsulfate as counter-ions.[126] However, only derivatives **20** and **21** adopt the required packing to form liquid-crystalline phases (Chart 9). Results suggest the formation of dimers or extended polymers via Ag-O interactions between the cation units and the triflate or sulfate groups. Interestingly, both metallomesogens form highly stable Col_h mesophases at room temperature and, additionally, they behave as luminescent materials due to the existence of excimers originated by argentophilic interactions between neighboring molecules.

Other kinds of compounds able to induce mesomorphism in their coordination complexes are pyrazoles. Cano's group demonstrated that ionic luminescent Ag(I) metallomesogens could be synthesized by using 3,5-bis(4-alkyloxyphenyl)pyrazole and 3-(4-alkyloxyphenyl)pyrazole) as ligands (Chart 10).[127,128] In the first case, Ag(I) complexes bearing disubstituted pyrazole ligands are self-assembled in a lamellar structure, forming SmA mesophases at *ca.* 100 ºC (Figure 7). Compounds **22** - **26** with counter-ions such as BF_4^-, PF_6^- and NO_3^- show relatively low melting temperatures ranging between 40 and 80 ºC. By contrast, monosubstituted pyrazole ligands only allow inducing mesomorphism at 47 ºC when the alkyl chain length is 12 and the counter-ion is PF_6^- (compound **27**). Regarding the photophysical behavior, it is noteworthy that silver metallomesogens emit light in solution, in the solid state, and also in the mesophase in some cases. The low melting and clearing temperatures avoid the typical quenching effect by the effect of non-radiative energy transfers.

Chart 10



R = $C_6H_4OC_nH_{2n+1}$; n = 12 -18; X = NO_3 (**22a-d**), BF_4 (**23a-d**), PF_6 (**24a-d**), PTS (**25a-d**), OTf (**26a-d**)
R = H; n = 12; X = PF_6 (**27**)

The pyrazole moiety offers great versatility when designing coordination compounds with different molecular shapes and functionalized groups. In 2010, Giménez and coworkers used 3,5-diarylpyrazolates bearing decyloxy chains at different positions of the benzene fragment to synthesize luminescent Ag(I) metallomesogens (Chart 11). The self-assembly of **28** forms open-chain oligomers that adopt a helical structure suitable for the formation of columnar mesophases (Col_h or Col_r

mesophases) at room temperature (Figure 8).[76] Photophysical measurements at room temperature demonstrate that the coordination-polymer Ag(I) metallomesogens exhibit luminescence in the mesophase (λ = 350–500 nm), which was unprecedented for this type of conformations.

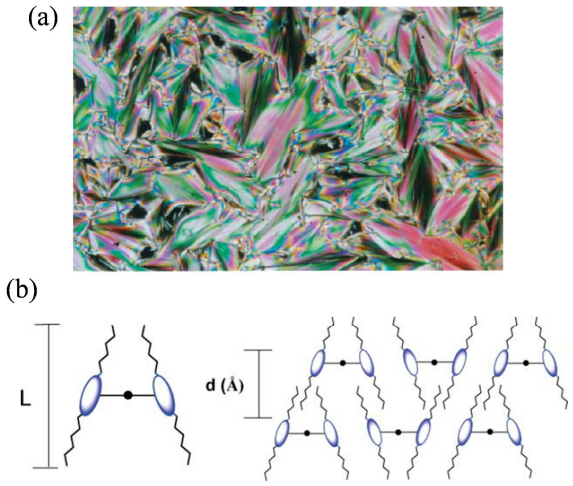
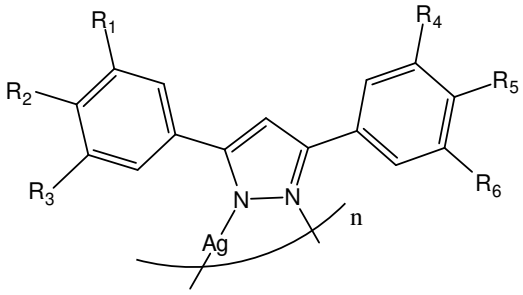


Figure 7. (a) POM microphotograph of the SmA mesophase observed for **24b** at 111 ºC. (b) Proposed schematic drawing of the lamellar organization of molecules in the SmA mesophase. [127] – Reproduced by permission of The Royal Society of Chemistry.

Chart 11



28a-f

a: $R_2 = R_5 = OC_{10}H_{21}$; $R_1 = R_3 = R_4 = R_6 = H$
b: $R_1 = R_2 = R_5 = OC_{10}H_{21}$; $R_3 = R_4 = R_6 = H$
c: $R_1 = R_2 = R_3 = R_5 = OC_{10}H_{21}$; $R_4 = R_6 = H$
d: $R_1 = R_2 = R_4 = R_5 = OC_{10}H_{21}$; $R_3 = R_6 = H$
e: $R_1 = R_2 = R_3 = R_4 = R_5 = OC_{10}H_{21}$; $R_6 = H$
f: $R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = OC_{10}H_{21}$

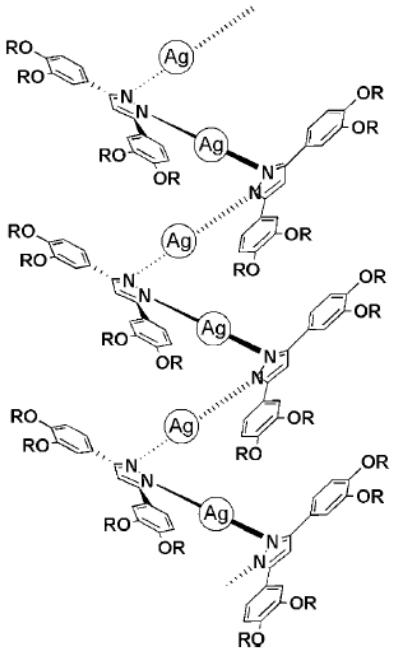


Figure 8. Self-assembly of the Ag(I) complexes in open-chain oligomers. Reprinted with permission from ref. 76. Copyright 2010 Wiley-VCH Verlag 14548 GmbH&Co. KGaA.

Luminescent ionic bis(3-(4-n-alkyloxyphenyl)-5-(2-pyridyl)pyrazole) Ag(I) metallomesogens **29a-d** and **30a-d** (Chart 12) with extended alkyl chains from 12 to 18 carbon atoms were reported by Cano et al. in 2013.[129] The formation of dimeric units via argentophilic interactions seems to be responsible of the liquid crystal properties found. The compounds have enantiotropic or monotropic behavior, forming SmA mesophases at moderate temperatures above 100-140 ºC. Nonetheless, thermal decomposition is only observed in a particular case, most likely due to the formation of an unstable mesophase. The ionic Ag(I) metallomesogens behave as luminescent materials in solution (λ = 392 - 405 nm) but, importantly, the authors demonstrate for the first time the use of these molecular systems to act as luminescence probes for Zn^{2+}, Cu^{2+} and Ag^{+} (Figure 9).

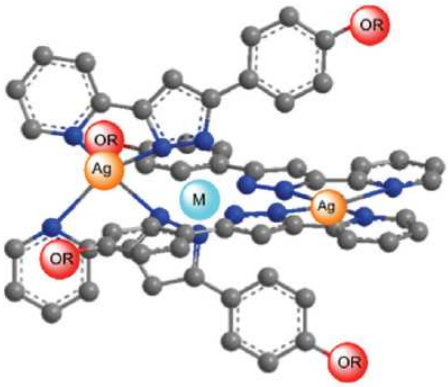
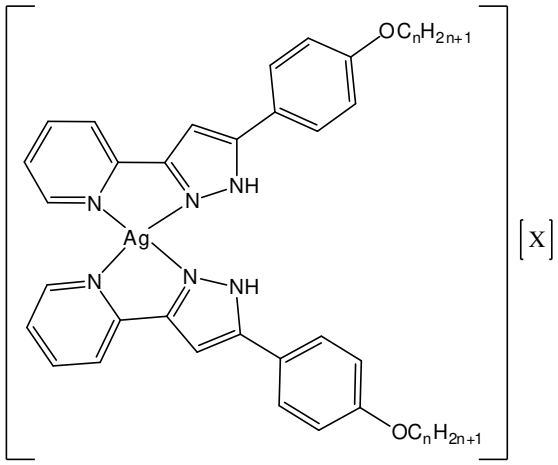


Figure 9. Schematic representation showing the binding mode of the pyrazole-based Ag(I) complexes towards Cu^{2+}. [129] – Reproduced by permission of The Royal Society of Chemistry.

Chart 12



29a-d, 30a-d

X = NO_3, BF_4, n = 12-18

The substitution of the pyrazolic proton by a pyridine group does not constitute a drawback to achieve the supramolecular assembly required in the mesophase. The related Ag(I) metallomesogens **31-33** (Chart 13) containing NO_3^- as counterion, which is bonded to the Ag(I) center via O,O, have been found to exhibit enantiotropic mesomorphism and fluorescence behavior in solution and solid state.[75] These compounds form dimers, adopting an H-like molecular shape (Figure 10) that improves the liquid crystal properties in comparison with the free ligands. Also, molecular asymmetry was introduced in the pyrazole ligand, a notable decrease in the melting and clearing temperatures is produced. The emission band appear centered at around 360 – 420 nm as a function of the functionalization of the pyrazole ligand, and the quantum yield reaches values of up to 0.3.

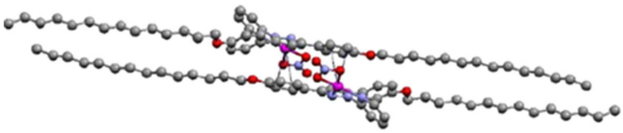
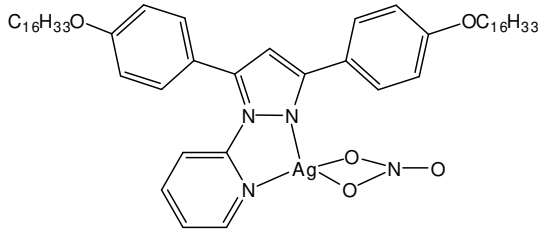
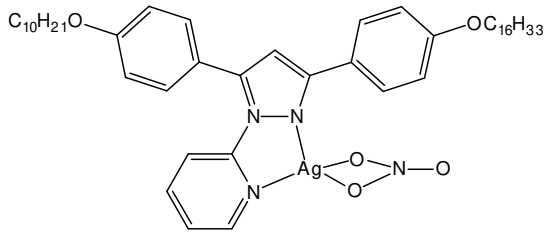


Figure 10. H-like molecular shape originated by the formation of dimmers. Reprinted with permission from ref. 75. Copyright 2014 Elsevier Ltd.

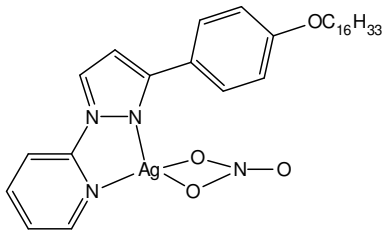
Chart 13



31



32



33

By using the same pyridylpyrazole-type compounds in their deprotonated form, new Ag(I) complexes were synthesized by the same authors.[130] The complexes **34a-c** are self-assembled into cyclic trimers in the solid state, as shown in Chart 14. However, complexes are reorganized in solution, and the cyclic trimers are opened to form one-dimensional oligomers. This feature is associated with the mesomorphic behavior observed in these species at high temperatures, which exhibit SmA mesophases (Figure 11). Moreover, the formation of the oligomers in solution induces luminescence properties (λ = 386 nm, Φ = 0.07).

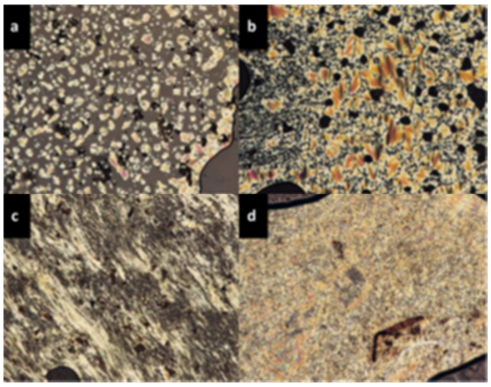
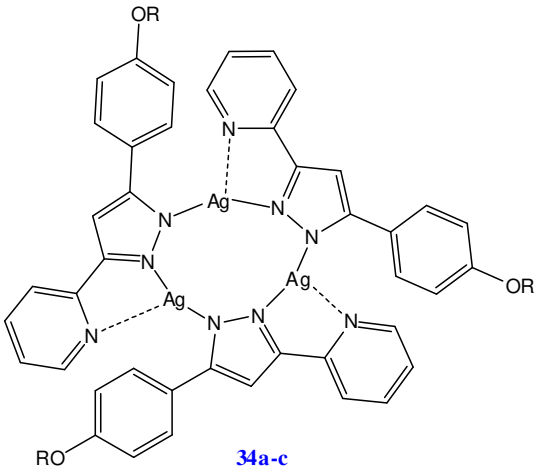


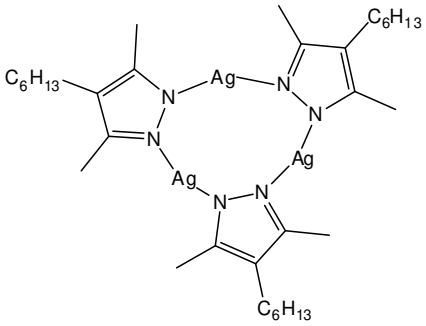
Figure 11. POM microphotographs taken in the mesophase of (a) **34a** at 139 ºC on heating, (b) **34b** at 160 ºC on cooling, (c) **34b** at 131 ºC on cooling, and (d) **34c** at 227 ºC on heating. Reprinted with permission from ref. 130. Copyright 2016 Elsevier Ltd.

Chart 14



34a-c

R = OC_nH_{2n+1}, n = 12, 16, 18

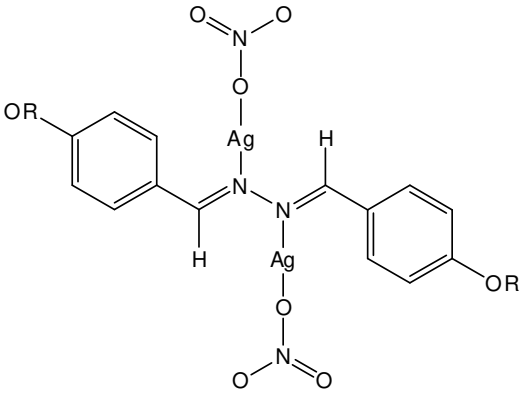


35

A cyclic trinuclear Ag(I) complex supported by 4-hexyl-3,5-dimethylpyrazolate (complex **35**) was also prepared shortly after. On heating, a Col_r mesophase is formed at high temperatures of 186 ºC, and it is maintained up to 193 ºC.[131] The compound behaves as a phosphorescent material at 77 K as a result of the formation of ^{3}AgAg excimers (λ = 448 nm).

Al-Karawi recently reported a series of Ag(I) complexes based on functionalized azines that show liquid crystal and luminescence properties.[132] Although the nature of the species reported could be different, the authors suggest the formation of dinuclear silver complexes with a lineal coordination of the silver atoms as a favorable element to achieve an elongated molecular shape that originates smectic mesophases in three of the compounds described (Chart 15), which also emit blue light in the solid state (λ = 394 nm). Temperature-dependent fluorescence studies reveal that the structural changes occurred during the solid-mesophase transition does not quench the emission properties, and compounds **36a-c** continue to be emissive up to reaching the clearing temperatures.

Chart 15

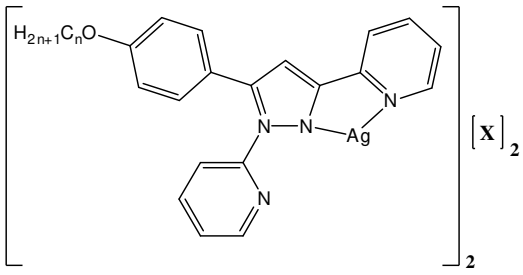


36a-c

R = C_nH_{2n+1}, n = 6-8

Non-mesomorphic 1,3-dipyridylpyrazole compounds have been proved to induce mesomorphism in their corresponding dimeric Ag(I) complexes **37-41** (Chart 16). In general terms, all the compounds with extended alkyl chains of 14, 16 or 18 carbon atoms form SmA mesophases whose stability ranges can be modulated by choice of the counter-ion.[74] Although they are poorly emissive (Φ < 0.01), the silver complexes show ionochromic behavior and highly-emissive heterobinuclear and heterotrinuclear species can be obtained *in situ* upon the addition of Zn^{2+}, Cd^{2+} and Pb^{2+} ions, reaching quantum yields of up to 0.27 (Figure 12).

Chart 16



n = 12-18

X = NO_3(**37a-d**), BF_4(**38a-d**), ReO_4(**39a-d**), PF_6(**40a-d**), PTS (**41a-d**)

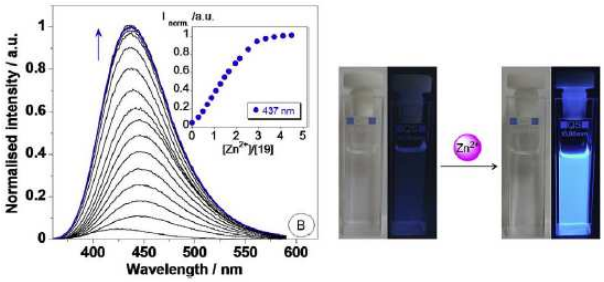


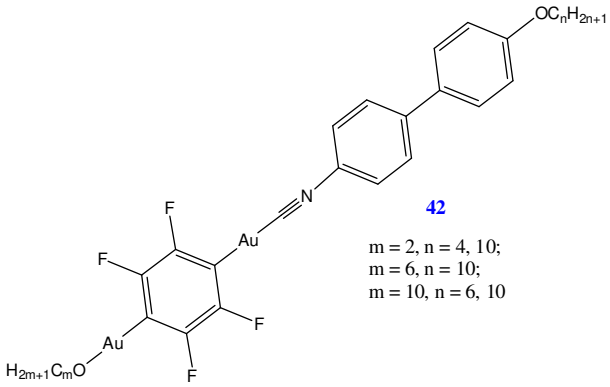
Figure 12. Spectrofluorimetric titration of **40c** in the presence of Zn^{2+} ions. (b) Image of the emission nature before and after the titration. Reprinted in part with permission from ref. 74. Copyright 2017 Elsevier Ltd.

3.2. Luminescent Au(I) metallomesogens

Gold(I) metal complexes commonly possess luminescence, and this phenomenon is regularly attributed to the Au···Au interactions. One of the first examples of luminescent Au(I) metallomesogens was reported in 2005 by Pablo Espinet and co-workers, in which the presence of an isocyanide ligand was the key factor to achieve a bifunctional behavior (Chart 17).[133] All complexes of the family **42** were liquid crystals as shown in Figure 13, exhibiting SmA, SmC and/or N mesophases in agreement with their elongated molecular shape. The metallomesogens show photoluminescence in the mesophase, solid state as well as in solution.

The reported compounds were luminescent at room temperature. In the solid state, a luminescence yellow-green light was observed when irradiated at 365 nm. The emission band observed at around 384 nm shows a lifetime shorter than 10 μs, whereas the bands at *ca*. 490 and 524 nm present a lifetime of 39 μs. This difference suggests two natures, one involving the intraligand localized π···π* orbitals, with no contribution to the Au atoms, and the longer attribute to phosphoresce nature.

Chart 17



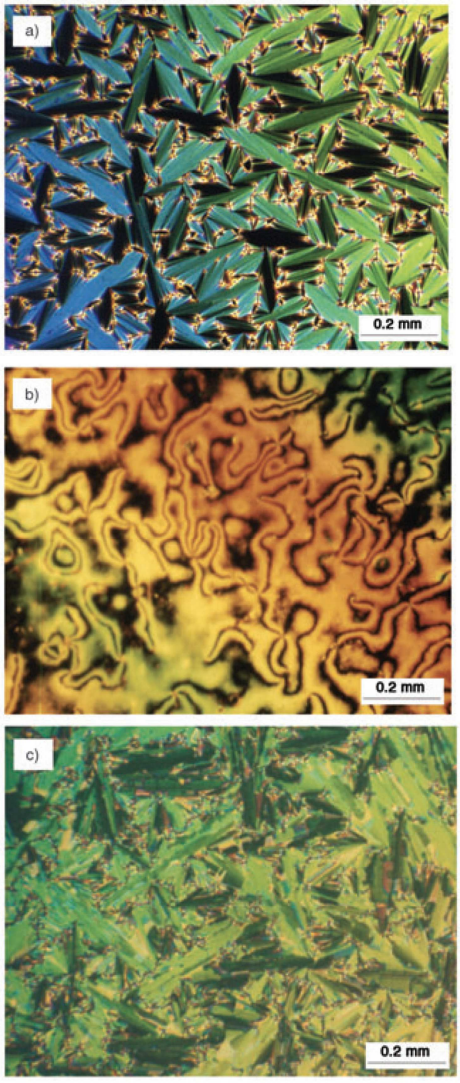


Figure 13. POM microphotographs showing the (a) SmA, (b) N, and (C) SmC mesophases of the Au(I) complexes **42**. Adapted with permission from ref. 133. Copyright 2005 Wiley-VCH Verlag GmbH&Co. KGaA.

A year later, the same research group reported a most sophisticate system based on dinuclear arrangements (Chart 18).[134] All gold(I) complexes **43** display thermotropic liquid crystal behaviour. Even although the free ligands were not mesomorphic, all Au(I) complexes shown mesomorphism, giving rise to a nematic mesophase at temperatures below 100 ºC with stability ranges that reach 80 ºC in some cases (Figure 14). All complexes show photoluminescence in the solid state and in solution.

Chart 18

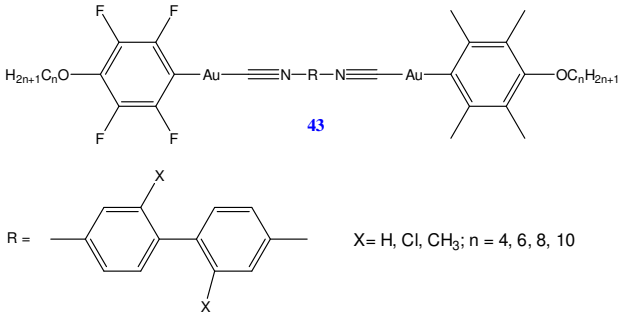
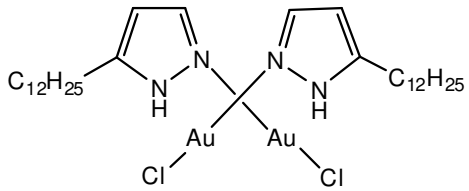


Figure 14. POM microphotograph of the nematic mesophase for the reported complex [μ–(4,4'-CN-C_6H_3Cl-C_6H_3Cl-CN][Au($C_6F_4OC_6H_{13}$)]$_2$] **43**, taken at 152ºC on heating. Reprinted with permission from ref. 134. Copyright 2006 American Chemical Society.

Based on the coordination of pyrazole and pyrazolate-type ligands, Cano and coworkers report in 2007 a series of Au(I) complexes that are luminescent at low temperature (77K).[135] The emission spectra show bands ranging between 395-500 nm, attributed to ligand-to-metal charge transfer (LMCT) transitions. Only one of the reported complexes, [AuCl($Hpz^{R(12)}$] **44** (Chart 19), became liquid crystal at *ca.* 70 ºC on cooling (Figure 15). The authors suggest that a SmA mesophase is formed despite it is difficult confirm it due to POM microphotographs were taken without crossed polarizers. At that time this example was one of the first gold complexes exhibiting both liquid crystal and luminescent properties.

Chart 19



44

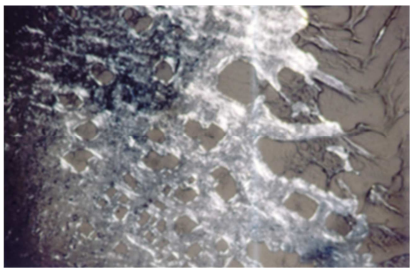
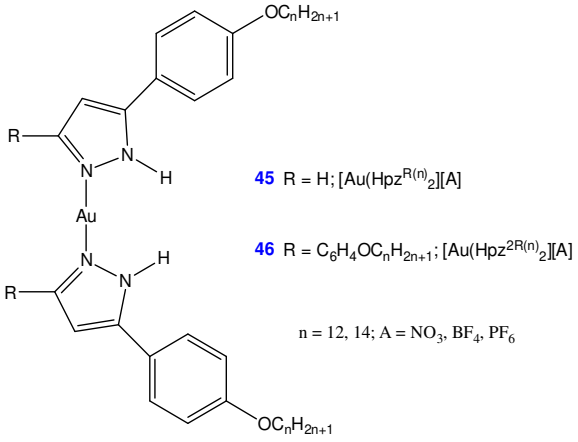


Figure 15. POM microphotograph showing the texture of the mesophase of **44** at 60ºC on cooling. Reprinted with permission from ref. 135. Copyright 2007 Elsevier B.V.

Complexes of the type Au-bispyrazolate were reported by the same research team in 2008, isolated as white products.[127] The gold compounds **45** and **46** exhibit mesomorphism and are emissive in solution and in the solid state (Chart 20, Figure 16). Melting temperatures are found to be rather low of about 70-90 ºC, and even in some instances the SmA mesophase is formed at 40 ºC. Complexation of the $Hpz^{2R(12)}$ ligand induces a slight red-shift in all cases, but no significant differences attributed to the influence of the BF_4^-, PF_6^- or NO_3^- counterions used were observed. The luminescence behavior was explored at different temperature from the solid state to the isotropic liquid. As a general trend, it was observed that the intensity of the luminescence decreases upon temperature increases, and at the clearing temperature the emission almost disappears.

Chart 20



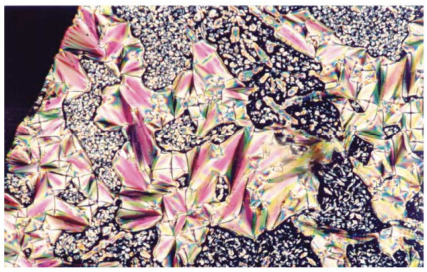
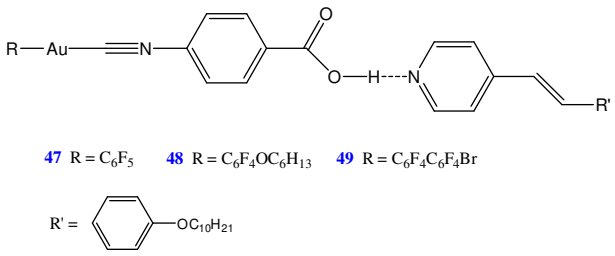


Figure 16. Texture of the SmA mesophase observed by POM for **46** (n = 12, A = PF_6) at 103 ºC. [127] - Adapted by permission of The Royal Society of Chemistry.

Following in the line of Au(I) complexes, Espinet et al. reported several supramolecular liquid crystals incorporating external coordination sites, as decyloxystilbazole units or isocyanide-crown ethers **47** – **49** (Chart 21).[136,137] All metallo-acids were luminescent materials. In these cases, the carboxyl group acts as hydrogen donor sites towards the hydrogen acceptor decyloxystilbazole. The compound shown in Figure 17 was a mesogen with rod-like structure giving rise to a SmC mesophase. The compound was luminescent at room temperature in solution and solid state. The spectra consist in a unique strong band with a maximum at 395 (THF) and 468 (KBr) nm.

Chart 21



47 R = C_6F_5 **48** R = $C_6F_4OC_6H_{13}$ **49** R = $C_6F_4C_6F_4Br$

R' =

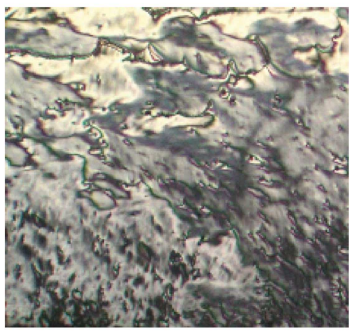
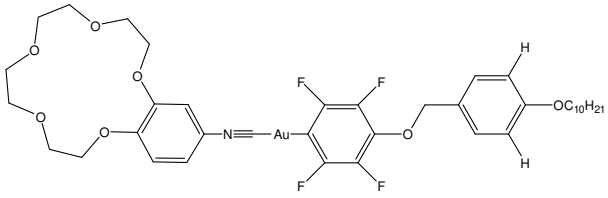


Figure 17. Schlieren texture of the SmC mesophase of **49** observed by POM at 165 ºC on heating. Reproduced from ref. 136 with permission from The Royal Society of Chemistry.

These authors described that the introduction of the crown ether unit allows the coordination of sodium(I) atoms close to the gold(I) complexes, affording bimetallic complexes with luminescent and liquid crystal properties.[137] These compounds were synthesized by dehydration of the corresponding formamide group. All of gold(I) derivatives were luminescent at room temperature in the solid state with emission maxima in the range 405–550 nm, and emits at 77 K from 410 to 572 nm. As an example, compound **50** represented in Chart 22 behaves as a monotropic liquid crystal (Figure 18). As the isotropic liquid was cooling down, these derivatives became very viscous, and the mesophase appears very slowly at temperatures close to room temperature. Unfortunately, after coordination to the sodium(I), the mesogenic behavior was lost.

Chart 22



50

Figure 18. Schlieren texture of the Smc mesophase observed in **50**. Reprinted with permission from ref. 137. Copyright 2008 American Chemical Society.

In 2013 the research group of Tsutsumi reported some novel liquid crystalline gold(I) complexes **51a-d** with a rod-like molecular structure based on very simple ligands including an isocyanide group (Chart 23).[138] The ligand simplicity prevents the steric hindrance and enhance the intermolecular aurophilic interactions necessary to developing efficient photoluminescent properties. All above reported gold (I) complexes were dimers in the crystalline phase, thus acting as mesogen units in the mesophase. In most cases, the nematic mesophase is formed at temperatures below 100 ºC (Figure 19).

Chart 23

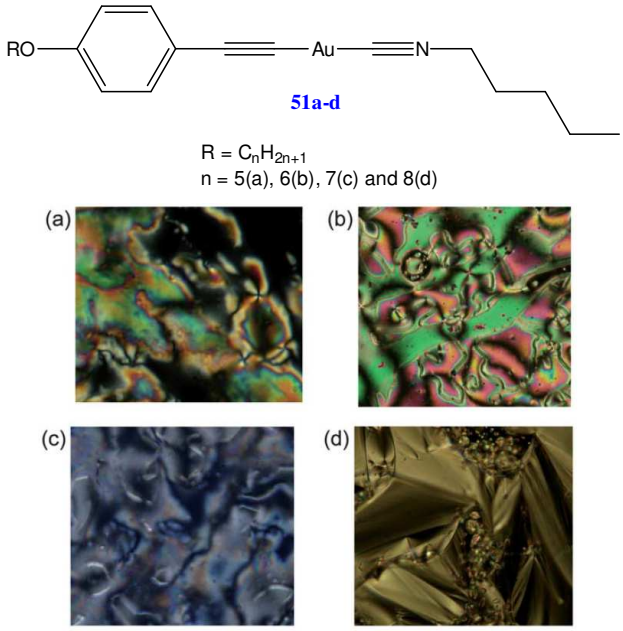
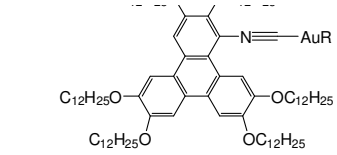
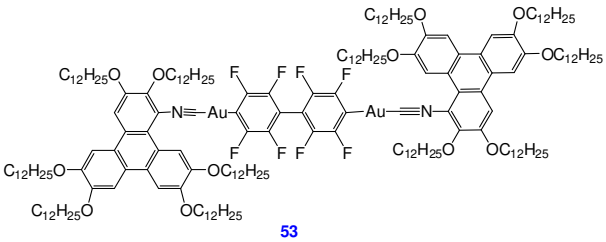


Figure 19. POM microphotographs showing the Schlieren texture of the nematic mesophases of (a) **51a** at 85 ºC, (b) **51b** at 78 ºC and (c) **51c** at 80 ºC, and (d) the focal-conic texture of the smectic mesophase of **51d**. Reproduced from ref. 138 with permission from The Royal Society of Chemistry.

S. Coco and coworkers reported in 2016 a fascinating group of stable organometallic complexes (**52a-d**) containing the ligand 1-isocyano-2,3,6,7,10,11-hexadodecyloxytriphenylene (CN-TriPh) (Chart 24).[139] Several metal complexes of gold, copper, silver and platinum with those ligands were prepared and discussed. Regarding the mononuclear gold(I) complexes all display enantiotropic mesomorphic behavior in a range of temperatures from 5 to 220 ºC (Figure 20a,b). Likewise, the dinuclear gold(I) compound **53** containing two isocyanide trans ligands forms a Col_r mesophase between 102 and 122 ºC, followed of a N one that remains stable until 172ºC (Figure 20c,d). All reported complexes were luminescent, with a fluorescent emission centered on the triphenylene core. The same group of researchers reported a year later several metal complexes of gold, copper, palladium and platinum with a similar triphenylene-based ligand (CNR = 2-(6-(4-isocyanophenoxy)hexyloxy)-3,6,7,10,11-pentakisdodecyloytriphenylene.[140] All complexes show liquid crystal behavior and charge transport properties in the mesophase. Interestingly, the metal ion was capable of modulating the thermal and electronic properties in these materials. Regarding the liquid crystal properties, all complexes containing more than one triphenylene ligand diplay columnar mesomorphism.

Chart 24





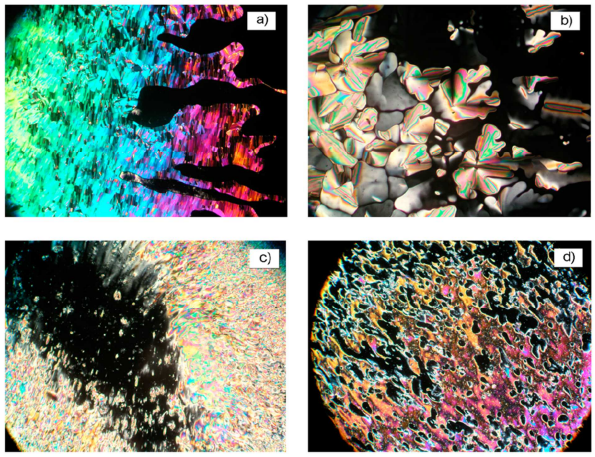
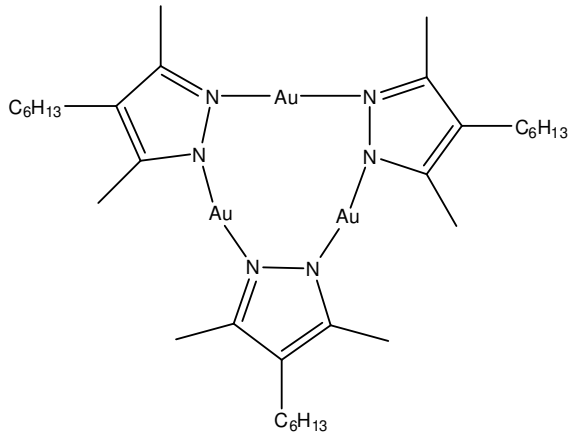


Figure 20. POM textures observed in the mesophase of (a) CN-TriPh at 120 °C on cooling, (b) **52a** at 217 ºC on cooling, (c) **53** at 135 ºC on heating, and (d) **53** at 150 ºC on cooling. Reprinted with permission from ref. 139. Copyright 2016 American Chemical Society.

Polynuclear complexes can also generate also liquid crystalline behavior and luminescence properties. In this field, Giménez et al. reported a family of trinuclear complexes based on pyrazolate moieties.[131] The complexes of Au(I), Ag(I) and Cu(I) were synthesized and characterized. The gold complex **54** drawn in Chart 25 shows columnar liquid crystal phases at temperatures higher than 140 ºC, as it occurs in the analogous Ag(I) derivative (Figure 21). Several PMMA films doped with the gold(I) complex show phosphorescence turn on upon cooling, with excellent quantum yields of 90%, being by now one of the highest values reported for compounds at room temperature.

Chart 25



54

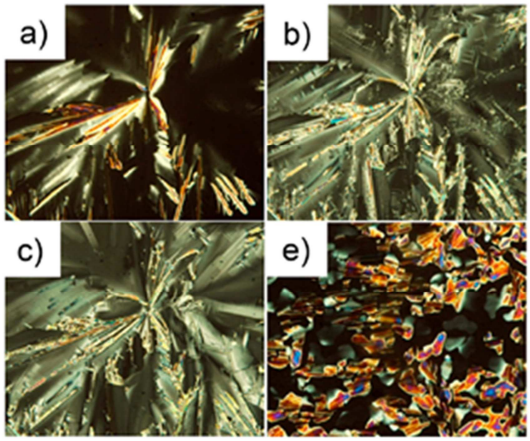


Figure 21. POM microphotographs of the textures observed for **54** on cooling from the isotropic liquid at (a) 145 ºC, (b) 142 ºC, (c) 139 ºC, and (e) 191ºC. Reprinted with permission from ref. 131. Copyright 2018 American Chemical Society.

4. Molecular architectures based on Zn(II) complexes

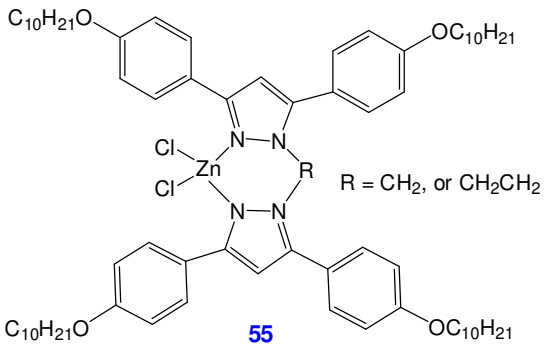
Zinc belongs to group 12. The oxidation state of most compounds is +2, being very rare the +1. Having an electronic configuration of $[Ar]3d^{10}$ it is considered a post-transition metal ion. The most common coordination structures are tetrahedral, where regularly the metal center is coordinate to four donor atoms, or octahedral with six-coordination, sometimes five and seven coordination can be imposed by the nature of the ligand. Zinc(II) can coordinate with a vast number of N and N, O donor molecules, displaying interesting luminescent properties for LED devices and sensors.[141]

Regarding the Zn(II) metallomesogens reported in the literature, they have shown variable coordination geometries such as square planar with porphyrin ligands or trigonal-bipyramidal with ligands such as dithiobenzoates and tridentate pyridines. Nevertheless, tetrahedral or octahedral zinc complexes with mesomorphic properties have continued a hedged objective for a long time.

4.1. Tetra- and six-coordinative Zn(II) complexes

The tetrahedral environment is not very convenient in metallomesogens, and in most of these compounds, this coordination has been proven to be a significant drawback for mesomorphism. However, some complexes have appeared in the literature with liquid crystal properties.

Chart 26



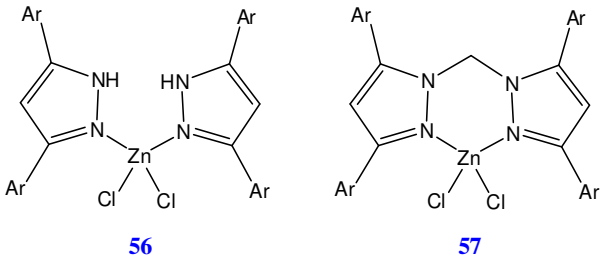
55

In 2004, Serrano et al. used the pyrazole derivative bis[3,5-bis(p-decyloxyphenyl)pyrazolyl]ethane as a ligand to synthesize the first thermotropic Zn(II) metallomesogen (**55**) with luminescence properties (Chart 26).[142] Interestingly, although the compound has a tetrahedral coordination environment, it shows two consecutive smectic mesophases in the temperature range of 95 - 134 ºC and 134 – 154 ºC, respectively, which were identified as SmA and SmC mesophases. Additionally, the new derivative behaves as an emissive material, showing the emission band centered in the ultraviolet region at 365 nm.

Giménez et al. synthesized several metallomesogens with liquid-crystalline behavior at room temperature using 3,5-diarylpyrazoles and bis(pyrazolyl)methane as ligands to be coordinated to Zn(II) ion (compounds **56** and **57** shown in Chart 27).[143] Their molecular structures consist of a nonplanar nucleus because of the tetrahedral coordination of the 3,5-diarylpyrazoles to the Zn(II) center, or the methylene spacer in the bis(pyrazolyl)methane ligands, forming a coordination environment far from the typical rod-like and flat disc-like geometries). The complexes exhibit lamellar and columnar mesophases, which depends directly from the number of alkyl chains present in the pyrazole ligands and not of the nature of the ligand itself. Compounds decorated with only two alkyl chains do not show mesomorphism. By contrast, the Zn(II) compounds that present three or four chains are generally self-assembled in lamellar structures forming smectic (SmA and/or SmC) mesophases (Figure 22b,c), whereas those with five or six alkyl chains exhibit Col_h mesophases (Figure 22a).

In general, all reported complexes exhibit luminescence in $CHCl_3$ solution from 350 nm until 437 nm depending on the number of carbon atoms present in the side chains. Unfortunately, it was not reported the luminescent quantum yield for these molecular complexes.

Chart 27



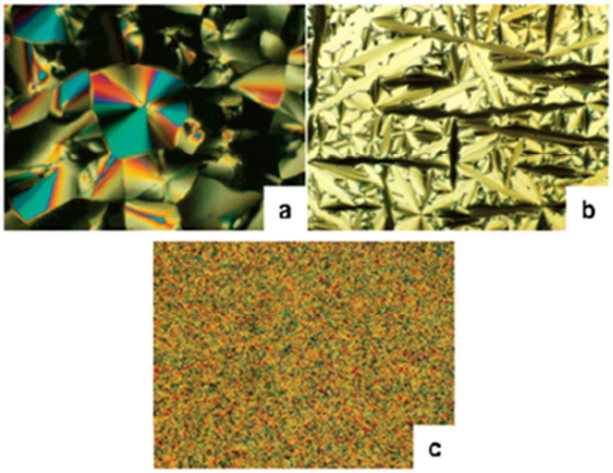
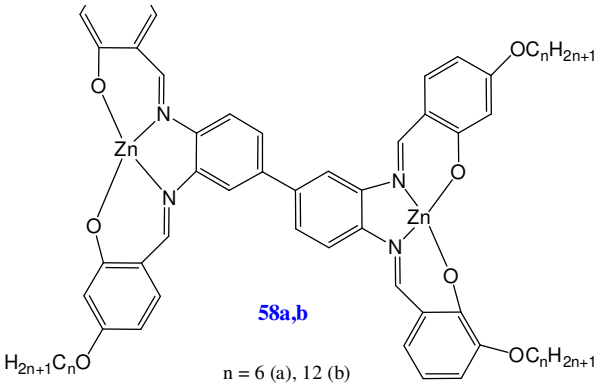


Figure 22. Different textures observed by POM for this type of Zn(II) metallomesogens, which exhibit (a) columnar, (b) SmA, and (c) SmC mesophases. Reprinted with permission from ref. 143. Copyright 2007 American Chemical Society.

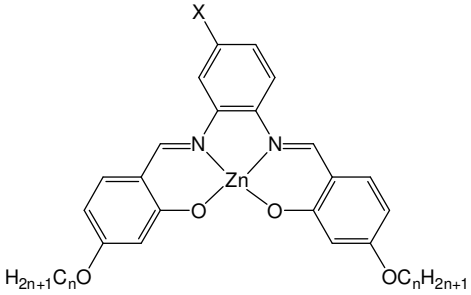
A similar strategy was used by Bhattacharjee et al. in many works with the use of different salicylaldiimine derivatives Schiff base as tetradentate ligands containing one or two N_2O_2 set, originating distorted square planar coordination environments (Chart 28).[144,145,146,147] The distortion of the typical tetrahedral geometry toward a square-planar one allowed obtaining bifunctional species with liquid crystal and luminescence properties. The bimetallic Zn(II) dimers formed from **58** show nematic or SmC mesophases, most likely due to their elongated molecular shape (Figure 23a,b). However, the Zn(II) monomers **59** and **60** are self-assembled *via* antiparallel dimeric arrangements to adopt a columnar stacking in the mesophase (Figure 23c). It is noteworthy that smectic mesophases are reached at lower temperatures (70 – 95 ºC) than the columnar ones, whose melting points are found to be over 120 ºC in all cases.

Chart 28



58a,b

n = 6 (a), 12 (b)



X = CH_3 (**59a-c**), n = 14 (a), 16 (b), 18 (c)
X = Cl (**60a-d**), n = 12 (a), 14 (b), 16 (c), 18 (d)

Regarding the luminescence properties, the dimeric complexes exhibit an emission band center at around 450 nm (violet-blue light) in solution, being observed at *ca.* 504 – 538 nm for the monomers (green light). In the solid state, all the complexes emit a greenish light with the maximum emission ranging between 515 and 558 nm. In some of the reported cases a blue-shifted in the fluorescence band was observed by the coordination effect, since the excited states in these complexes involve a typical ligand-centered (LC) band in nature due to the inability of the d^{10} metal center to participate in low-energy charge transfer for metal-centered transitions. The aggregation induced emissive strategy was also explored with asymmetric Schiff bases.[148] A non-mesomorphic ligand induces liquid-crystalline behavior after Zn(II) coordination. The aggregation phenomenon was explored in different solvents by the authors. The complexes showed blue luminescence with emission maxima centered at ~ 424 nm and an emission quantum yield of ~ 23% in solution, but it was lower than 5% in the solid state upon irradiation with 330 nm UV light. The observed fluorescence emission is originated from metal-perturbed π···π* ligand-centered transitions.

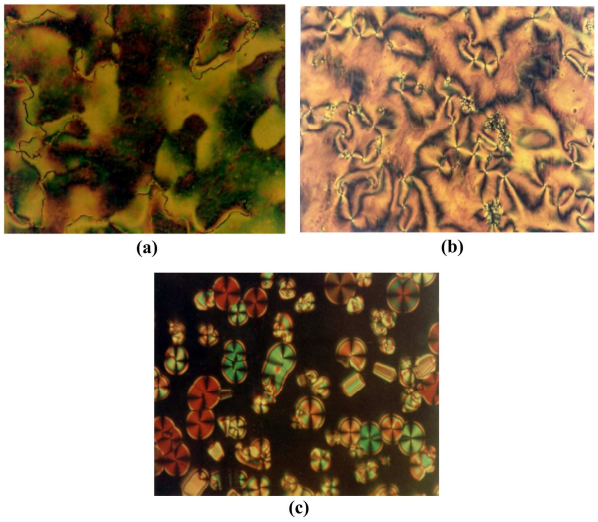
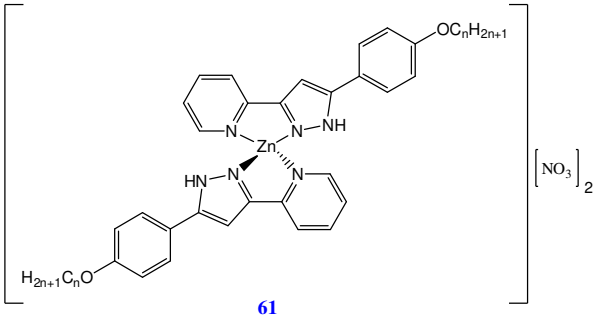


Figure 23. Mesophases observed by POM for the reported Zn(II) metallomesogens. (a) Mesophase of **58a** at 128 ºC; (b) Mesophase of **58b** at 117 ºC. Adapted with permission from ref. 144. Copyright 2012 Elsevier B.V. (c) **59b** at 169 ºC. Adapted with permission from ref. 145. Copyright 2010 Elsevier Ltd.

Cano et al. reported the use of pyridine-functionalized pyrazole ligands as chelators towards Zn(II) ions. Compounds **61** and **62** shown in Chart 29 exhibit the typical fan-shaped and focal-conic textures of the SmA mesophase. Although several octahedral metallomesogens were reported by Giroud-Godquin and Rassat,[149] Swager,[150,151] Bruce,[152,153,154,155,156,157,158,159,160,161] Ghedini,[162] and more recently by Watanabe,[163] these species constitute one of the few octahedral Zn(II) species that show mesomorphism.[164] The liquid crystal behavior of these zinc derivatives depend notably on the chain length, the molecular geometry and the nature of the counter anions used. By increasing the chain length, the melting point of the complexes is decreased regardless of the counter anion present, which suggests that the increase of the van der Waals interactions is a determinant of the mesophase ordering.

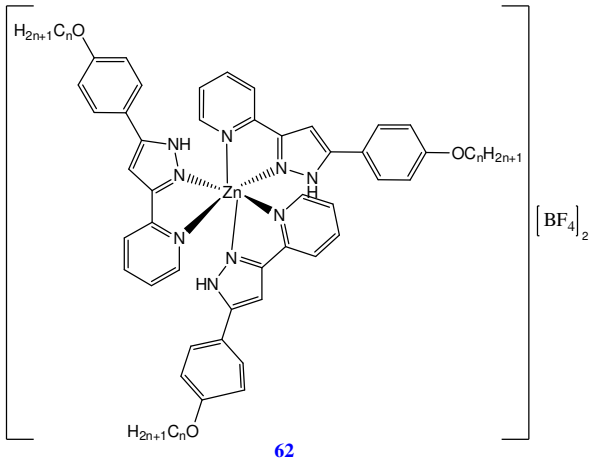
Extending the chain length of the ligands, and introducing more rigidity in the structure, Pucci et al. reported in 2009 the use of dimeric salicylaldimine, 2,2′-bipyridine or 1,10-phenathroline derivatives as di or hexacatenar ligands to form highly stable Zn(II) complexes.[165,166,167] In the series of mesogenic zinc(II) complexes **63** obtained with the dimeric salicylaldimine ligand (Chart 30), mesomorphism was observed to have a significant dependence on the length of the alkyl chains (L_c) and the central bridge (L_b). Thus, compounds in which L_c is smaller than L_b show nematic mesophases, whereas SmC mesophases are identified when both values of length are similar. The complexes show a blue luminescence centered at 432 - 440 nm with a luminescence quantum yield from 20% (in solution) to *ca*. 8 % (in the mesophase and in the solid state). Authors remark that the described species are very interesting blue emitters combining properties as fluidity and orientation ability sensible to external changes in the single molecular tectons.

Chart 29



61

n = 12 - 18

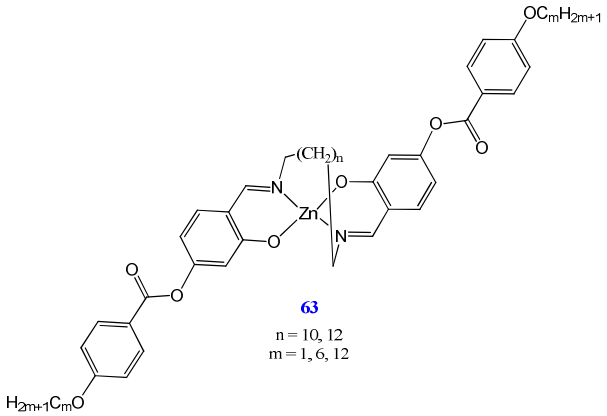


62

n = 12 - 18

In relation to the complexes with rigid core obtained using the 2,2′-bipyridine or 1,10-phenathroline central cores, tetra-, penta- and hexa-coordinated zinc complexes were formed. The extra coordination ligands were chloride, sulfur or diketonate derivatives. See as examples in Chart 31 the complexes **64** and **65** using the phenathroline and the bipyridile units. As expected, the presence of six terminal alkyl chains induced the establishment of columnar mesophases, in some cases, at low temperatures of *ca*. 36 ºC. The most interesting remark on these species is the red-shifted emission observed. The bands vary between 454 to 562 nm with fluorescent quantum yields from 0.80% (very low emissive) to 22.0% depending on the nature of the ligands used.

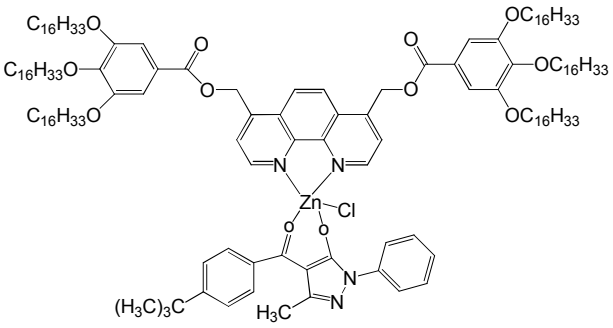
Chart 30



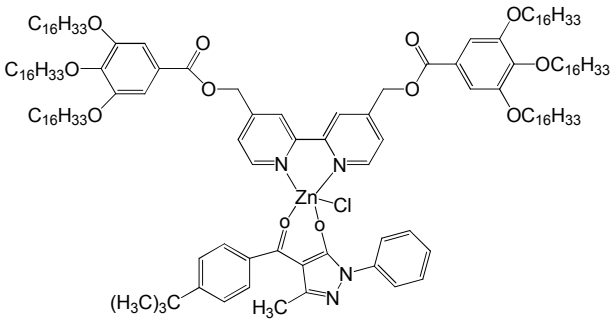
63

n = 10, 12
m = 1, 6, 12

Chart 31



64

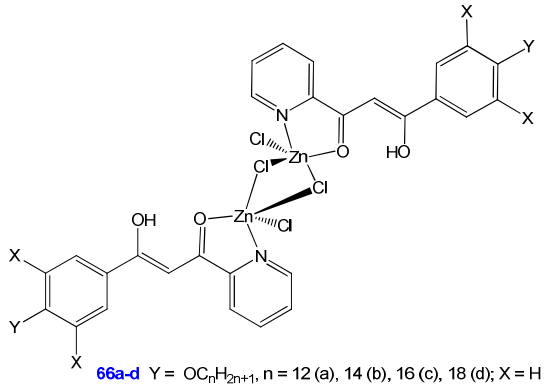


65

4.2. Zn(II) complexes with other coordination environments

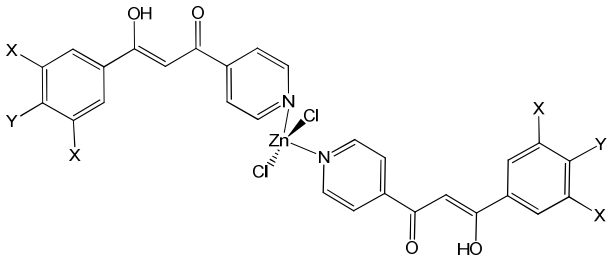
Cano, Lodeiro and coworkers have reported one of the few examples in tetrahedral complexes with the system 1-(pyridil)-3-(alkoxyphenyl)propane-1,3-dione.[168] Monomeric compounds having a hockey-stick shape are found for the monocatenar species, which were not liquid crystals. By contrast, a lamellar columnar mesomorphism (Col_L) was found on the dicatenar free ligand. The self-assembly of two hemidiscotic molecules originated the essential disc-like shape of four-chained functionalized molecules. The reactions with Zn(II) dichloride afforded to four new families of Zn(II) compounds, as shown in Chart 32. The complexes **66** and **68** bearing the monocatenar ligands with the pyridinic nitrogen atom both in 2- and 4-position were liquid crystal materials (Figure 24), showing SmA mesophases and so, indicating that mesomophic behavior is induced by complexation with the metal. However, the Zn(II) complexes **67** and **69** carrying dicatenar ligands were not liquid crystal materials. Most of the Zn(II) complexes also exhibit green/blue emission at room temperature in solution.

Chart 32



66a-d Y = OC_nH_{2n+1}, n = 12 (a), 14 (b), 16 (c), 18 (d); X = H

67a-d X = OC_nH_{2n+1}, n = 12 (a), 14 (b), 16 (c), 18 (d); Y = H



68a-d Y = OC_nH_{2n+1}, n = 12 (a), 14 (b), 16 (c), 18 (d); X = H

69a-d X = OC_nH_{2n+1}, n = 12 (a), 14 (b), 16 (c), 18 (d); Y = H

Bruce and coworkers explored the mesomorphism of different hexasubstituted terpyridine ligands coordinate to zinc(II) ions. The authors examined two types of ligands derived from the terpyridine with or without a fused cyclopentene ring on each non-central pyridine fragment (Chart 33). All Zinc(II) complexes **70** and **71** with long alkyl chains were found to be liquid-crystalline materials and exhibited columnar mesophases (Figure 25), properties depending directly on the complexation.[79] The Zinc complexes show the expected distorted trigonal bipyramidal geometry around the zinc center linked to the terpyridine ring, completing the coordination sphere with two chloride ligands. Both showed enantiotropic liquid-crystalline properties exhibiting an emission band center between 464 and 541 depending on the solvent used, hexane, cyclohexane, THF or DCM, being the most emissive in cyclohexane with a quantum yield of 0.394.

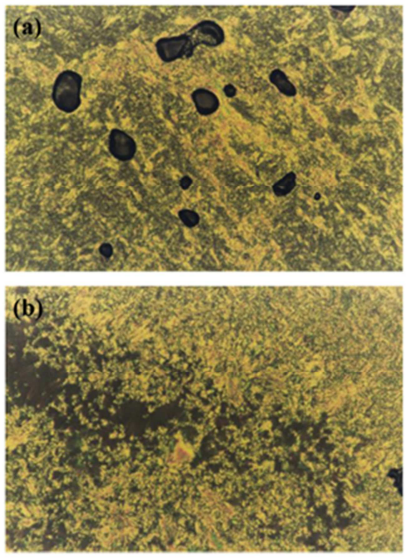
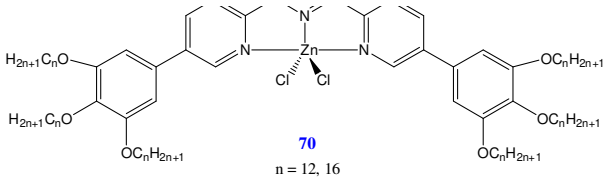
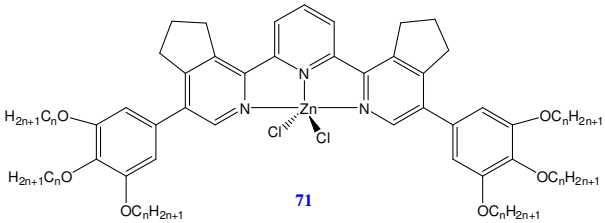


Figure 24. Texture observed under polarized light for the Zn(II) complexes (a) **68a** at 155 ºC on heating, and (b) **68b** at 148 ºC on cooling. Reprinted with permission from ref. 168. Copyright 2017 Elsevier Ltd.

Chart 33

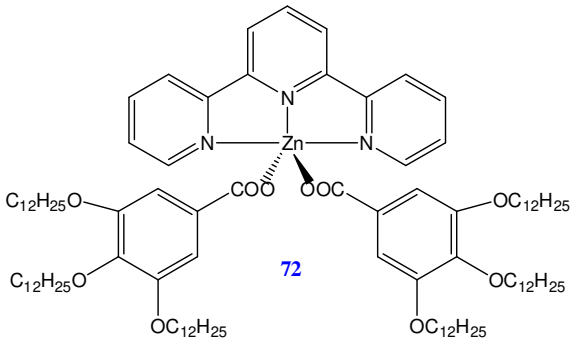




Using an equivalent strategy, Szerb and coworkers have used the terpyridine non-functionalized molecule as a central ligand core to be complexed to the zinc ion, using two ancillary ligands based on gallate units not covalently connected to the terpy unit (Chart 34).[169] The Zn complex **72** exhibits mesomorphism from room temperature up to 101°C. POM textures at 80°C in the mesophase and at room temperature, obtained on cooling from the isotropic state, display pseudo focal-conic defects and homeotropic domains that which indicates the formation of an untitled Col_h mesophase. The luminescent complex formed shows an intense emission quantum yield of 24.5 % with a lifetime of 2.7 ns in solution, however, this emission was quenched in the columnar mesophase.

Figure 25. POM microphotograph of the mesophase found in **71**-16 at 207 ºC on cooling. Reprinted in part with permission from ref. 79. Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA.

Chart 34



5. Phosphorescent Pt(II) and Ir(III) metallomesogens

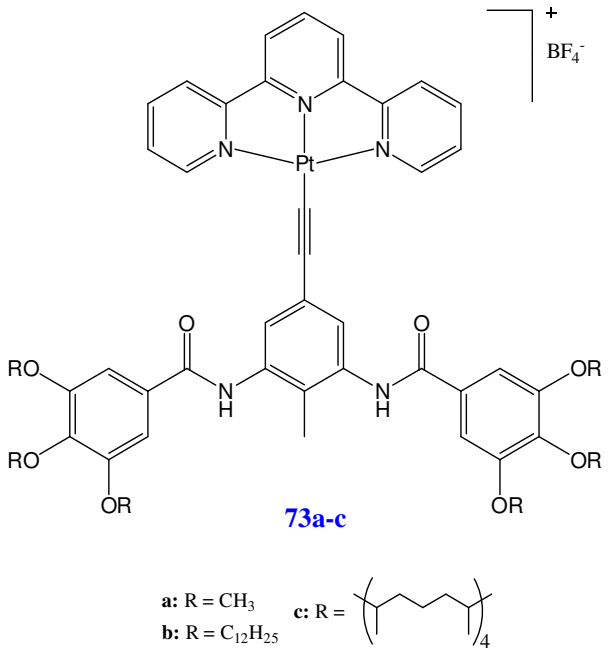
5.1. Square-planar Pt(II) complexes

Platinum appears mainly in two oxidations states +2 and +4. The +1 and +3 oxidation states are much less common and are often stabilized by metal bonding in bimetallic (or polymetallic) species. Regularly the tetracoordinate platinum(II) species tends to adopt the 16-electron square planar structures being very favorable for reaching the packing required in the liquid crystalline phases.

Camerel et al. observed in a family of phosphorescent σ-alkynyl platinum(II) terpyridine complexes that intermolecular Pt···Pt, Pt···π, and π–π* interactions not only can be responsible of the origin of a solvatochromic behavior, but also of the formation of extended columnar mesophases (Chart 35).[170] For example, compound **73b** was found to exhibit a bright near-infrared emission in dodecane solution (λ_{em} = 830 nm), which was un-

doubtedly attributed to the presence of ^{3}MMLCT excited states. However, the addition of a mixture of methanol in dichloromethane (25% v/v) caused a bluish-shift of the emission band from 830 to 644 nm as a result of the molecular disaggregation and the consequent rupture of the Pt···Pt interactions. The extraordinary ability of these complexes to be self-assembled in Pt(II) aggregates was also observed in the solid state for the particular case of **73c**. Temperature-dependent XRD studies revealed the formation of a highly-stable hexagonal columnar mesophase driven by Pt···Pt interactions in the temperature range of 20 – 200 ºC.

Chart 35



73a-c

a: R = CH_3 **b:** R = $C_{12}H_{25}$ **c:** R =

The search for bifunctional Pt(II) compounds combining phosphorescence and liquid crystal properties opened a new research line at the end of the 20th century. It was well known that the Pt(II) compounds can exhibit phosphorescence at room temperature, which attracted significant attention in the field of metallomesogens. If phosphorescence could be maintained in the liquid crystal state, Pt(II) compounds could behave promising candidates for the next generation of OLEDs. In 2008, Swager and his research team described a series of *ortho*-platinated metallomesogens bearing 2-phenylpyridines and 2-thienylpyridines that showed phosphorescence at both 77 and 298 K (λ_{em} = 494 – 576), with lifetimes from 0.5 to 11.3 μs (Chart 36).[171] As expected, the nature of the mesophase depends on the number of terminal alkyl chains. In compounds decorated with four alkyl chains (compounds **74**, **78a**), the mesophases were identified as SmA, whereas the presence of at least six chains in compounds **75**-**77**, **78b** and **79** induces the formation of highly-stable Col_h or Col_r ones (Figure 26).

The terdentate N,C,N-coordinated Pt(II) compound **82** also exhibit phosphorescence at room temperature, as well as liquid crystal properties when the alkyl chains present six or more carbon atoms (Chart 37).[172] The mesophases were found to be Col_r for **80b-e** and Col_h for **81**, but in all cases the emission spectrum recorded the typical structured band of Pt(II) monomers with the maximum at 575 nm. Bruce and coworkers performed further studies with the main goal of controlling the supramolecular organization in the columnar mesophases, and analyzing its influence in the optical behavior. Interestingly, by fast cooling the sample from the isotropic liquid, molecules establish intermolecular associations, and an excimer-like emission is observed (λ_{em} = 660 nm) (Figure 27). Similar results were achieved when the compounds were spin-coated over a glass surface to create a thin film. Temperature-dependent experiments revealed that after heating the film at temperatures above the melting point and cooling again to room temperature, the monomer emission could be partially recovered. Otherwise, the excimer emission returns when the film was grinded at room temperature. These studies demonstrated that it is possible to modulate the luminescence properties of the Pt(II) by controlling their supramolecular self-assembly in the mesophase.

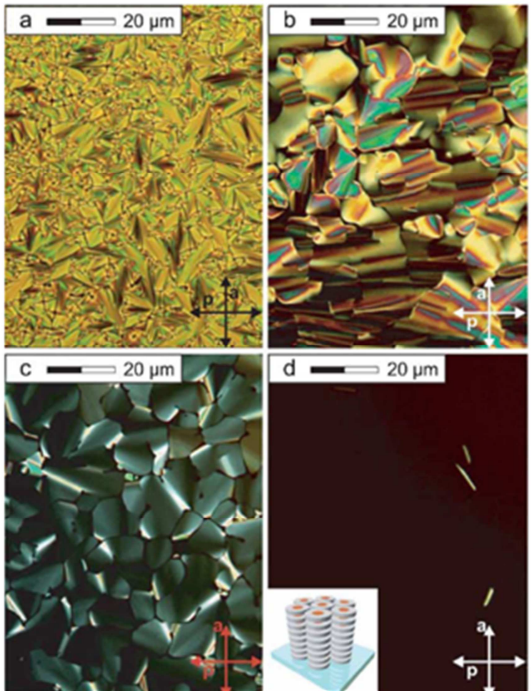
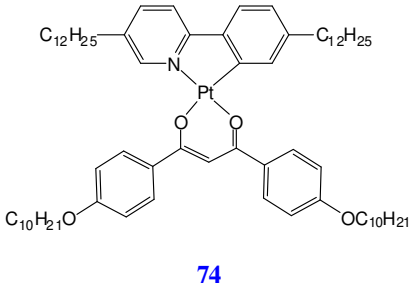
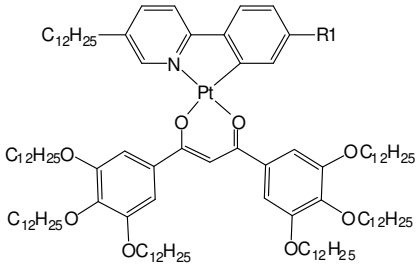


Figure 26. POM microphotographs of the mesophases of (a) **78a** at 118 ºC, (b) **76a** at 120 ºC, (c) **76a** upon cooling, and (d) **76a** after annealing at 160 ºC. Reproduced from ref. 171 with permission from The Royal Society of Chemistry.

Chart 36

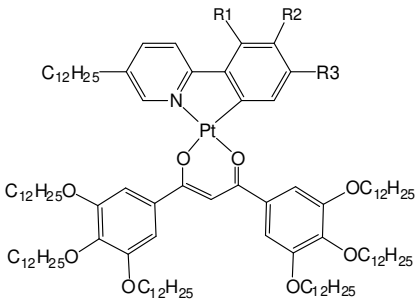


74



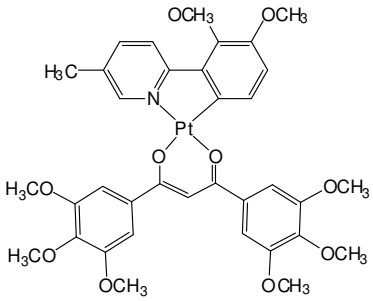
75a,b

a: R1 = $C_{12}H_{25}$ / **b:** R1 = $OC_{12}H_{25}$

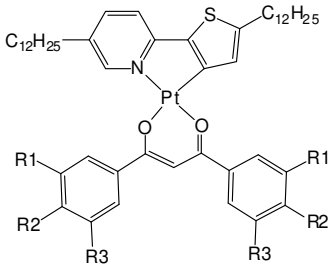


76a,b

a: R1, R2 = $OC_{12}H_{25}$; R_3 = H
b: R1 = H; R2, R3 = $OC_{12}H_{25}$

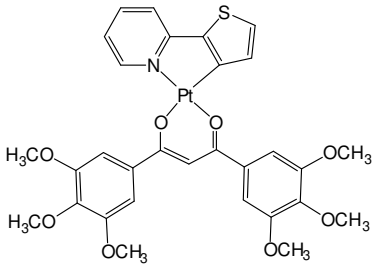


77



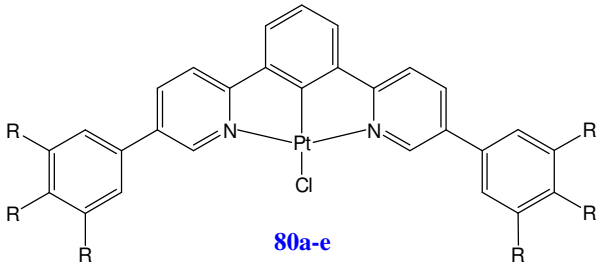
78a,b

a: R1, R3 = H; R2 = $OC_{10}H_{21}$
b: R1, R2, R3 = $OC_{12}H_{25}$



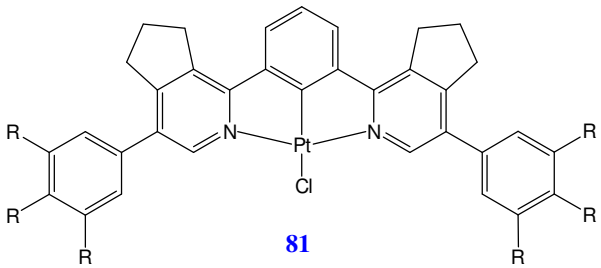
79

Chart 37



80a-e

R = OC_nH_{2n+1}, n = 4 (a), 6 (b), 8 (c), 10 (d), 12 (e)



81

R = OC_nH_{2n+1}, n = 10 - 12

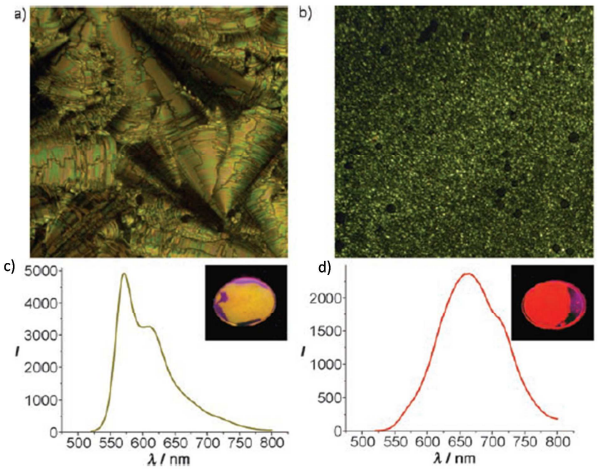


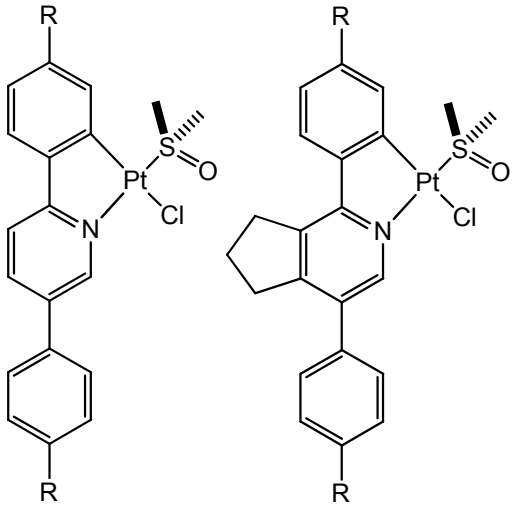
Figure 27. Texture of the Col_r mesophase found in **8ob** at room temperature after fast cooling (a) from the mesophase, and (b) from the isotropic liquid. (c, d) Corresponding emission spectra, and images showing the luminescence nature of this compound. Reprinted with permission from ref. 172. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA.

Following the same research line, Bruce also described several families of Pt(II) metallomesogens based on 2-phenylpyridines (Chart 38), which forms smectic and nematic mesophases at temperatures around 100 – 150 ºC.[173] All of them are bifunctional materials and present luminescence in solution and in the solid state. Remarkably, the compounds **84a-d**, **85a-d** bearing β-diketonate ligands showed high emission quantum yields of *ca*. 0.5 - 0.6 and lifetimes of 27 μs at room temperature. Thus, they were used as dopants of a polycarbonate matrix to fabricate luminescent thin films. Inside the polymer, the Pt(II) metallomesogens maintain the monomer emission regardless of its concentration, although the band attributed to the excimer-like emission begins to appear at dye concentrations above 50%. It was also observed that 100% films emit a bright orange emission (λ_{em} = 600 nm) at temperatures close to the melting point, which demonstrated for the first time efficient molecular aggregation of Pt(II) metallomesogens within a polymer matrix.

Some new Pt(II) metallomesogens with luminescence properties were reported over the following years, and two key factors were established to achieve optimized functional materials. On the one hand, the platinum metal center stabilizes the liquid-crystalline phase in comparison with other analogous metal complexes and concomitantly induces luminescence behavior.[174] On the other hand, the establishment of intermolecular $Pt(d_z^2)\cdots Pt(d_z^2)$ interactions in the solid state or in neat film favors the formation of aggregates with strong emission and large lifetimes.[175,176,177,169] Isomerism in phosphorescent Pt(II) metallomesogens has been also investigated by Bruce et al.[178] Results show that the presence of structural isomers does not constitute a drawback to achieve the required supramolecular assembly in the mesophase. Phosphorescent ionic species are also capable of being self-assembled in columnar mesophases even when the ligand bears a unique terminal alkyl chain.[179] Thus, based on these results and keeping in mind that liquid crystals can be easily aligned, luminescent Pt(II) metallomesogens have been early positioned as promising candidates for the development of polarized phosphorescent OLEDs.

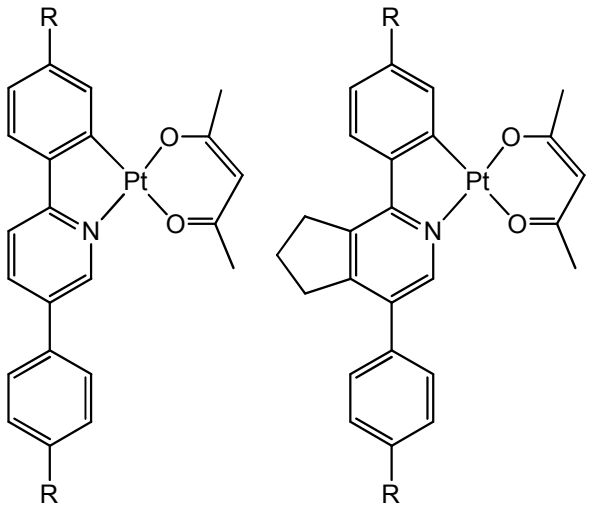
One of the first species of metallomesogens with high polarized emission was described at the beginning of the 21st century. The use of 2-phenylpyridine and 2-(3-fluorophenyl)pyridine as ligands allowed to obtain two series of cyclometalated Pt(II) complexes **86** and **87** that form smectic mesophases at low temperatures of about 50 – 90 ºC (Chart 39).[77] Taking advantage of the supramolecular organization in the mesophase, Wang *et* al. prepared liquid-crystalline thin films in which the molecules maintained the same organization of the mesophase at room temperature. As a result, the emission intensity of these films undergoes drastic changes as a function of the measurement direction, achieving a polarization ratio of 2.7. Encouraged by these results, the same authors prepared new thin films of the Pt(II) metallomesogens by using an aligned polyimide as a substrate. The new composites showed an emission intensity 10.5 times higher at the parallel direction.

Chart 38



82a,b **83a,b**

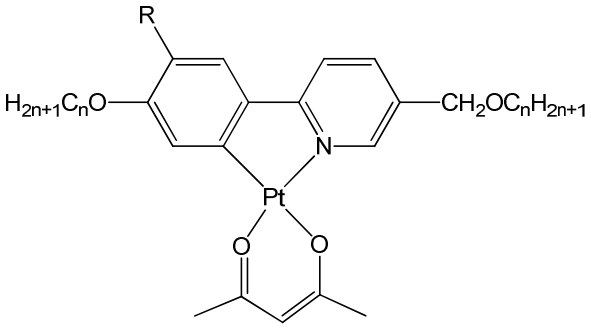
R = OC_nH_{2n+1}, n = 6 (a), 10 (b)



84a-d **85a-d**

R = OC_nH_{2n+1}, n = 6 (a), 8 (b), 10 (c), 12 (d)

Chart 39

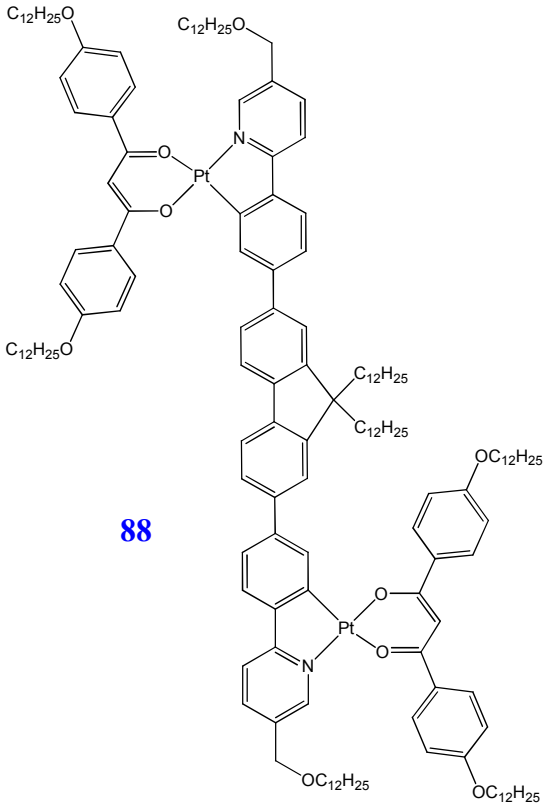


86 R = H, n = 4, 8, 12, 16
87 R = F, n = 8, 12, 16

Using the same alignment method, Wang *et* al. also reported a dinuclear Pt(II) metallomesogen bearing phenylpyridine and β-diketonate ligands, and incorporating the 9,9-dioctylfluorene moiety as a linkage in order to improve the luminescence behavior of this type of cyclometalated complexes (Chart 40).[180] The thermal and luminescence properties were similar to those found in the previous Pt(II) metallomesogens synthesized by the same authors. Compound **88** exhibits a smectic mesophase and displays polarized emission with dichroic ratios of 1.3 and 10.3 when the films are prepared on a glass or an aligned polyimide substrate, respectively. As a novelty, the complex shows hole mobility of 8.4 x 10^{-4} $cm^2/(V\ s)$, being a potential candidate for the design of polarized OLEDs.

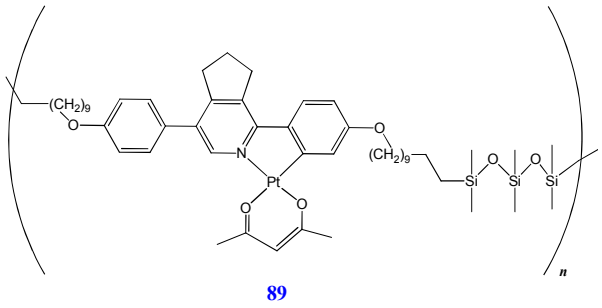
When designing a liquid crystal device based on OLED technology it is crucial not only to achieve that the Pt(II) metallomesogens exhibit polarized emission, but also that the alignment is retained. To this aim, Bruce proposed the use of liquid-crystalline polymers since these materials can be quickly processed and aligned. Thus, by combining the luminescence properties of particular cyclometallated Pt(II) complexes based on 2,5-disubstituted pyridine and β-diketonate ligands, and the flexibility of 1,1,3,3,5,5-tetramethyltrisiloxane, Bruce and coworkers synthesized a novel multifunctional polymer with liquid crystal behavior and polarized emission (Chart 41).[181] The new polymer shows a SmA mesophase in the temperature range of 64 – 150 ºC, so that it can be easily processed without causing the thermal degradation of the sample (Figure 28). Polarized photoluminescence studies revealed that **89** does not present a promising dichroic ratio (2.5 at λ_{em} = 528 nm), but the authors demonstrated for the first time that alignment could be mechanically induced and retained in this type of metallomesogens by taking advantage of their flexible nature.

Chart 40



88

Chart 41



89

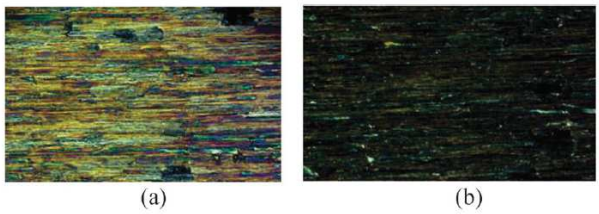
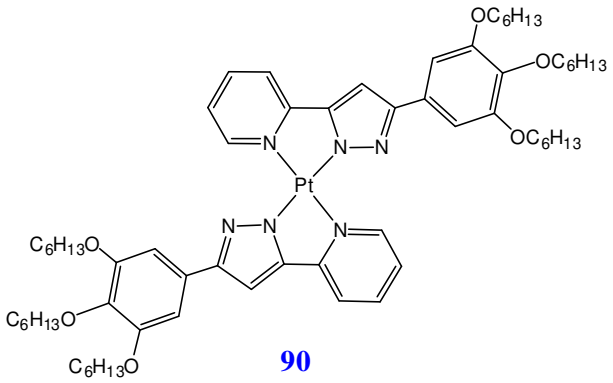


Figure 28. POM microphotograph of **89** after annealing. Images were taken with the polarizers at (a) 0 º, and (b) 90 º. Reproduced from ref. 181 with permission from The Royal Society of Chemistry.

Some few Pt(II) metallomesogens with improved polarized emission properties or hole mobility were reported shortly after.[182,183,184,185,186] The compounds form columnar, smectic and nematic mesophases and display polarized emission with dichroic ratios of up to 3, 6-7 or 24, respectively. It is interesting to note that this behavior seems to be directly related to the supramolecular organization in the mesophase. Nematic structures are more disordered than smectic and columnar ones, so that they are easier to align, and concomitantly, exhibit good dichroic ratios, which makes them excellent candidates for the development of technological devices. However, the first prototype of polarized OLED based on Pt(II) metallomesogens was fabricated in 2011 by S.-H. Liu *et al.* taking advantage of the hexagonal columnar ordering of the bispyrazolate Pt(II) compound **90** (Chart 42).[183] The device was developed by combining the phosphorescent Pt(II) metallomesogen **90** with penta[9,9-bis(2-methylbutyl)fluorene], a mesogenic fluorene oligomer that acts as the host, and PEDOT:PSS, a conducting polymer which is used as the alignment layer. As a result of the alignment, the Pt(II) molecules adopt a columnar stacking in which the columnar axis is maintained perpendicular to the rubbing direction, originating ^{3}MMLCT excited states *via* intermolecular Pt···Pt interactions (Figure 29). Curiously, in contrast than conventional polarized OLED, this fact causes that the emission measured perpendicular to the rubbing direction is two times stronger than that measured in the parallel direction, exhibiting a brightness of 2000 cd/m^2 and a current efficiency of 2.4 cd/A.

Chart 42



90

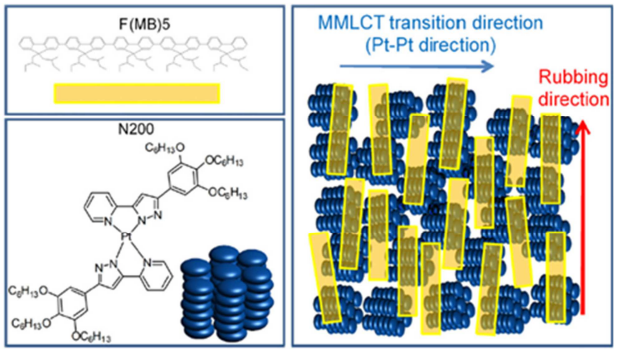


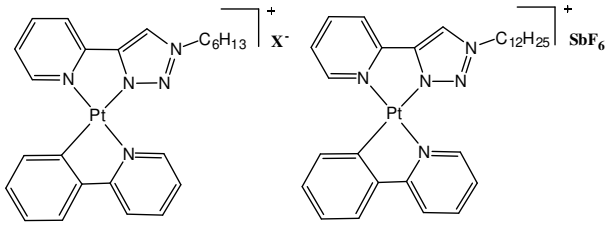
Figure 29. Schematic drawings displaying the molecular alignment of **90** in the aligned film built to fabricate the OLED device. Reprinted with permission from ref. 183 Copyright 2010 Elsevier B.V.

Materials exhibiting circularly polarized electroluminescence have raised significant attention in OLEDs in recent years because they can improve these devices' performance. In 2019 it was demonstrated that a nematic liquid crystal doped with a chiral emitter and a triplet donor boosts the luminescence dissymmetry factor, and therefore also the circularly polarized luminescence, in the induced chiral nematic liquid crystal state.[187] Based on these results, Bruce and coworkers synthesized two new cyclometalated Pt(II) compounds bearing a chiral moiety that shows N* and SmA* mesophases.[188] Circularly polarized luminescence was not observed in solution either in the pristine state, but films annealed at 100 ºC in the N* mesophase shown a maximum luminescence dissymmetry factor of 0.02. Then, circularly polarized organic light-emitting diodes (CP-OLEDs) were fabricated using these complexes. Interestingly, devices with 40 wt% dopant concentration exhibit the highest luminescence dissymmetry factor reported to date in chiral metallomesogens (~ 0.06), with an external quantum efficiency of 11.3%. These promising results establish the basis to improve the luminescence dissymmetry factor in metallomesogens using chiral induction as a strategy.

The interest in Pt(II) metallomesogens took a significant turn in the last years, and a new research line on stimuli-responsive luminescence properties arose. Swager and coworkers described in 2014 a series of cationic Pt(II) complexes bearing phenylpyridine and pyridyltriazole ligands that exhibit mesomorphism and mechanochromic properties (Chart 43).[87] The new compounds **91**, **92** have a unique terminal alkyl chain but, despite this fact, they can self-assemble into columns *via* Pt(II)···Pt(II) interactions to form Col$_h$ mesophases at temperatures over 100 ºC. Nevertheless, the real novelty of these materials lies in their solid-state luminescent behavior. Because of the intermolecular Pt···Pt interactions are permutable, the typical greenish emission of the Pt(II) monomers (λ_{em} = 500 nm) can be converted to an orange-red emission (λ_{em} = 550 -800 nm) upon grinding the sample (Figure 30). The origin of this dramatic change was attributed to the presence of ^{3}MMLCT excit-

ed states as a consequence of the formation of a new polymorph. Moreover, reversibility was observed; the addition of dichloromethane or the heating of the sample allow recovering the initial luminescence emission, so that the compounds exhibit reversible mechano- and thermochromic properties.

Chart 43



91a-d **92**

X = SbF_6 (a), PF_6 (b), BF_4 (c), OTf (d)

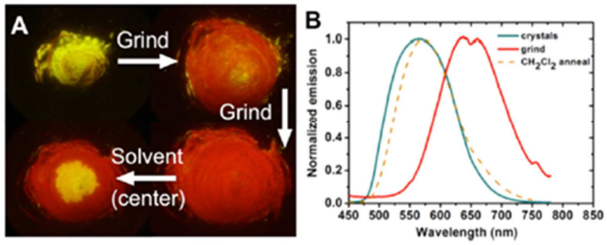
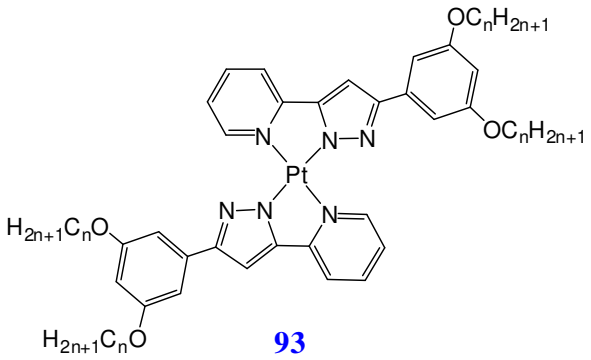


Figure 30. Mechanochromic properties of **91a**; (a) Images of the reversible behavior by adding CH_2Cl_2. (b) Emission spectra of **91a** as prepared, after grinding, and upon annealing with CH_2Cl_2. Reprinted with permission from ref. 87. Copyright 2014 American Chemical Society.

In the same year, Cano et al. reported a novel family of multifunctional tetracatenar bis(pyridylpyrazolate) Pt(II) metallomesogens, **93**, in which the Col_h mesophase induces the formation of ^{3}MMLCT excited states (Chart 44).[189] All the compounds emit a greenish light (λ_{em} = 500 nm) in the solid state, which is progressively turn-off by increasing the temperature from RT to the melting point, reached to *ca.* 100 ºC. Then, the Pt(II) molecules are self-assembled in a columnar stacking through intermolecular Pt···Pt interactions, originating ^{3}MMLCT excited states and reviving the luminescence properties of the complexes in the mesophase (λ_{em} = 605 nm). This photophysical behavior was exploited to fabricate thermo-responsive PMMA thin films that allow detecting if an object or a technological device has been exposed to high temperatures.

Chart 44



93

n = 4, 6, 8, 10, 12, 14, 16, 18

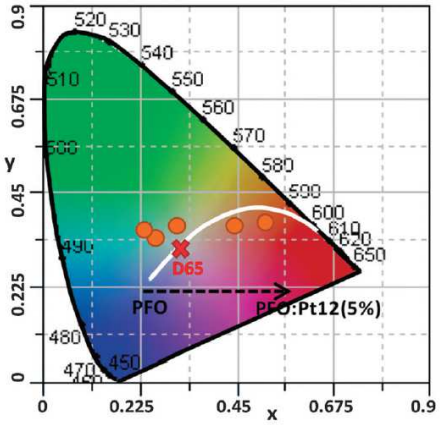


Figure 31. CIE coordinates of the polymer OLED fabricated with the Pt(II) metallomesogen **93** (n = 12). [190] – Reproduced by permission of The Royal Society of Chemistry (RSC) on behalf of the Centre National de la Recherche Scientifique (CNRS) and the RSC.

Otherwise, these Pt(II) metallomesogens also exhibit electroluminescence properties, and one of them (n = 12) was selected as a prototype to develop polymer OLEDs.[190] The idea, described by the same authors, was taking advantage of the chromic response of the Pt(II) complex and the emission properties of PFO and fluorenone to fabricate workable white-emitting (W-OLEDs). Results have shown that in those devices fabricated by doping the PFO matrix with just only 3% of the Pt(II) complex, Pt···Pt interactions are induced and, concomitantly, the greenish emission of Pt(II) monomers turned on a bright orange one. The combination of the bluish, greenish and orange colors from PFO, fluorenone and the Pt(II) complex, resulted in an emission very close to that perceived as white by the naked eye (Figure 31), proving once again the potential of phosphorescent Pt(II) metallomesogens for new technologies.

Few Pt(II) metallomesogens have been described to exhibit similar luminescence properties in the liquid

crystal state, because of mesophases are usually achieved at high temperatures, when thermally-activate non-radiative process occur. In this context, the applicability of a luminescent metallomesogen noticeably increases if it is possible to maintain the luminescence emission during the mesophase, or even enhancing it. Espinet et al. recently reported an interesting liquid-crystalline material formed by a benzoquinoline-platinum fragment decorated by six disc-like triphenylene moieties (Figure 32).[191] The new hybrid system forms a hexagonal columnar lattice driven by Pt···Pt and π···π interactions, giving rise to Col_h mesophases at low temperatures that do not exceed 30 ºC. Moreover, the core stack of benzoquinoline-platinum groups is responsible for the orange emission that the compounds show in the mesophase, which is associated with the presence of triplet excited states originated by the metallophilic interactions.

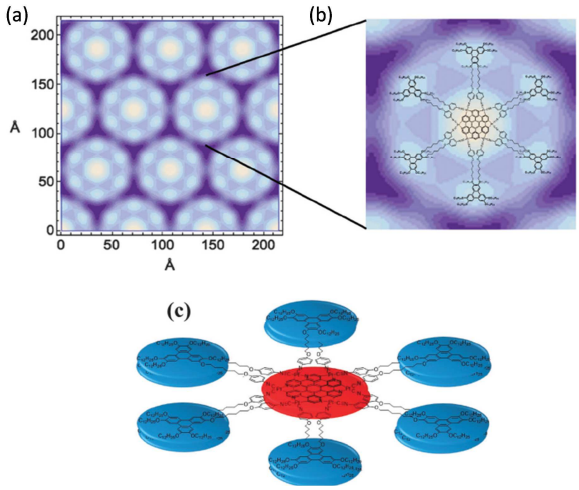
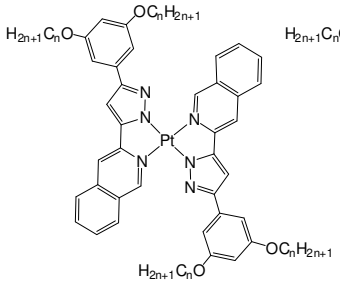


Figure 32. (a.b) Charge density map for compound **94** established from X-ray measurements. (c) Molecular structure of **94** showing the internal disc-like organization. Reproduced from ref. 191 with permission from The Royal Society of Chemistry.

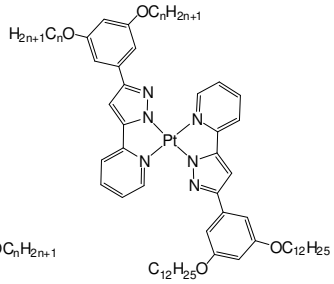
Following the research line on tetracatenar bispyrazolate Pt(II) metallomesogens, Cano's group reported a series of isoquinoline-functionalized bispyrazolate Pt(II) complexes **95** (Chart 45), which behave as liquid crystal materials exhibiting Col_t and Col_h mesophases in surprisingly-wide temperature ranges of up to 300 ºC (Figure 33).[192] Although the compounds are practically non-emissive in the solid state, the columnar stacking *via* Pt···Pt interactions adopted by the molecules in the mesophases produces ^{3}MMLCT transitions that result in a bright orange emission (λ_{em} = 615 nm). Mechanical grinding also causes a similar aggregation-induced emission enhancement (AIEE) in the solid state at room temperature. In both cases, good reversibility is observed after the addition of dichloromethane or the exposure of the sample to their vapors. Further studies revealed that aggregation of these Pt(II) complexes inside polymer matrixes as PMMA and PVP is possible, which allowed fabricating stimuli-responsive films useful as temperature and pressure sensors (Figure 34).

Chart 45



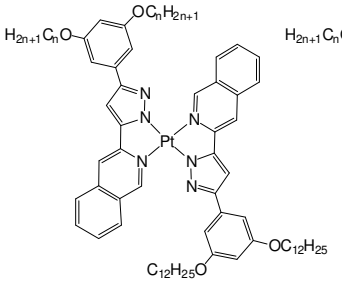
95

n = 4, 6, 8, 10, 12, 14, 16, 18



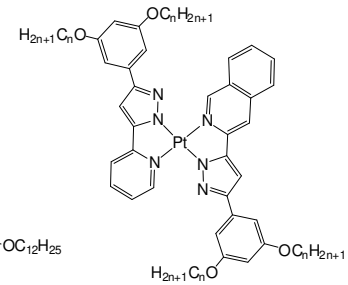
96

n = 4, 6, 8, 10, 14, 16, 18



97

n = 4, 6, 8, 10, 14, 16, 18



98

n = 4, 6, 8, 10, 12, 14, 16, 18

Since the columnar mesophases can revive the photophysical properties of this type of bispyrazolate Pt(II) metallomesogens, it is essential that mesophases are reached at low temperatures to achieve high quantum yields. To this respect, Cano and the research group evaluated the effect of the introduction of asymmetry in the molecular structure of the above-described complexes. The new series of derivatives 96 - 98 shown melting temperatures near to RT, further expanding the stability range of the Col_h mesophases and concomitantly, improving their luminescent behavior (Figure 35).[193,84,39] The fluidic nature of the mesophase also provide a suitable platform for proton conduction, proving for the first time that luminescent Pt(II) metallomesogens can be promising candidates for application in PEM fuel cells.

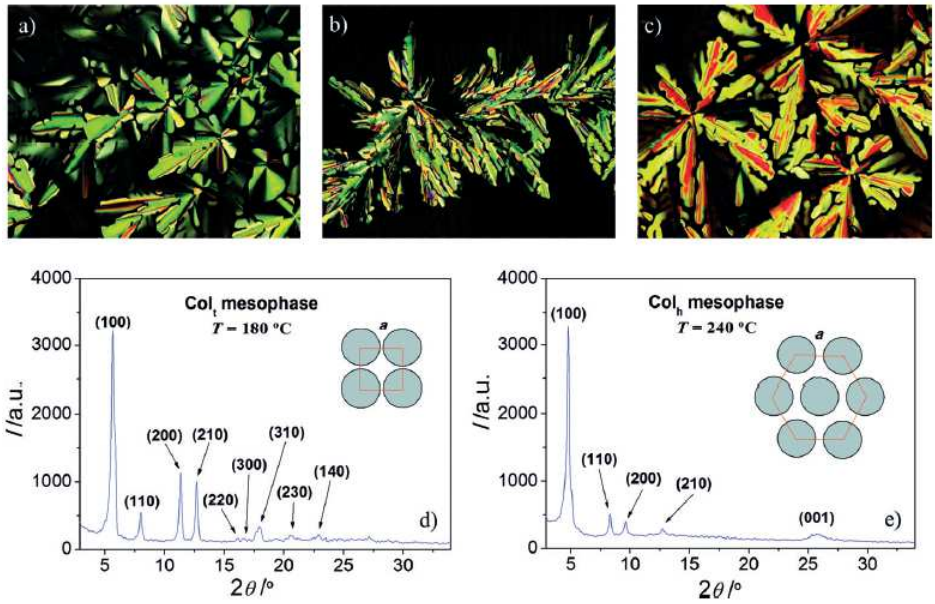


Figure 33. Textures observed in the mesophase of the Pt(II) compounds **95** with (a) n = 10 at 244 ºC, (b, c) n = 12 at 348 and 306 ºC, respectively. All microphotographs were taken upon cooling. (d, e) X-ray diffractograms showing the typical pattern of the Col_t and Col_h mesophases for **95** with n = 4. Reprinted with permission from ref. 192. Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA.

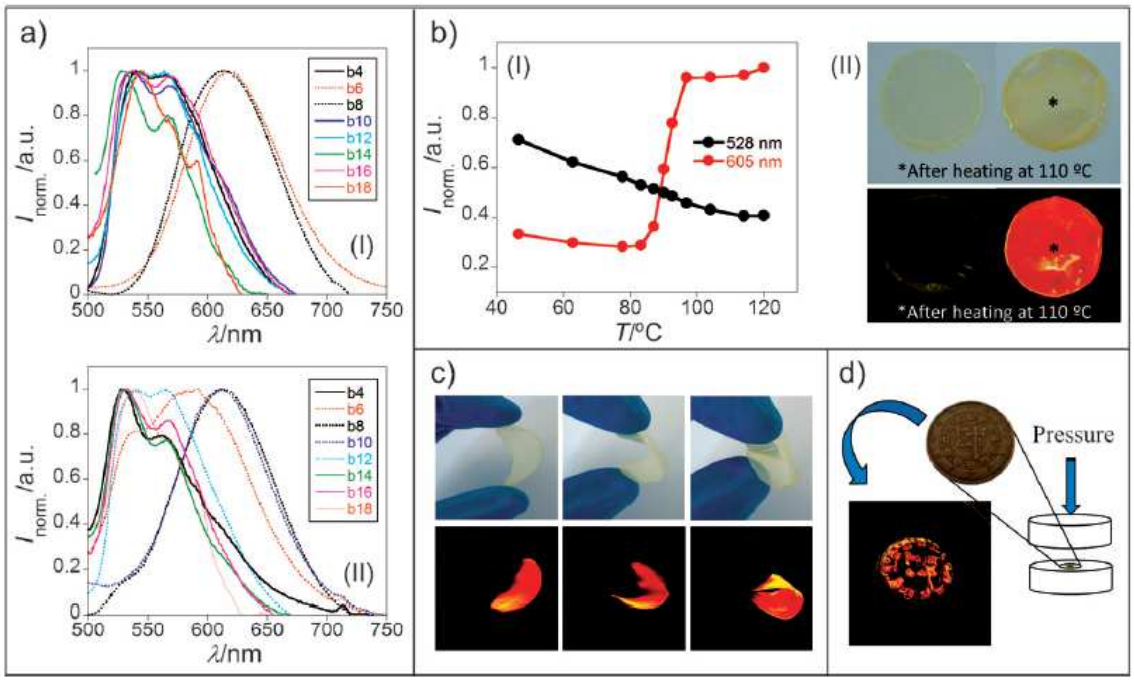


Figure 34. Luminescence properties of the stimuli-responsive thin films doped with the series of Pt(II) compounds **95**: (a) Emission spectra of the PMMA and PVP films; (b) Normalized emission intensity as a function of temperature, including images taken at 25 and 110 ºC; (c) Images showing the flexibility of the polymer before and after heating; (d) Image showing the piezochromic response of the doped PMMA polymers. Reprinted with permission from ref. 192. Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA.

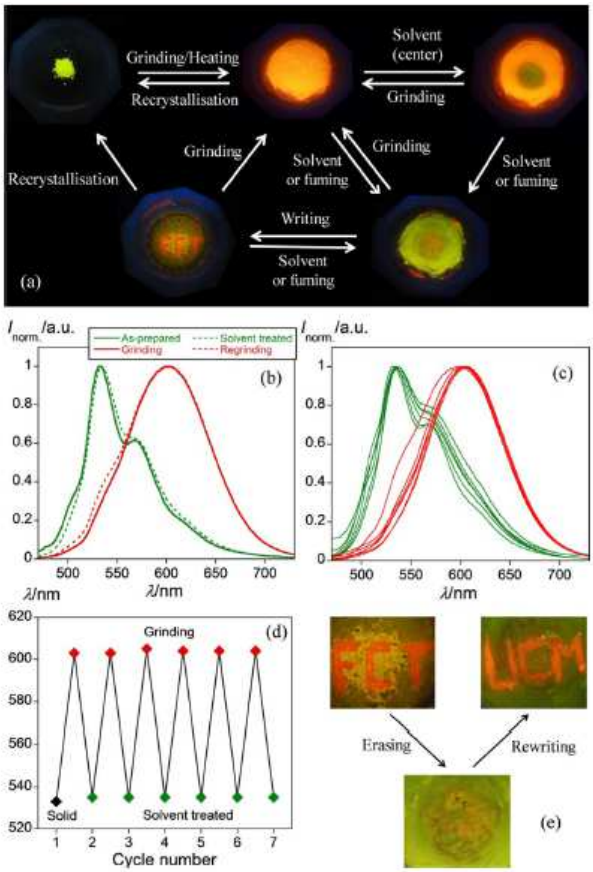


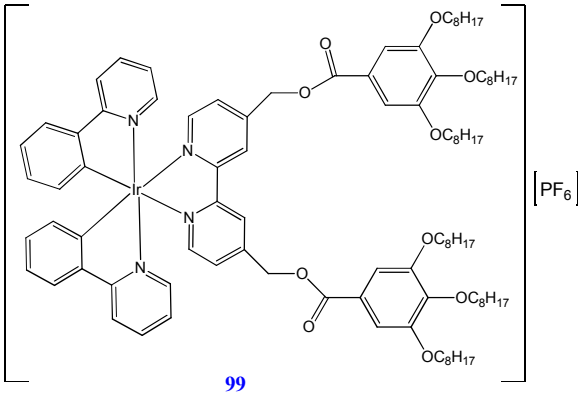
Figure 35. (a,b,c) Mechano-, solvato-, and vapochromic behavior of **98** (n = 18). (d) Reversibility found in the mechanochromic behavior of **98** (n = 18) after successive grinding/solvent cycles. (e) Images showing the rewritable ability of this series of Pt(II) compounds. Reprinted with permission from ref. 84. Copyright 2019 Wiley-VCH Verlag GmbH & Co. KGaA.

5.2. Ir(III) complexes

The usefulness of the luminescent Ir(III) complexes for the development of OLEDs has been widely demonstrated during the last years.[194,195] As the Pt(II) complexes, these materials have strong spin-orbit coupling constants, which gives access to room-temperature phosphorescence with high quantum yields. After the discovery of luminescent metallomesogens and, particularly, seeing the ease of processing that offer these materials, the idea of combining the phosphorescence nature of Ir(III) complexes with the fluidic nature of liquid crystals gained strength in the last decade. Although few Ir(III) metallomesogens have been reported to date due to the octahedral geometry constitutes a great drawback for inducing mesomorphism, Ir(III) complexes have shown to be good candidates to develop electroluminescence devices with an internal quantum efficiency (IQE) near to 100%.[196]

The first phosphorescent Ir(III) metallomesogen was described in 2010 by Ghedini and coworkers.[197] Compound **99** is ionic in nature as shown in Chart 46. In the cationic complex, the Ir(III) center is bonded to two phenylpyridine ligands and one 2,2-bipyridine ligand, which is functionalized with terminal octyloxyphenyl groups at the 4,4'-positions. Accurately, the presence of these extended alkyl chains allows to the ionic complex adopting the required organization to form a Col_h mesophase upon fast cooling from the isotropic phase at 130 ºC. The mesophase is maintained as a frozen liquid crystal phase when the room temperature is reached, exhibiting a bright yellow emission (λ_{em} = 560 nm, Φ = 0.39). It is interesting to remark that **99** also emits orange (λ_{em} = 600 nm, Φ = 0.12) or green light (λ_{em} = 520 nm, Φ = 0.48) in solution and its crystalline form, respectively, so that the increase of order seems to cause a blue-shift in the emission band. In fact, the luminescence properties of the ionic Ir(III) complex in thin film can be controlled by the application of several stimuli that cause changes in its structural packing, such as heating or mechanical gridding.

Chart 46

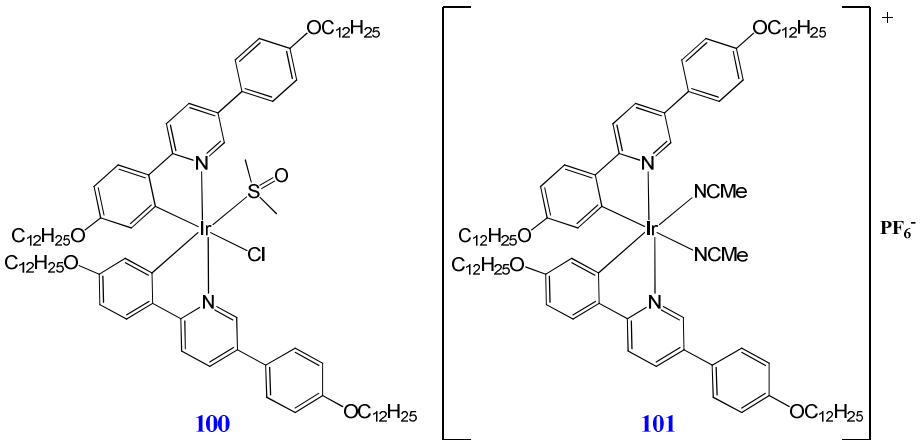


99

One year later, Bruce's group reported the first kind of neutral and ionic Ir(III) metallomesogens bearing monocatenar 2,5-diphenylpyridine ligands (Chart 47).[198] Complex **100** exhibits lamellar and columnar rectangular mesophases at temperatures around 100 ºC, although its luminescence properties (λ_{em} = 580 nm, Φ < 0.01) and the stability over time are not very promising. Likewise, the analogous cationic complex **101** shows a columnar mesophase in a short stability range of temperatures of 145 – 163 ºC (Figure 36a), and slightly improved luminescence behavior (λ_{em} = 532 nm, Φ < 0.013).

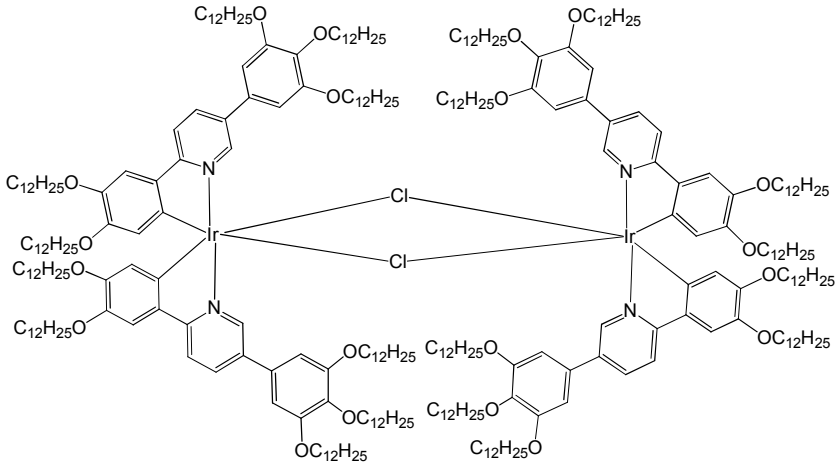
Based on these results, which were unprecedented in the field of luminescent Ir(III) metallomesogens, Bruce et al. were interested in to synthesize related Ir(III) compounds based on polycatenar 2,5-diphenylpyridine ligands. Interestingly, the functionalization of the ligands with five and six terminal alky chains allows inducing

Chart 47



100 **101**

Chart 48



102

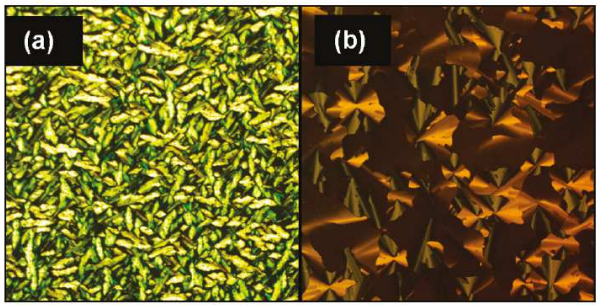
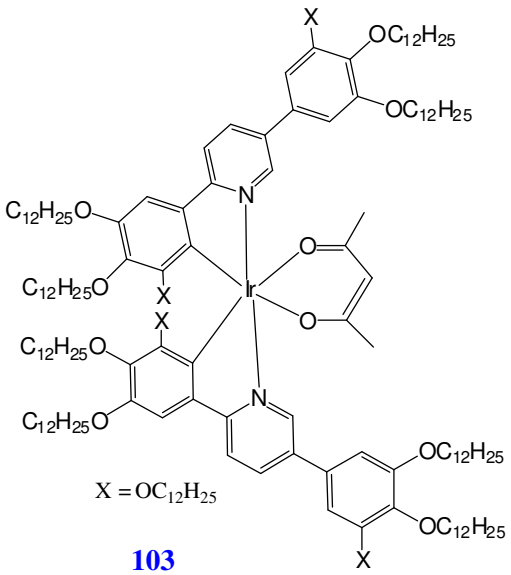


Figure 36. POM microphotographs taken on cooling in the mesophase of (a) **101** at 155 ºC, and (b) **102** at 43 ºC. Reprinted with permission from ref. 198. Copyright 2011 American Chemical Society.

mesomorphism in the dimeric complex **102** (Chart 48) and the monomeric one **103** (Chart 49).[198] In the first case, **102** forms a stable hexagonal columnar mesophase at room temperature, which is maintained until 75 ºC (Figure 36b). This complex emits yellow light with the emission maximum centered at around 570 nm and a low quantum yield below 0.01. Complex **103** shows similar mesomorphic behaviour, exhibiting hexagonal columnar mesophase at near room temperatures between 31 and 66 ºC. Regarding the luminescence properties, the emission band appears centered at 582 nm, and the quantum yield notably increases with respect to the pentacatenar Ir(III) complex, reaching values of 0.09.

Chart 49



103

A few months later, and following the above-described research line, Bruce and coworkers reported a new series of diphenylpyridine-based binuclear Ir(III) metallomesogens by using 1,1,2,2-tetraacetylethane as a bridging ligand (Chart 50).[199] In these compounds, the asymmetry of the Ir(III) center originates two diastereomers that could be separated but not identified, the *meso* form and the racemate one, with ΛΔ-stereochemistry, and ΔΔ- and ΛΛ-stereochemistry, respectively. Results revealed that diphenylpyridine ligands decorated with one terminal alkyloxy chain at each phenyl moiety do not allow inducing liquid crystal properties in their corresponding Ir(III) complex **104**. By contrast, compounds **105**, **107**-**109** bearing polycatenar ligands exhibit mesomorphic behaviour (Col_h mesophases) except for compound **106** (Figure 37). Interestingly, all the Ir(III) complexes show orange emission at room temperature with quantum yields ranging between 0.4-0.6. This fact demonstrates that the bridging tetraacetylethane ligand is an excellent candidate to synthesize bifunctional dimeric complexes, in comparison with the analogous low-emissivity dimeric complex **102**, in which chloride ligands are used as binding ligands.

The luminescence and mesomorphic properties of the Ir(III) complexes can be modulated by the strategical design of their coordinated ligands, as demonstrated Bruce, Baranoff and coworkers in 2015. On the basis of the probed usefulness of the phenylpyridine ligands to induce mesomorphism, the authors synthesized two series of Ir(III) complexes **110**-**113** with 2-phenylpyridine, 2-(2,4-difluorophenyl) pyridine and difluorobiphenylcyclohexyl compounds as ligands (Chart 51).[200] Complexes **110** and **112** show green phosphorescence (λ_{em} = 517 nm) with lifetime and quantum yields of around 1.5 μs and 0.5, respectively, whereas the presence of the fluoride atoms in the phenylpyridine ligands of the complexes **111** and **113** originates a bright blue emission (λ_{em} = 482 nm, Φ ~ 0.65, τ ~1.1 μs). Regarding the phase behavior, all the Ir(III) complexes form SmA mesophases, **110** and **111** exhibiting monotropic behavior, and **112** and **113** showing enantiotropic one. Moreover, upon thermal annealing, these species show high hole mobilities ranging between 10^{-4} – 10^{-3} cm^2 V^{-1} s^{-1}, which makes them to be the first multifunctional Ir(III) metallomesogens for potential application in the fabrication of phosphorescent OLEDs.

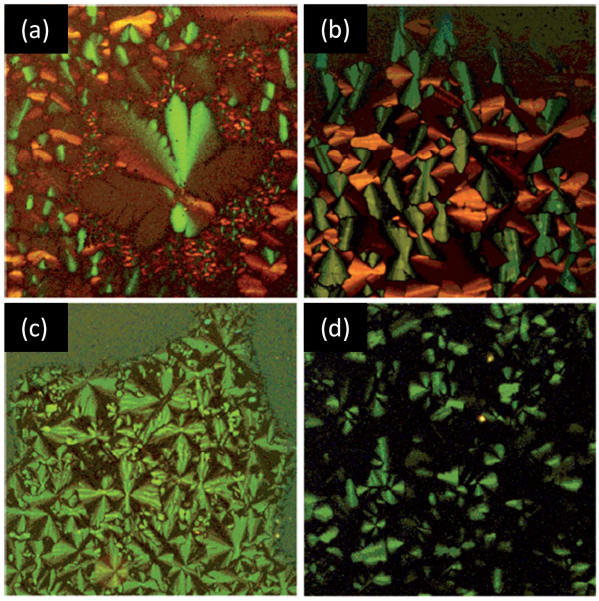
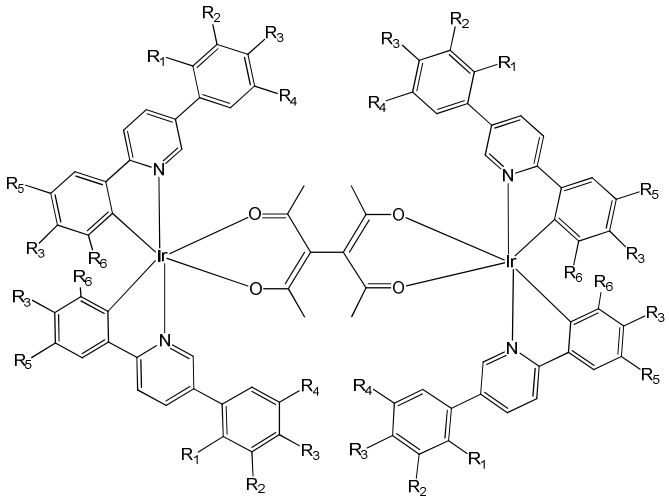


Figure 37. POM microphotographs of (a) **107** (isomer 1) at 100 ºC, (b) **107** (isomer 2) at 60 ºC, (c) **105** (mixture of diastereoisomers) at 85 ºC, and (d) **109** (mixture of diastereoisomers) at 133 ºC. All photographs were taken on cooling. Reprinted with permission from ref. 199. Copyright 2012 Wiley-VCH Verlag GmbH & Co. KGaA.

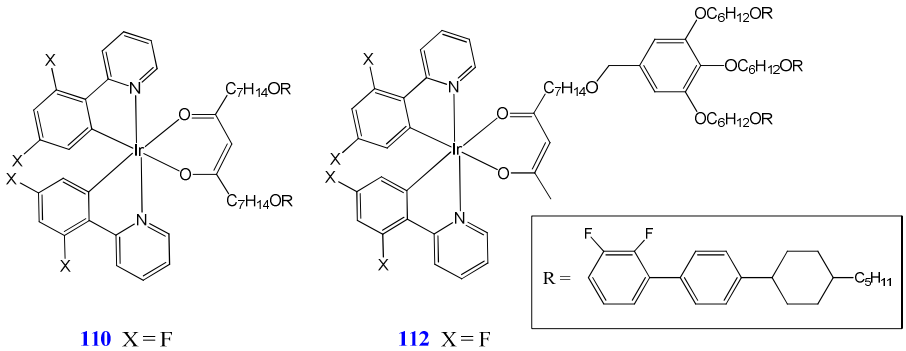
Hexacatenar terpyridine-functionalized Ir(III) complexes **114** and **115** (Chart 52) were found to exhibit improved properties because they maintain their phosphorescence emission in the mesophase.[79] Both species exhibit stable Col_r and Col_h mesophases in a wide temperature range from *ca*. 40 ºC to about 230 ºC. In particular, **114** is highly emissive in solution, in the solid state and the liquid crystal phase at high temperature, this later feature being unprecedented in the field of luminescent Ir(III) metallomesogens to date. Notably, the solid-mesophase phase transition does not cause the quenching of the emission, as it occurs in most of metallomesogens. Temperature does not have that effect either. The emission intensity is maintained below 150 ºC, and only decreases when the isotropic phase is formed. Moreover, a red-shift of the emission maximum from 619 to 655 nm is observed at 175 ºC and it is attributed to an excimer-like emission in the mesophase (Figure 38). The finding of the thermal and photophysical behavior of this Ir(III) metallomesogen opens a great variety of potential applications in the field of optoelectronics and, particularly, in the development of polarized phosphorescent OLEDs.

Chart 50



(104) $R_3 = OC_{12}H_{25}$; $R_1, R_2, R_4, R_5, R_6 = H$
(105) $R_2, R_3, R_5 = OC_{12}H_{25}$; $R_1, R_4, R_6 = H$
(106) $R_2, R_3, R_4, R_5 = OC_{12}H_{25}$; $R_1, R_6 = H$
(107) $R_1, R_2, R_3, R_5 = OC_{12}H_{25}$; $R_6 = H$
(108) $R_2, R_3, R_4, R_5, R_6 = OC_{12}H_{25}$; $R_1 = H$
(109) $R_3, R_5, R_6 = OC_{12}H_{25}$; $R_1, R_2, R_4 = H$

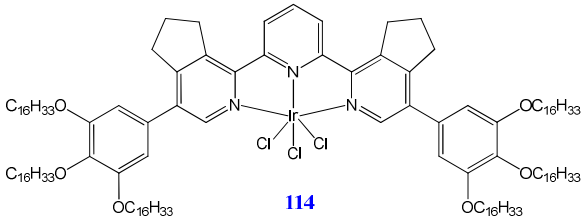
Chart 51



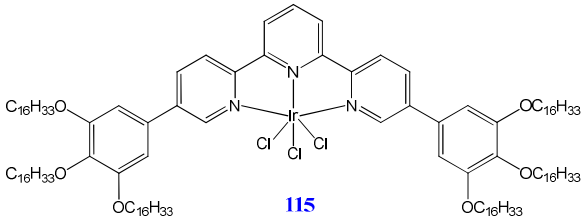
110 X = F
111 X = H

112 X = F
113 X = H

Chart 52



114



115

Luo et al. recently reported a new family of Ir(III) complexes supported by two 2,5-diphenylpyridine ligands and one pyridyltetrazole ligand, all of them carrying terminal alkyl chains of 6 or 12 carbon atoms.[201] Although all of them emit yellow light (λ_{em} = 563 nm), only the Ir(III) complexes bearing 10 or 15 alkyl chains with 12 carbon atoms, i.e. compounds **116** and **117** (Chart 53), behave as liquid crystal materials, exhibiting Col_h mesophases at room temperature. Ambipolar carrier mobility was also found for **117**, with maximum hole and electron mobility values of the order of 10^{-4} and 10^{-5} cm^{-2} V^{-1} s^{-1}, respectively, when the sample is aligned in the thin film. Results seem to suggest that the Ir(III) molecules are self-assembled into columnar structures via intermolecular π···π interactions, originating continuous pathways that favor the carrier mobility (Figure 39).

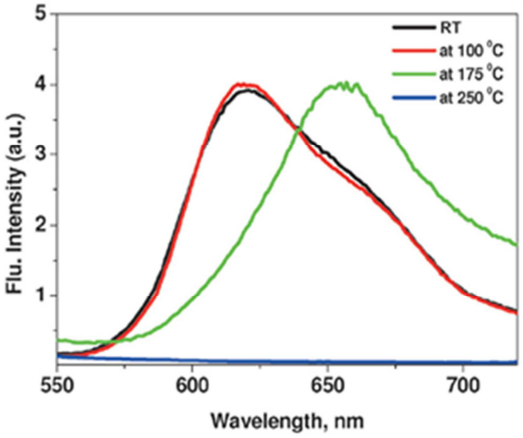
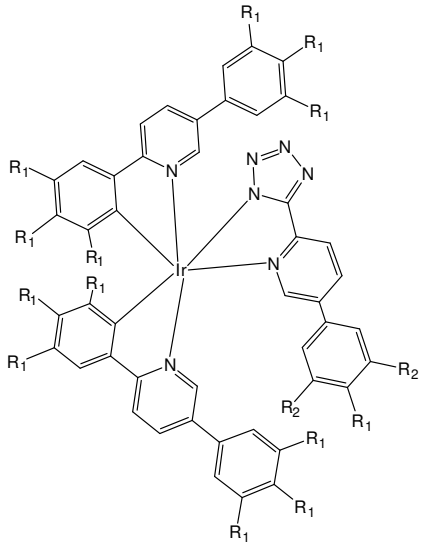


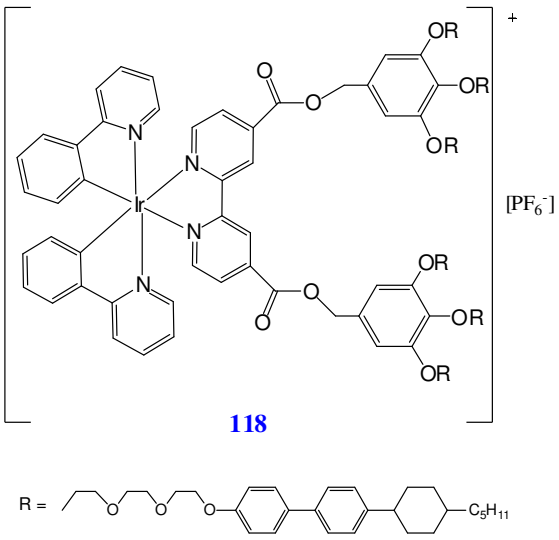
Figure 38. Temperature-dependent emission spectra of **114**. Reprinted in part with permission from ref. 79. Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA.

Liquid crystal properties constitute an important factor when fabricating electrooptical devices since low melting temperatures erase the thermal annealing processes, and low clearing temperatures avoid decomposition. These features were found in the Ir(III) metallomesogen **118** reported by Bruce and coworkers in 2018 (Chart 54),[202] which shows SmA mesophase in a stability range of 156 -177 ºC. For the first time, the authors demonstrated that Ir(III) metallomesogens could be used to develop workable polarized OLEDs. The electroluminescence spectra generally show a broad band centered at around 640 nm and, although the EQE brush 1% in most cases, the dichroic ratio reaches values of up to 4 (Figure 40), which is an unprecedented and promising result in the broad field of metallomesogens



116 $R_1 = OC_{12}H_{25}$; $R_2 = H$
117 $R_1 = R_2 = OC_{12}H_{25}$

Chart 54



118

Chart 53

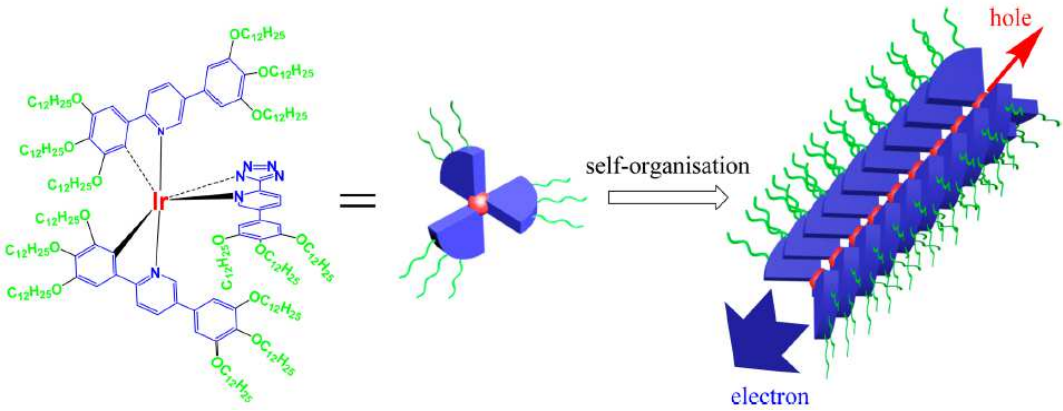


Figure 39. Self-assembly of **117** into columnar structures that originate the carrier mobility. Reprinted with permission from ref. 201. Copyright 2018 American Chemical Society.

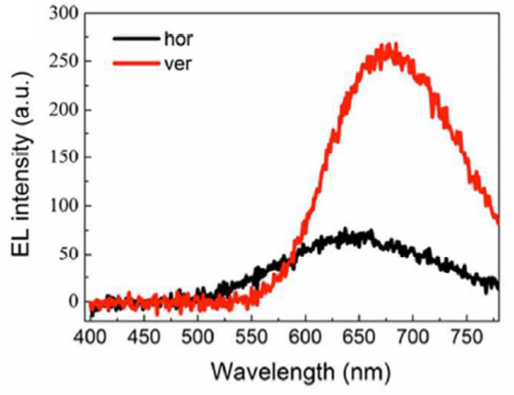


Figure 40. Electroluminescence spectra of one of the devices fabricated with **118**, recoded in two orthogonal directions. Reproduced from ref. 202 with permission from The Royal Society of Chemistry.

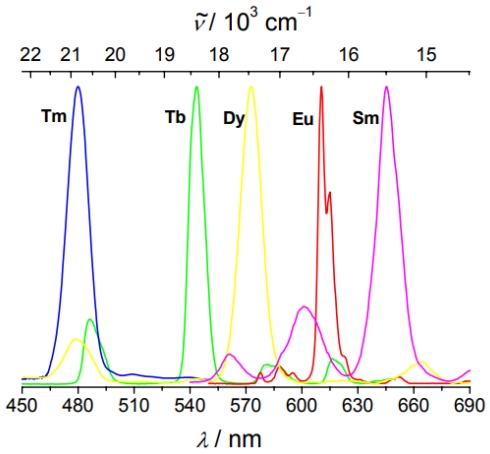


Figure 41. Emission spectra of different lanthanide complexes. Reprinted with permission from ref. 206. Copyright 2006 Wiley-VCH Verlag GmbH & Co. KGaA.

6. Lanthanide metallomesogens and the antenna effect

Lanthanide luminescent materials (LnM) are fascinating due to their intrinsic photoluminescence properties.[203,204,205,206] In general, LnM emission results in a high color purity of the emitted light. However, the choice of the organic compounds that will be used as ligands is rather essential to take advantage of the phosphorescent nature induced by the metal center. Some ligands can act as an "antenna" absorbing light and transferring it to the lanthanide center to generate metal-centered excited states. This complexation protects the metal ion from vibrational coupling and enhance the light absorption by the "antenna effect".[207] However if the ligand coordination does not protect the metal center from water coordination, the complexes became non emissive. The consequence of the coordination of the different type of ligands has been analyzed, as well as the influence of the lanthanide center in the luminescence and liquid-crystal behaviors of the complexes. These LnM materials can emit luminescence in the visible (400–800 nm) or near-infrared (NIR) (800–1700 nm) spectral regions (Figure 41). The most studied ions are Eu^{3+} (that emits red light), and Tb^{3+}(emitting green light), however many examples have been produced using Sm^{3+} that emits orange light, Tm^{3+} generates blue light and finally Dy^{3+} white or near-white light in the visible region. Other lanthanide ions such as $Yb^{3+,}$ Nd^{3+}, Er^{3+} and others show NIR emissions.

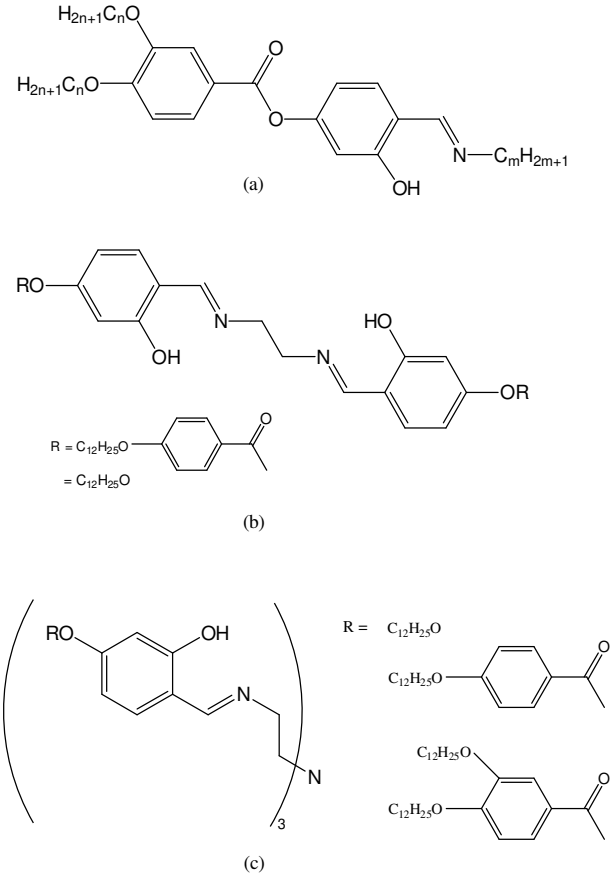


Figure 42. Molecular structure of the (a) mono-, (b) di-, and (c) tri-imine ligands.

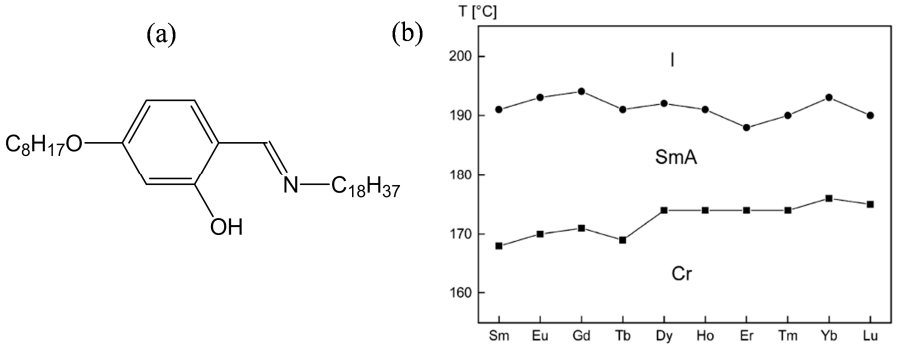
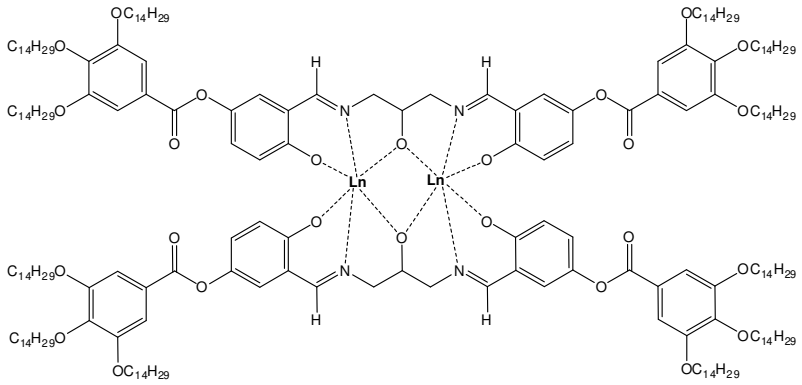


Figure 43. (a) Molecular structure of the Schiff base ligand. (b) Melting and clearing temperatures found for different Schiff-based lanthanide complexes. Adapted with permission from ref. 211. Copyright 2001 Elsevier Science B.V.

Chart 55

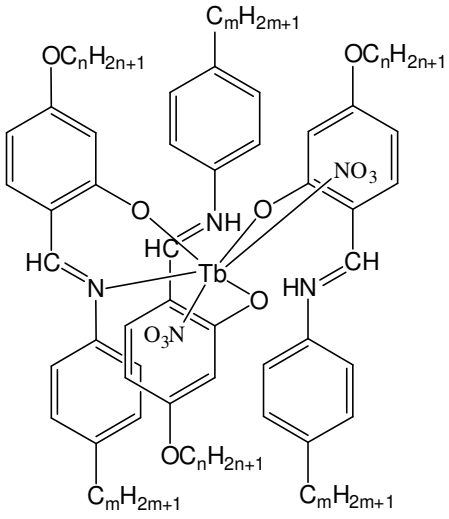


Ln = Nd(III) (**119**), Sm(III) (**120**), Gd(III) (**121**)

When the organic ligand shows a liquid crystalline behavior, very interested lanthanidomesogens can be potentially generated.[208,209] Using imine ligands, Binnemans and coworkers produce a series of Lanthanide liquid crystals with potential magnetic properties.[210] Some of ions as La^{3+}, Dy^{3+}, Nd^{3+}, Ho^{3+} and Er^{3+} coordinated to mono-, di- and ter-imine ligands gave rise to metallomesogenic materials (Figure 42), producing SmA mesophases established for the focal conic fan textures and the presence of homeotropic areas. Unfortunately, the authors do not report any results concerning the photophysical properties of their materials.

Lately, the same author described some lanthanide containing Schiff base ligands (Figure 43a), using chloride as counter-ions.[211] In all complexes, it was observed an enantiotropic SmA phase characterized by polarized optical microscopy, differential scanning calorimetry (SDC) and X-ray diffraction measurements. All complexes present rather high melting and clearing temperatures (Figure 43b). The transition temperatures observed were rather high and consequently, some complex decomposition occurs.

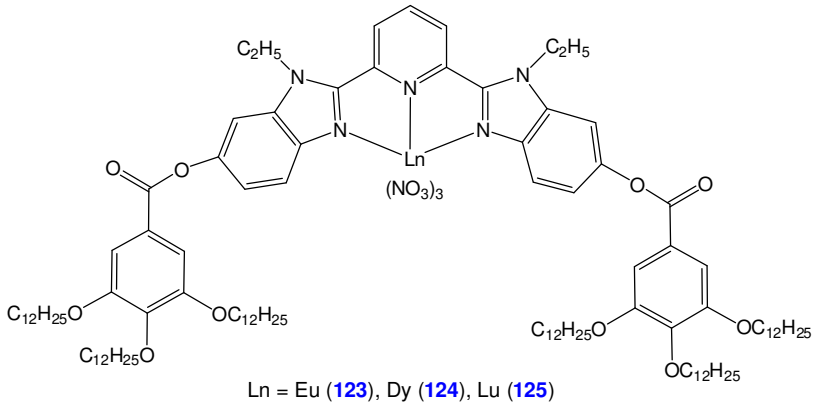
Chart 56



122a-c

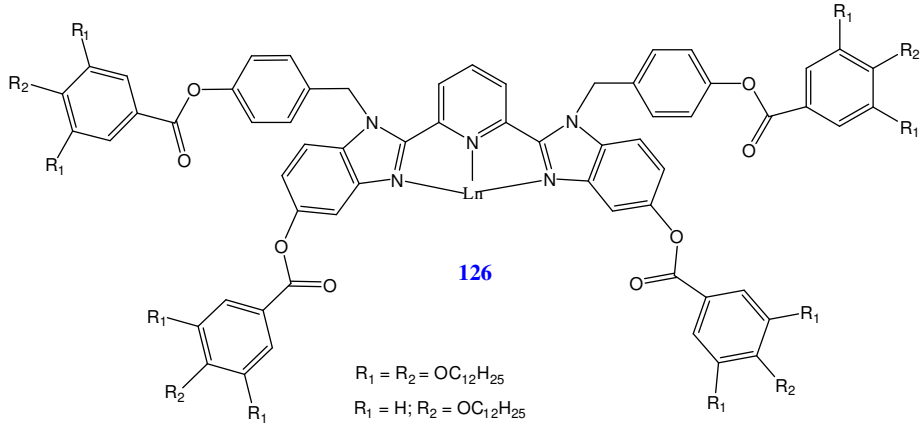
n = 10; m = 4 (a), 10 (b), 14 (c)

Chart 57



Ln = Eu (**123**), Dy (**124**), Lu (**125**)

Chart 58



126

$R_1 = R_2 = OC_{12}H_{25}$

$R_1 = H$; $R_2 = OC_{12}H_{25}$

Ln = La - Lu; $Ln(NO_3)_3$ and $Eu(CF_3CO_2)_3$

In order to prepare neutral lanthanide-based complexes, Binnemans et al. synthesized an organic ligand by condensation of 3-formyl-4-hydroxyphenyl-3,4,5-tris(tetradecyloxy)benzoate in the presence of 1,3-diamino-2-propanol.[212] The compound formed stable dinuclear structures with the lanthanide ions Nd(III), Sm(III) and Gd(III) (complexes **119**-**121** in Chart 55), creating neutral metallomesogens with Col_r mesophases, in a wide stability range of temperatures.

Schiff base ligands possessing a N-aryl moieties have been used by Rao and coworkers to prepare different Ln(III) complexes with mesomorphic properties.[213] A modification between the calamitic lamellar to discotic columnar phase was reported and controlled by the chain length incorporated in the terminal N-aryl ring of the Tb(III) complexes **122a-c** shown in Chart 56.

The same authors report one year later, a series of similar lanthanide(III)-salicylaldimine complexes using their nitrate precursors. The nitrate groups chelate to the metal in the bidentate fashion completing the nine-coordination sphere. All complexes exhibit enantiotropic viscous SmA mesophases in temperatures ranging between 60 and 185ºC, as shown in Figure 44.[214] The lanthanide complexes were emissive in the visible range of 465 to 670 nm after excitation at 350 nm.

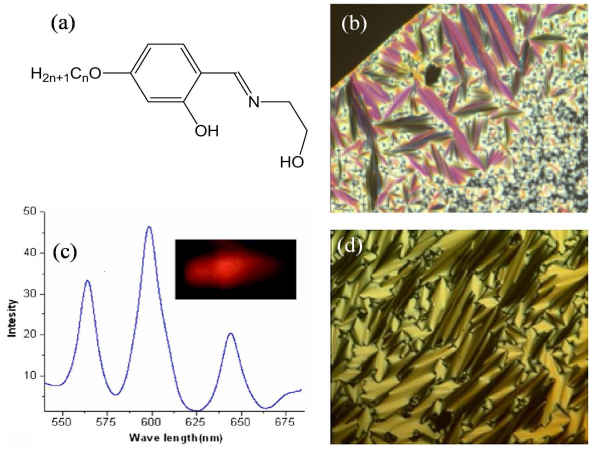
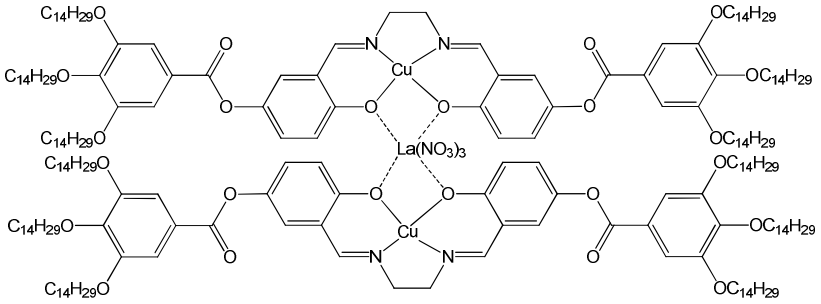
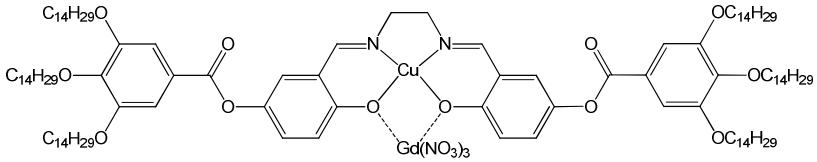


Figure 44. (a) Molecular structure of the salicylaldimine ligand. (b) Texture observed by POM for the salicylaldimine ligand (n = 14) at 74 ºC. (c) Emission spectrum of the corresponding Sm(III) complex in the solid state. (d) POM microphotogarph of the corresponding Pr(III) complex at 155 ºC. Adapted with permission from ref. 214. Copyright 2011 Elsevier Ltd.

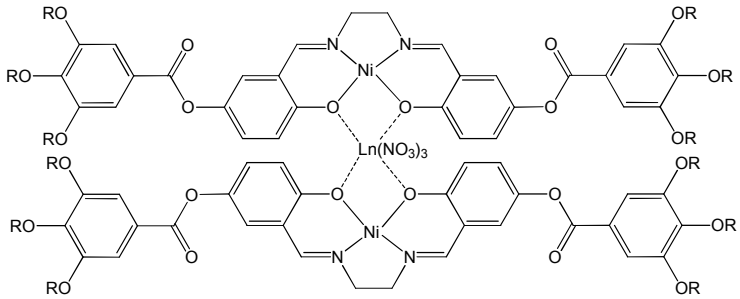
Chart 59



127



128



Ln = La (**129**), Gd (**130**)

R = $C_{12}H_{25}$; $C_{14}H_{29}$; $C_{16}H_{33}$; $C_{18}H_{37}$

The atomic radio of the trivalent lanthanide ions is a very critical factor in defining the final liquid crystal properties in these kinds of complexes. Using dodecanoic acid (lauric acid) the team of Binnemans obtained several complexes with the lanthanide(III) series from Y(III) to Lu(III). All compounds have been found to exhibit a lamellar bilayer structure in the solid state; however the mesophase was only formed with the lighter elements: La(III), Ce(III), Pr(III) and Nd(II), being no mesomorphic the other synthesized complexes.[215] No data about emission properties were reported for these lauric acid derivate materials.

Terazzi and coworkers observed the same size-tune by the lanthanide ion size. In this case, several tridentade receptors containing a pyridine head were used (Chart 57). The authors observed a modulation between columnar mesophases in Lu(III) to cubic phases in Eu(III) and Dy(III) complexes.[216] Unfortunately, due to the thermal degradation observed the clearing temperatures of the mesophases could not be determined. Later on, Terazzi et al. report a dinuclear Ytrium(III) complex formed by a large bis-terdentade ligand originating a SmA-type liquid crystalline phase with a rodlike dinuclear structure.[217]

Escande et al. reported in 2007 a similar tridentate aromatic ligand connected to twelve peripheral dodecyloxyl chains (Chart 58).[218] The molecular system **126** shows room temperature mesomorphism and keep this exciting property when coordinate to the lanthanide(III) ions (La-Lu). Low temperature melting processes generate room temperature hexagonal or lamellar columnar liquid-crystalline phases in the complexes. Steady-state emission studies reveal the typical sharp bands for the lanthanides ions in the solid state at 77K, obtaining Gd(III), Tb(III), and Eu(III) emissive materials.

Mixed d-f metallomesogens are up-and-coming materials since they combine the inherent properties of the transition metal used with the photophysical properties of the lanthanide metal. The team of Koen Binnemans has studied a series of complexes mixing copper(II) or nickel(II) with the nitrate of La(III) and Gd(III) using the salen-type ligand as a chelator.[219,220,221] For copper(II)-lanthanide(III) complexes **127** and **128**, different stoichiometries were found depending on the radio of the lan-

thanide used. By contrast, for the analogous nickel(II)-lanthanide(III) compounds **129** and **130**, the lanthanide was not critical, and the stoichiometry obtained was always 1:1, Ni-Ln (Ln = La-Gd) (Chart 59). All the complexes show Col_h mesophases in a wide range of temperatures (Figure 45). Unfortunately, no luminescence studies were reported for these systems.

Chakrabarty et al. prepared a series of multifunctional lanthanide(III) complexes using a non-centrosymmetric flexible Schiff-base ligand derived from the condensation of 4-alkoxy substituted ketone with the amine, 2-aminoethanol.[222] The resulting tridentate ligand chelate to the lanthanide(III) ions (in a ratio 3:1) to form the compounds **131-134** (Chart 60), which exhibit a partial bilayer type SmA mesophase. It is interesting to remark that in the case of the Tb(III) complex **133**, luminescence was observed even in the mesophase.

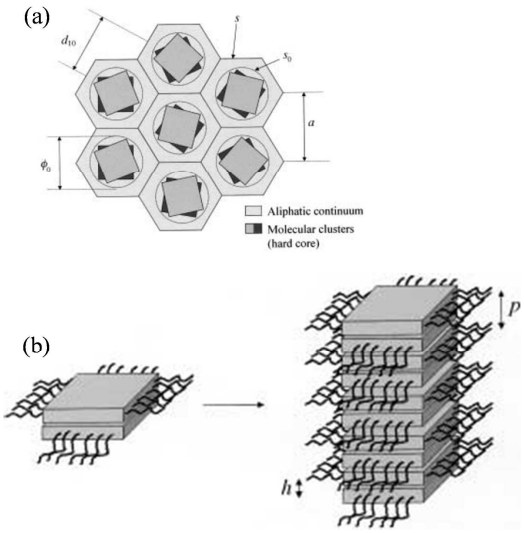
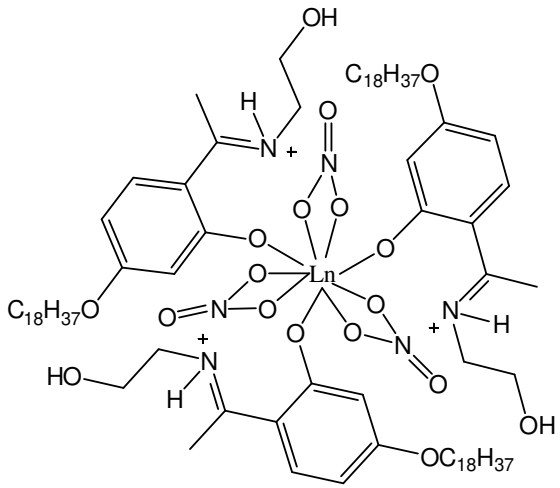


Figure 45. Schematic drawings showing (a) the hexagonal organization in the mesophases of the reported compounds, and (b) the columnar stacking of **127** in the Col_h. Adapted with permission from ref. 221. Copyright 2002 WILEY-VCH Verlag GmbH.

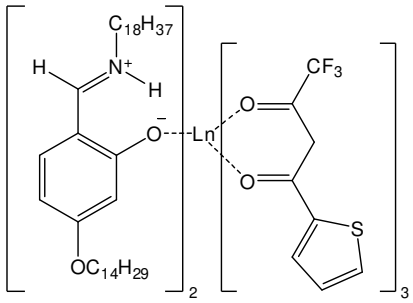
Metallomesogens **135** and **136** exhibiting a mesophase close to room temperature were reported by Yang and coworkers employing a long chain salicylalmine Schiff base ligand and the β-diketonate compound tris(2-thenoyltrifuoroacetonate) (Chart 61). In all cases, the mesophases were identified as SmA ones.[223] The lanthanide(III) complexes obtained with Eu(III), Sm(III), Nd(III) and Er(III) show photoluminescence. The luminescence behavior was studied in the mesophase at room temperature (Figure 46). The visible spectra represent the typical bands predicted for each metal studied.

Chart 60

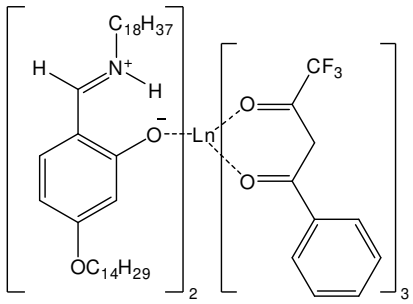


Ln = La (**131**), Dy (**132**), Tb (**133**), Yb (**134**)

Chart 61



135



136

Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Tb, dy, Ho, Er, Tm, Yb, Lu

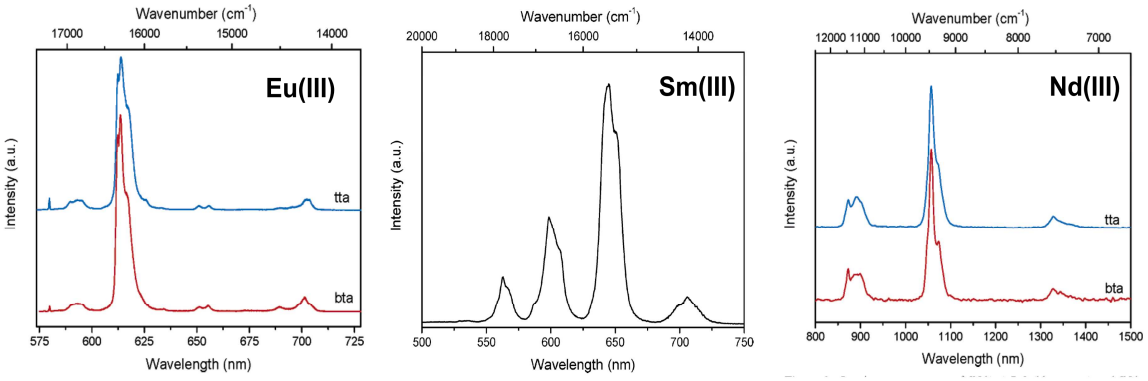
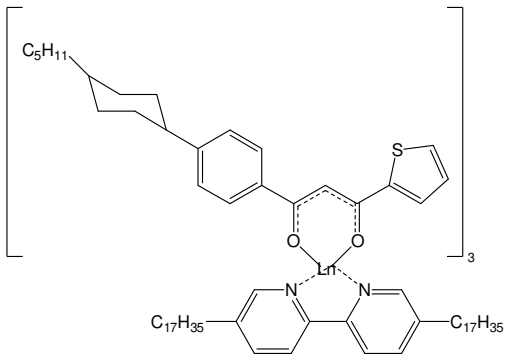


Figure 46. Emission spectra recorded in the mesophase at 25 ºC for some selected Ln(III) complexes. Adapted with permission from ref. 223. Copyright 2006 American Chemical Society.

Chart 62



137

Ln = La(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Ho(III), Er(III), Yb(III), Lu(III)

Different *β*-diketonate lanthanide(III) complexes have also been prepared by Knyazev and coworkers (Chart 62). The photoluminescence of the Eu(III), Sm(III), Yb(III), Er(III) and Nd(III) adducts was reported.[63] All complexes formed with the 5,5′-di(hepadecyl)-2,2′-bipyridine ligand as cooligand, **137** (Figure 47), show thermotropic mesomorphism, giving rise to SmA or SmB mesophases whose melting and clearing temperatures depend on the lanthanide ion.

Very recently employing the β-diketone strategy, Cano et al. studied the series of Eu(III) emissive ionic complexes **138** using long-chained symmetrical and unsymmetrical substituted 1,3-dialkyloxyphenyl-β-diketones as ligands (Chart 63).[224] The alkyl chains varied from 4 to 16 carbon atoms. All complexes exhibit mesomorphism with a smectic A mesophase, and, additionally, luminescence (Figure 48). However, the strategy used to modify the alkyl length chain did not show any effect in the liquid crystal properties. Some of the complexes were studied as dopants of PMMA polymer matrix and evaluated as temperature and anion sensors.

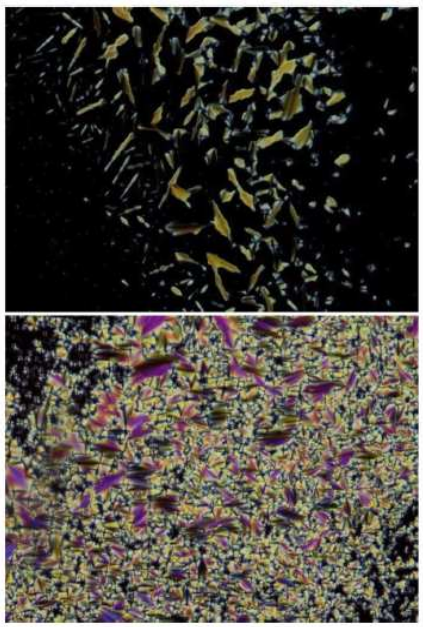
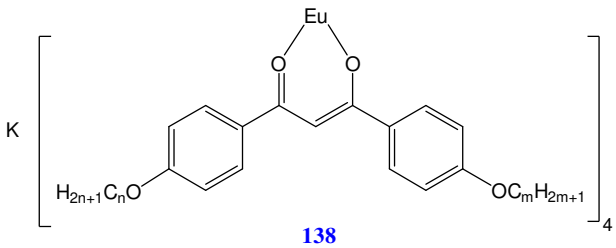


Figure 47. Textures observed for the Sm(III) complex during the formation of the SmA mesophase at 220 ºC (top) and 160 ºC (down) upon cooling. Reprinted with permission from ref. 63. Copyright 2017 Elsevier Ltd.

Chart 63



138

n = m = 8, 10, 12, 14, 16
n = 4; m = 12, 16
n = 8; m = 12, 16
n = 12; m = 16

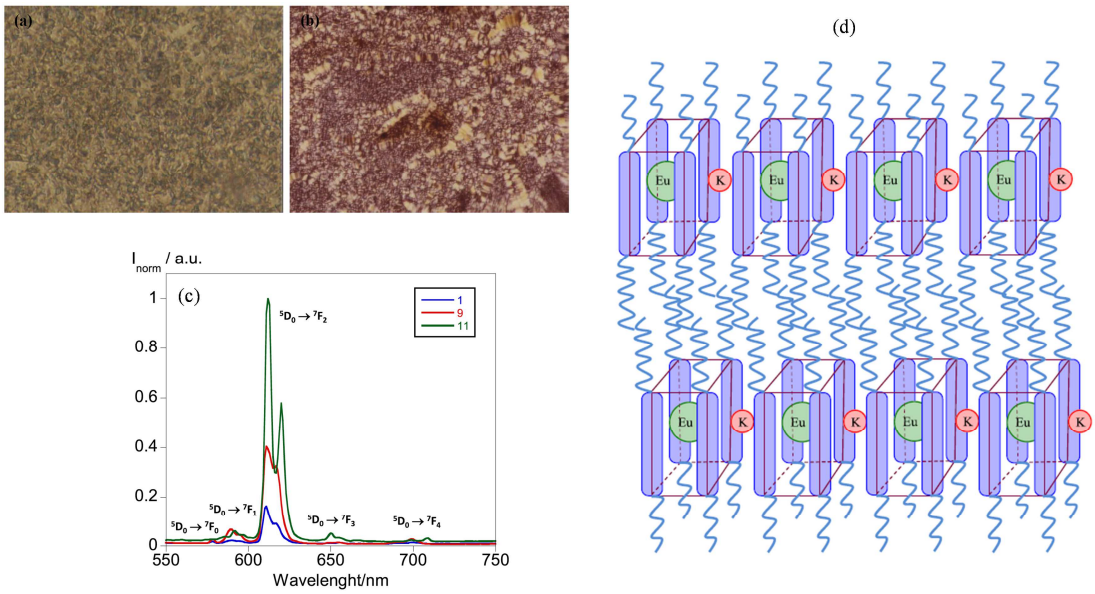
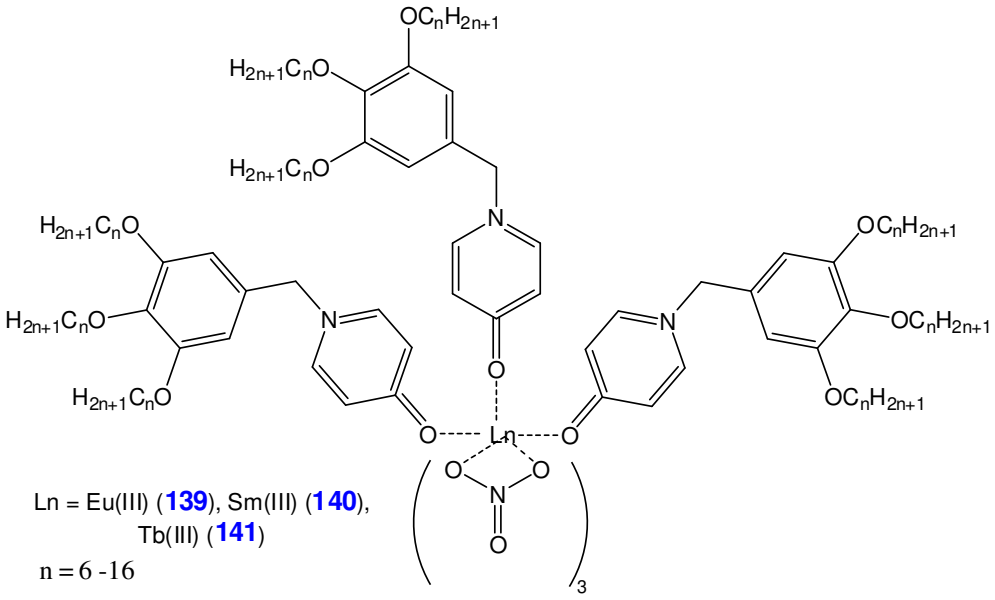


Figure 48. (a,b) POM microphotographs showing the SmA mesophases for the complexes **138** bearing alkyl chains with (a) n = m = 12, and (b) n = m = 14 carbon atoms. (c) Emission spectra of selected complexes recorded in the soli state. (d) Proposed schematic representation of the supramolecular organization in the SmA mesophase. Adapted with permission from ref. 224. Copyright 2017 Elsevier Ltd. 2018 Elsevier Ltd.

Chart 64



Lyotropic metallomesogens with lanthanide(III) ions are very attractive materials for biochemical and materials-science applications. Mesogenic and luminescent complexes were reported by Selivanova and coworkers employing non-ionic surfactants such as decaethylene glycol monododecyl ether and tetraethylene glycol-monododecyl ether with the Eu(III) and Tb(III) nitrates.[225] Their results suggest to form hexagonal mesophases for $C_{12}EO_{10}$/Ln(III) in H_2O-D_2O system, and lamellar mesophases for the $C_{12}EO_4$/Ln(III) system in H_2O-D_2O. In relation with the fluorescent properties, time-resolved luminescence spectroscopy demonstrate that the hexagonal Eu(III) organization is 2-fold more luminescent than that of the lamellar Tb(III) species, being very sensitive to any change in solvents, and surfactant-metal ratio.

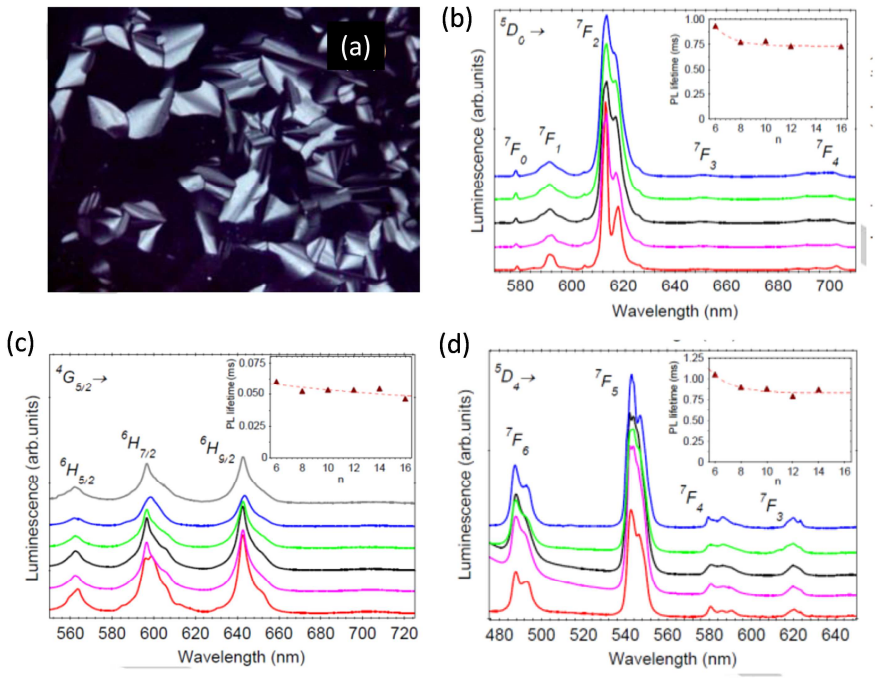


Figure 49. (a) POM microphotograph showing the texture of the Eu(III) complex **139** (n = 14) at 210 ºC. (b,c,d) Emission spectra of complexes **139**, **140** and **141**, respectively, recorded at room temperature in the solid state. Adapted with permission from ref. 93. Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA.

Later on, the Itaya´s group reported the synthesis of several europium(III) and terbium(III) complexes using the dendritic amphiphile 3,4,5-tris(dodecyloxy)benzoate. All complexes exhibit thermotropic liquid crystalline mesophases.[226] The propeller-like central core with nine long surrounding alkyl chains exhibit columnar hexagonal type mesophases, and the lanthanide(III) ions arranged linearly. Both types of complexes shows the typical emission bands for Eu(III) and Tb(III) metal ion composed materials, at 614 nm for Eu(III) and 585 nm for Tb(III), both in solution and in liquid crystal state

Exquisite results have been reported by Circu et al. employing some 4-pyridone derivatives to synthesized Eu(III), Sm(III) and Tb(III) complexes **139** – **141** (Chart 64). These novel liquid crystal materials display an enantriotropic behavior with lamellar phases (SmA) for the shorter chains compounds (6 to 8 carbon atoms), or hexagonal columnar (Col_h) phases for the higher number of carbon atoms (12 to 18) species (Figure 49a).[93] Moreover, they show luminescence emission in the solid state (Figure 49b-d).The fluorescence decay curves showed single exponential decays with the characteristic times in the ms range (0.75-0.90 ms for Eu(III), 0.045-0.060 ms for Sm(III) and 0.75-1.05 ms for Tb(III), respectively).

Few examples can be found in the literature related to liquid crystals using macrocyclic functionalized ligands. Bünzli et al have studied some complexes with a pro-mesogenic 18-membered diaza-substituted core and with for four lateral chains.[227] The nitrate complexes 142 and 143 show luminescent both as powders and as liquid crystals in a range of temperatures between 87 to 195 ºC (Figure 50). The Eu(III) complex is clearly mesogenic with possible columnar phase.

A fascinating example using a phthalocyanine derivative as a ligand was reported by Veciana´s group in 2010.[228] The Terbium(III) complex 144 drawn in Chart 65 presents a behavior of single-molecule magnet introducing chirality. The double-decker terbium complex behaves as a liquid crystal at room temperature and lower temperatures. POM studies show that the complex is mesomorphic at room temperature with a clearing temperature at 304 K. After cooling from the isotropic liquid, dendritic textures could be observed. These results evidence the formation of a Colh mesophase. The synthesis of this molecule was essential in the future findings of room temperature liquid crystals molecular material, including chirality.

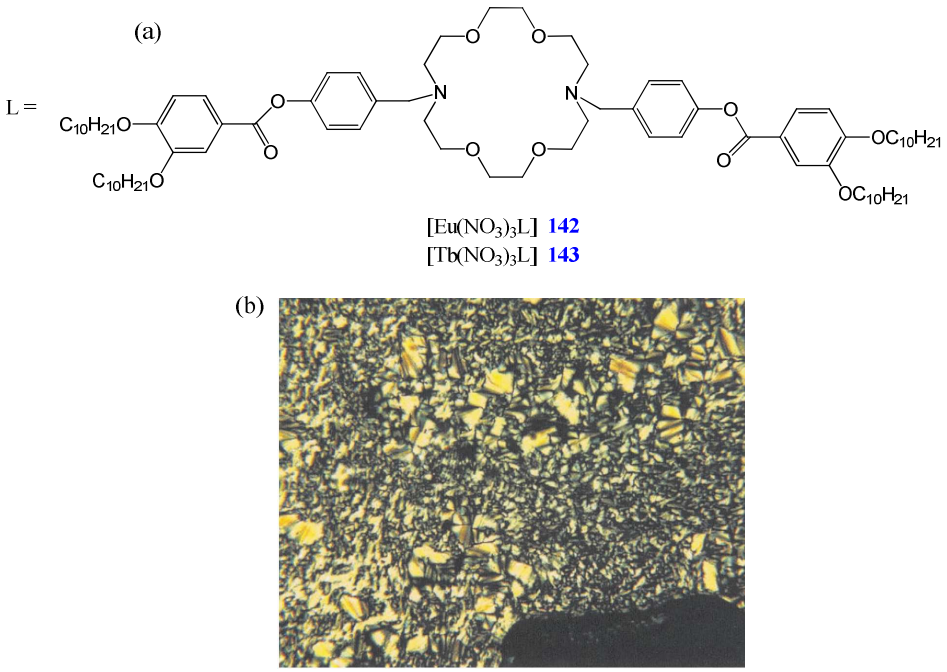
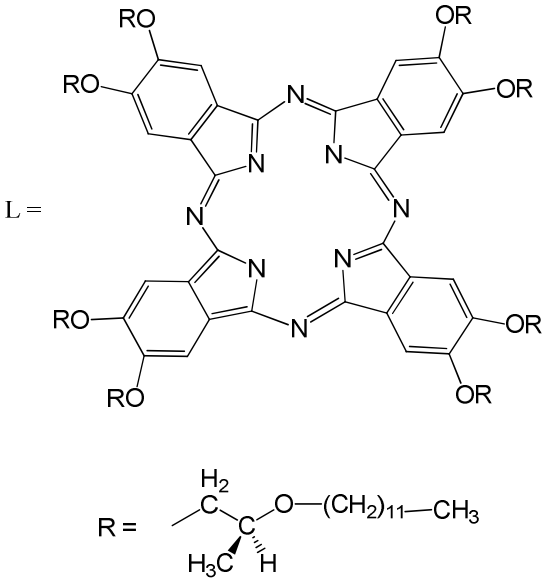


Figure 50. (a) Molecular structure of the macrocyclic used for the synthesis of $[Eu(NO_3)_3L]\cdot 0.25H_2O$ (**142**) and $[Tb(NO_3)_3L]\cdot 1THF$ (**143**) complexes. (b) POM microphotograph obtained for **142** in the mesophase at 110ºC. Adapted from ref. 227 with permission from The Royal Society of Chemistry.

Chart 65



7. Conclusions and outlook

The past decades have seen tremendous advances in the design and synthesis of liquid crystal materials, being at the first mainly organic, but latter metallomesogenic compounds have strongly crashing in the field of these kind materials. Their incorporation in modern displays as LCDs and OLEDs components has been critical. In a world of continuous technological expansion, any improvements in commercial applications are essential. We have lived a worldwide health crisis with the Covid19 pandemic, where once again science reactions, modifications, and knowledge have been crucial to surviving. From technical and engineering applications to nanoscale in biomedical and environmental fields, the needed for more sophisticate organic and inorganic smart materials became a subsistence issue.

Among the typical elements explored in this review as metal centers towards Ag(I), Au(I) and Pt(II) metallomesogens, other less expensive metals must be studied in the future, to reduce the cost of production and in consequence the final commercial price of technology. Some metals than could induce essential changes in the emission properties such as Cu(I), Zn(II), Al(III) or Ga(III) could be promising cheaper candidates to be explored. On the other hand, among the metal centre, the optical properties of the organic ligands, and the potential ability to stabilize different oxidations states, become prevailing. This review also evidences the transcendence of the molecular geometry to achieve the bifunctional nature of the new materials. This research could be the focus of two attractive features for new optical materials that go far beyond the typical uses in sensor and LED technology. The first remains in better imaging properties with more substantial brightness and efficiency, and the second will be the option of performing measurements on a nanoscale in fields as medicine

and environmental media. Temperature and pressure sensors to be used in fingerprint technology also will be groundbreaking.

The results presented in this review show the impressive progress that has been made in metallomesogenic materials exhibiting optical properties. However it is a none ending history, the future is in our hands as designers and synthetic chemist, to perform new environmental, economical materials, to explore new spectroscopies, to conquer new optoelectronic and microelectronic components for sustainable technology, and do not forget three crucial areas in the future, health, energy and data processing.

AUTHOR INFORMATION

Corresponding Author

* Cristián Cuerva. BIOSCOPE Research Group, LAQV@REQUIMTE Chemistry Department, NOVA School of Science and Technology, NOVA University Lisbon, 2829-516 Caparica, Portugal. E-mail: c.alaiz@fct.unl.pt.
Current address: Department of Inorganic Chemistry, Complutense University of Madrid, Ciudad Universitaria, 28040 Madrid, Spain. E-mail: c.cuerva@ucm.es

* Carlos Lodeiro. BIOSCOPE Research Group, LAQV@REQUIMTE Chemistry Department, NOVA School of Science and Technology, NOVA University Lisbon, 2829-516 Caparica, Portugal. E- mail: cle@fct.unl.pt; clodeiro@bioscopegroup.org

Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

The authors would like to dedicate this manuscript to the late Prof. José Vicente Heras and Prof. José Antonio Campo, full professors at the UCM research team for their contributions in the field of metallomesogens.

Biographies

Dr. Cristián Cuerva graduated in Chemistry at the Complutense University of Madrid in 2012, and completed his professional career with a Master in Chemical Sciences and Technologies in 2013 (MSc award). Four years later, he received his Ph.D. in Advanced Chemistry (Outstanding PhD Thesis Award - European Mention) by the same Institution. During this time, C. Cuerva worked on stimuli-responsive luminescent liquid crystals and nanostructured metallomesogens. In 2019 he moved to the NOVA University Lisbon as a postdoctoral researcher. Its research focuses on the development of water-soluble luminescent nanocrystals and polymer nanoparticles taking advantage the self-assembly behavior of certain metallomesogens and other coordination compounds.

Prof. Mercedes Cano is full professor of Inorganic Chemistry, main researcher of several research projects since 1985, and co-head of the research group "Molecular and Polymer Materials based on Coordination Compounds" from the Complutense University of Madrid until 2020. She has a high level of experience with more than 40 years working on compounds including metal-metal bonds, functional materials with non-linear optical properties and liquid crystals materials. The latter line of research being currently developed with particular interest in to achieve luminescent soft materials.

Prof. Carlos Lodeiro graduated in Chemistry in 1995 in the University of Santiago de Compostela, Spain, and received his PhD in chemistry in 1999 by the same university. In 1999 he moved to the University NOVA of Lisbon (UNL) in Portugal as European Marie Curie postdoctoral researcher in a project concerning molecular devices and machines, and in 2004 he became a fellow researcher and invited assistant lecturer at the REQUIMTE-CQFB, Chemistry Department (UNL). In 2008 Dr. Lodeiro got the habilitation in Chemistry in Spain, and a year later in 2009 he moved to the University of Vigo, Faculty of Sciences of Ourense (FCOU), Spain as IPP (Isidro Parga Pondal) researcher-lecturer until 2012. Since 2012 to 2017 he was Assistant Professor at the Chemistry Department in the FCT, University NOVA of Lisbon. In 2017 got the habilitation in Inorganic Analytical Chemistry in Portugal at the FCT-UNL and became Associate Professor. His research interest comprises (i) physical-organic and physical-inorganic chemistry of fluorescence chemosensors and dyes, (ii) Synthesis of Functionalized Nanoparticles, Nanocomposites and Nanomaterials (iii) Applications of nanomaterials in environmental research, (iv) application of nanomaterials in bio-medical research, (v) Analytical proteomics, (vi) Onco and Nanoproteomics. (vii) Drug Delivery and Antibiotic Resistance Studies.

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ABBREVIATIONS

N, Nematic; SmA, smectic A mesophase, SmC, smectic C mesophase; Col_h, hexagonal columnar mesophase; Col_r, rectangular columnar mesophase; Col_t, tetragonal columnar mesophase; Col_L, lamellar columnar mesophase; OLEDs, organic light-emitting diodes; LCDs, liquid crystal displays; POM, polarized light optical microscopy; THF, tetrahidrofuran; DCM, dichloromethane.

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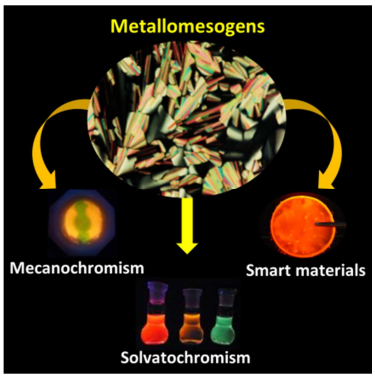
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