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An Overview of Phosphorescent Metallomesogens based on Platinum and Iridium

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KEYWORDS. Luminescent metallomesogens; Phosphorescence; Platinum complex; Iridium complex

ABSTRACT: Metal atom with excellent magnetic, electrical and optical properties that became integrated into liquid crystal molecules – metallomesogens – have attracted much attention by chemist and physicist and engineers and many materials based on, *e.g.* Ag, Pt, Pd, Ir, Ni, Cu and lanthanide ions have been reported. Though several reviews and books have been published on metallomesogens, few refer to their photophysical properties. Additionally, metallomesogens with good emission properties in solution or in neat film are still scarce. Owing to the 100% theoretical internal quantum efficiency, phosphorescent liquid-crystalline materials were developed recently. Here, a brief overview of recent research on such materials based on platinum and iridium complexes including their molecular design and structure-property relationships is reported. It is hoped that this review will stimulate further development of luminescent metallomesogens.

1. Introduction

Metallomesogens – that is liquid crystals containing metal centres – have attracted much interest due to their diverse properties.[1,2] For example, these metal-based liquid crystals can show interesting magnetic, electrical, optical and electro-optical properties.[3-8] The study of metallomesogens not only opened up novel strategies for the design of liquid crystals but also has provided a method for tuning their physical properties. Compared to the broader field of organic liquid crystals, metallomesogens are considered to be a relatively new area, flourishing in 1980s even if the first example was reported by Heintz in the 19th century.[9]

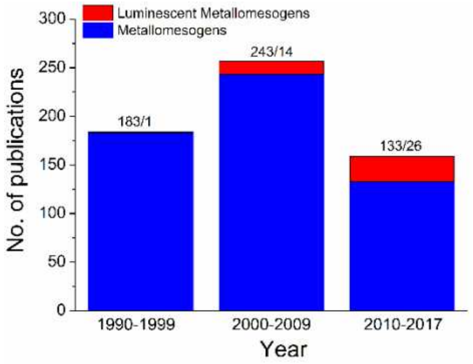


Figure 1. Publications on metallomesogens and luminescent metallomesogens from 1990 to 2017 (Dec.)

According to data obtained from *Scifinder* with the search topic of metallomesogens, there are 559 publications from 1990 to 2017 (actually, the phrase metallomesogens did not come into wide use until the 1990s – before that there were many phrases) (**Figure 1**). And, while numerous metallomesogens were designed and synthesised, investigation of their physical properties generally lagged far behind, especially of their luminescence.[10-19]

Recently, liquid-crystalline materials with emission property have received considerable attention due to their potential application as backlighting in displays. Thus, in, for example, a laptop display, the backlight is a solid LED emitting unpolarised light. The LCD is sandwiched between two crossed polarisers as usual, with each polariser removing about 50% of the light. However, owing to the ability to produce large-area, oriented films of liquid crystals, they can emit polarised light without the additional polariser and so could form a polarised OLED backlight. This would remove the need for the back polariser and so would double the amount of light passing through the LCD.

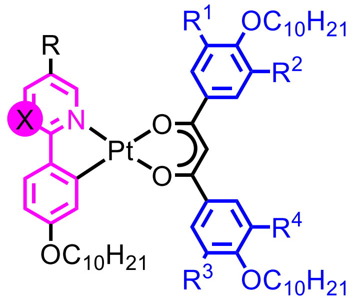
To date, numerous luminescent liquid crystal materials, including polymers, oligomers, small molecules, and metal complexes, have been reported (1202 publications from *Scifinder*).[20-33] However, most of the reported luminescent liquid crystals are fluorescent materials (singlet emitters) which utilise only singlet excitons leading to low emission efficiency. To address this issue, introducing liquid crystals into the concept of phosphorescence (triplet emitters) could combine mesogenic properties with high emission efficiency. Compared to fluorescent materials, phosphorescent materials in OLEDs could achieve four times greater efficiency.[34] However, purely organic phosphorescent emitters generally have very long radiative lifetimes due to weak spin-orbit coupling (SOC) between singlet and triplet state and consequently possess low emissive efficiency. On the other hand, phosphorescent materials bearing heavy-metal complexes, especially those containing third row transition metal, such as iridium, platinum, ruthenium, usually have strong SOC due to the "heavy-atom" effect, which could harvest both singlet and triplet excitons leading to theoretic 100% internal quantum efficiency.[34] With this in mind, luminescent metallomesogens bearing platinum, iridium, palladium, and lanthanide elements have been developed recently.[10-19,35] As seen from Figure 1, the number of the publications on luminescent metallomesogens has a distinct increasing trend from 1990s to the 2010s (**Figure 1**).

Although several reviews and books on the concept, development and structure-property relationship of metallomesogens have been published,[1,2,36] overviews on luminescent liquid crystals are still largely overlooked.[37-39] Three years ago, we summarised some typical luminescent liquid crystals and their application in polarised emission,[35] but as the field has moved on, it is appropriate to summarise recent progress in luminescent metallomesogens. In this review, luminescent metallomesogens based on platinum and iridium complexes (phosphorescent metallomesogens) will be emphasised due to their wide application in organic light-emitting diodes, which will be helpful to those with a general interest in this subject. Three different aspects of phosphorescent metallomesogens, namely the design, luminescence and mesomorphism will be discussed.

2. Cyclometallated, platinum-based luminescent metallomesogens

Cyclometallated platinum complexes are one of the most attractive candidates for organic light-emitting diodes due to the possibility of nearly 100% internal quantum efficiency resulting from harvesting both singlet and triplet excitons.[40,41] Additionally, cyclometallated platinum(II) complexes have a d^8 electronic configuration and square-planar geometry and, in some circumstances, can exhibit intermolecular Pt···Pt interactions, which has an effect on both self-assemble and emission behaviour.[42-8] Herein, typical luminescent, cyclometallated platinum complexes are selected for review and their structure-property relationships are discussed.

Cyclometallated Pt complexes with bidentate C^N ligands



1

X = N, R= C_7H_{15}

1a R^1 = H, R^2 = H, R^3 = H, R^4 = H;
1b R^1 = $OC_{10}H_{21}$, R^2 = H, R^3 = H, R^4 = H;
1c R^1 = $OC_{10}H_{21}$, R^2 = H, R^3 = $OC_{10}H_{21}$, R^4 = H;
1d R^1 = $OC_{10}H_{21}$, R^2 = $OC_{10}H_{21}$, R^3 = H, R^4 = H;
1e R^1 = $OC_{10}H_{21}$, R^2 = $OC_{10}H_{21}$, R^3 = $OC_{10}H_{21}$, R^4 = H;
1f R^1 = $OC_{10}H_{21}$, R^2 = $OC_{10}H_{21}$, R^3 = $OC_{10}H_{21}$, R^4 = $OC_{10}H_{21}$;

X = CH, R= OC_8H_{17}

1g R^1 = H, R^2 = H;
1h R^1 = $OC_{10}H_{21}$, R^2 = R^3 = R^4 = H;
1i R^1 = $OC_{10}H_{21}$, R^3 = $OC_{10}H_{21}$, R^2 = R^4 = H;

Figure 2. Chemical structures of platinum-based metallomesogens **1**. Adapted from ref. 50 and 51, copyright 2003 (ref. 50) and 2006 (ref. 51), Royal Society of Chemistry.

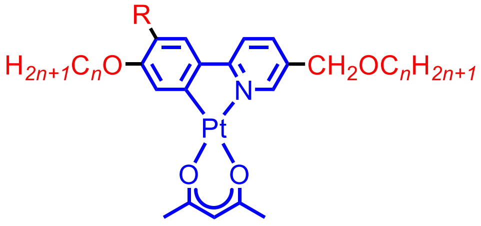
Cyclometallated platinum complex with bidentate C^N ligand is widely used in in OLEDs as an emitter, which. has realised high emission efficiencies both in the visible and near-infrared spectral regions.[49] Usually, this type of complex can normally be prepared under relatively mild conditions starting from $K_2[PtCl_4]$.[43]

At the beginning of 2000s, Tschierske and co-workers reported a series of cyclometallated platinum-based metallomesogens (**1**).[5051] In these complexes, a rod-like platinum skeleton was used as the mesogenic unit and emissive core, while the number, position and length of the peripheral chains allow to tune the liquid crystalline properties. This strategy therefore can maintain both the luminescence and mesophase, although there were suggestions by Swager and co-workers that the phenyl groups on the acac ligand could act to quench some of the emission.[52] As shown in **Figure 2**, the cyclometallated platinum employs 2-phenylpyrimidine (X = N) and 2-phenylpyridine (X = CH) ligands in the cyclometallation and alkoxy-substituted 1,3-diphenyl-1,3-diketonates as the ancillary ligand. The structure-property relationship in these complexes was explored thoroughly by variation of the number and length of attached peripheral flexible chains and the central metal atom. When X = N, all platinum complexes showed thermotropic mesomorphism and the organisation of the phase changed from lamellar to columnar as the number of alkyl chains on the 1,3-diketonate unit increased. Conversely, where X = CH, the complexes were crystalline solids without mesomorphism, the lack of mesomorphism being attributed to the increased torsion between the phenyl and pyridine rings, which disturbs the organisation in LC phases. However, other studies reported below would not readily support this assertion. All platinum complexes (X = N or CH) were luminescence in solution and in the solid state, although some aspects of the emission behaviour were curious. Thus, some of these cyclometallated platinum complexes showed one emission band below 440 nm (1b, 1c and 1e), while other platinum based metallomesogens displayed another additional emission band above 490 nm in solution (1a, 1d and 1f). Attributed by the author, this emission phenomenon mainly originated from the different Pt···Pt distance. Unfortunately, the decay lifetime and emission efficiency were absent in the report to enable this to be verified. To the best of our knowledge, this was the first report of a mesomorphic cyclometallated platinum complex.

Table 1. Phase transition temperatures of compounds **1**. Adapted from ref. 50 and 51, copyright 2003 and 2006, Royal Society of Chemistry.

Compound	R^1	R^2	R^3	R^4	Transition/°C
1a	H	H	H	H	Cr 137 SmA 145 Iso
1b	$OC_{10}H_{21}$	H	H	H	Cr 126 SmA 107 N 109 Iso[a]
1c	$OC_{10}H_{21}$	H	$OC_{10}H_{21}$	H	Cr 117 Iso
1d	$OC_{10}H_{21}$	$OC_{10}H_{21}$	H	H	Cr 62 Col_h 75 Iso[a]
1e	$OC_{10}H_{21}$	$OC_{10}H_{21}$	$OC_{10}H_{21}$	H	Cr 74 Col_h 151 Iso[a]
1f	$OC_{10}H_{21}$	$OC_{10}H_{21}$	$OC_{10}H_{21}$	$OC_{10}H_{21}$	Cr 76 Col_h 170 Iso[b]
1g	H	H	/	/	Cr 100 Iso
1h	$OC_{10}H_{21}$	H	/	/	Cr_1 56 Cr_2 77 Cr_3 87 Iso
1i	$OC_{10}H_{21}$	$OC_{10}H_{21}$			Cr_1 67 Cr_2 92 Iso

Abbreviations: Cr, Cr_1, Cr_2 = crystalline phases, SmA = smectic A phase, Col_h = hexagonal columnar phase, Iso = isotropic liquid state. [a]1:1 Mixture of stereoisomers. [b]Transition temperatures observed by polarised light optical microscopy only.



2

2a R = H; n = 4, 8, 12, 16
2b R = F; n = 8, 12, 16

Figure 3. Chemical structures of platinum-based metallomesogens **2**. Adapted from ref. 53, copyright 2010, Royal Society of Chemistry.

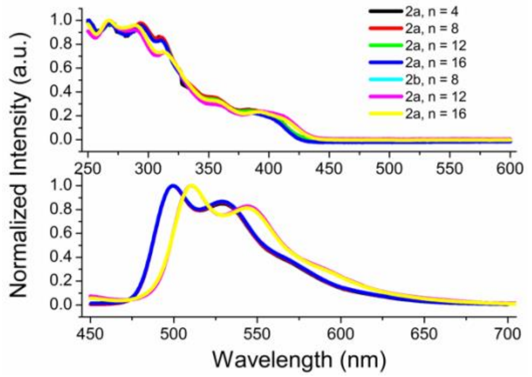
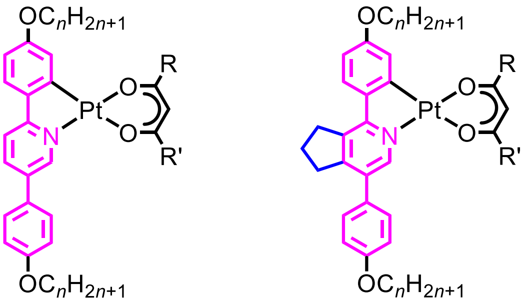


Figure 4. UV-vis spectra and PL spectra of complexes **2** in solution. Adapted from ref. 53, copyright 2010, Royal Society of Chemistry.

To seek the balance between high emission and mesogenic phase, Wang *et al.* reported two kinds of luminescent metallomesogens based on a cycloplatinated complex with fewer flexible chains (**2**, **Figure 3**).[53] In these molecules, the alkoxy chains were found only on the 2-phenylpyridine moiety and the acetylacetone was used as the ancillary ligand. In order to explore the influence of intermolecular interactions on the mesogenic property, a fluorine atom was further introduced into cyclometallating ligand (**2b**). Both platinum complexes showed a smectic phase except the complex with short alkoxy chain (n = 4) and their clearing point decreased with increasing length of the alkoxy chains. Complexes **2b** displayed a lower transition temperature and a higher clearing point than complexes **2a**, which implies that complexes **2b** possesses a broader mesophase range. Complexes **2** showed yellow-greenish emission with moderate emission efficiency (Φ_{em} = 0.12-0.15) in solution. As described in Figure 4, complexes **2b** presented a red-shifted absorption and emission spectra compared to complex **2a** due to the electron-withdrawing fluorine, which then contributes both to tuning the emission wavelength as well as influencing the mesomorphism. The complexes were then fabricated into aligned polyimide films by heating and annealing, and a dichroic emission ratio up to 10.5 was achieved, which is the first example for the polarised emission of metallomesogens based on a platinum complex.

Bruce and co-workers attached one additional phenyl ring onto a 2-phenylpyridine ligand to expand the rigid core, and prepared two series of luminescent metallomesogens based on rod-like platinum complexes with β-diketonate co-ligand (**3-10, Figure 5**).[54] Complexes **3** presented a sole SmA phase, while complexes **4** displayed monotropic SmA and N phases. This difference can be explained by the destabilisation of the mesophases of a rod-like material caused by the presence of the fused, lateral cyclopentane ring in complexes **4**. Both complexes **3** and **4** showed bright emission at *ca* 530 nm in solution with the Φ_{lum} (emission efficiency) up to 0.49, with the chain length having little influence on the solution luminescence. Afterwards, the same group varied the β-diketonate co-ligand (**5** – **10**, **Figure 5**), employing trifluoroacetylacetonate (tfac, **5** & **6** – note both isomers possible) hexafluoroacetylacetonate (hfac, **7** & **8**) and heptanedionate (hdn, **9** & **10**) to study the effect of ancillary ligand on both mesogenic and luminescence properties.[55] It was demonstrated that the substituent in ancillary ligand has a critical effect in the mesophase of their platinum complexes. For example, when the co-ligand is hfac, no mesomorphism is observed for either **5** or **6**, attributed to steric destabilisation of the mesophase. The hdn-based platinum complexes only gave a SmA phase but at significantly reduced temperatures, while the tfac-based complexes displayed a complicated phase behaviour that reflected the presence of isomers arising from the unsymmetric ancillary ligand. Notedly, platinum complexes **5**, **6**, **9** and **10** showed an intense emission in the green-yellow region with Φ_{um} of 0.5-0.7 at room temperature in CH_2Cl_2, amongst the highest reported for bidentate ligand-based platinum complexes. An interesting observation was that the two isomers of complex **5** appeared to have very different emission efficiencies so that Φ was very much greater (and the emission wavelength slightly shorter) for the isomer where R = Me and R' = CF_3. However, ground- and excited-state TD-DFT calculations could not provide an explanation of this observation. As well as lacking liquid crystal properties, complexes **7** and **8** did not prove to be emissive and calculations showed that this was because the LUMO in these complexes resided on the hfac ligand, whereas in the other complexes of this type, it is a mixture of 2-phenylpyridine and Pt orbitals.

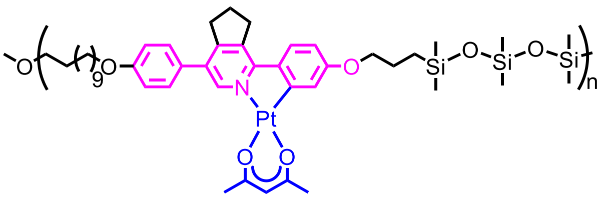


n = 6, 8, 10, 12

3 R = R' = Me
5 R = Me, R' = CF_3
7 R = R' = CF_3
9 R = R' = Et

4 R = R' = Me
6 R = Me, R' = CF_3
8 R = R' = CF_3
10 R = R' = Et

Figure 5. Chemical structures of platinum based metallomesogens **3-10**. Adapted from ref. 54 (**3** and **4**), copyright 2009, American Chemical Society. Adapted from ref. 55 (**5-10**), copyright 2012, Royal Society of Chemistry.



11

Figure 6. Chemical structures of platinum based metallomesogens **11**. Adapted from ref. 56, copyright 2009, American Chemical Society.

The same group then extended this work to the production of semi-flexible, main-chain polymer containing the platinum chromophore (**Figure 6**) and, while the dichroic ratios obtained were modest, they demonstrated the principle of polarised triplet emission from liquid crystal polymers.[56]

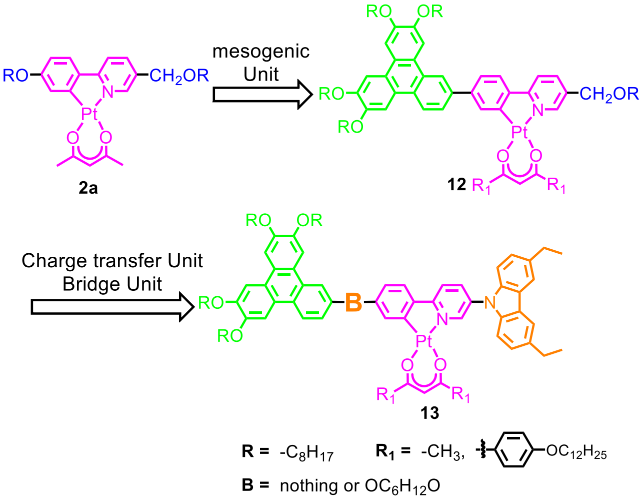


Figure 7. Structural evolutions of molecules **12** and **13**. Adapted from ref. 57 (**12**), copyright 2015, Elsevier Science. Adapted from ref. 58 (**13**), copyright 2016, Elsevier Science.

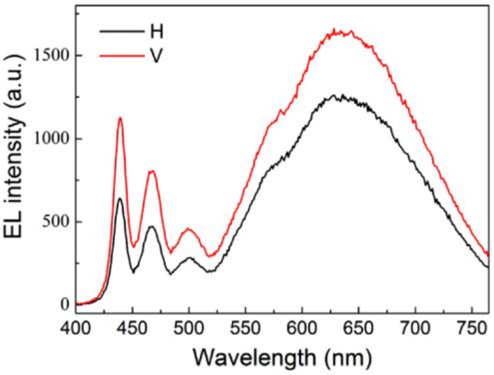


Figure 8. Polarised EL spectra of complex 12 (R = methyl and phenyl derivative) measured in OLEDs at 10 mA/cm^2 (H: parallel, V: perpendicular). Adapted from ref. 58, copyright 2016, Elsevier Science.

In a different synthetic approach, Wang and co-workers introduced a rigid, conjugated mesogenic unit into the platinum complex (**Figure 7**),[57,58] with obvious effects on the mesomorphism, so that complexes **12** (R = methyl and phenyl derivative) showed a columnar phase.[57] Further modifications then inserted a linkage unit between the triphenylene moiety and platinum core (**13**),[58] or introduced a carbazole group to extend the conjugation and enhance the emission efficiency. Both the mesogenic behaviour and the photophysics showed a strong dependence on the modified structure. For example, when triphenylene unit conjugated with platinum skeleton, a columnar mesophase was observed. As the linker length increases, mesomorphism becomes suppressed. Both complexes **12** and **13** displayed intense emission in solution (Φ_{lum} = 0.22-0.35) and in the solid state. This led to the materials being evaluated in a device fabrication where the emitter were aligned by a combination of rubbing and annealing to obtain polarised emission. Compound **12** (R = phenyl derivative) used were such that the emitted light was white (due to the incomplete energy transfer, dual emission from host matrix and guest were obtained.) and, while the dichroic ratio was modest at 4:1 (**Figure 8**), the fabrications were unique examples of polarised WOLEDs containing platinum luminophores.

Zou *et al.* then reported a series of Pt complexes (**14** and **15**) in which the 2-phenylpyridine moiety was functionalised with a hexadecyloxy chain on the pyridine ring and flexibly linked cyanobiphenyl on the phenyl ring with either an acac (**14**) or a picolinato (**15**) *co*-ligand.[59] The complexes were liquid-crystalline and for complexes **14** with one cyanobiphenyl group, a SmA phase was observed while for **15** with $R_3 = R_n$, a nematic phase was seen. The complexes were emissive in solution with the Φ_{lum} = 0.1 to 0.30, but the nature of the emission depended on the state of organisation, with a bathochromic shift, most likely arising from direct Pt···Pt interactions, in the solid state when compared with the liquid crystal phase. Using aligned polyimide films as the substrate, polarised photoluminescence (PL) with polarised ratio of 24.6 was achieved for complex **15** ($R_3 = Rn$, m = 12, **Figure 10**), which we believe to be the highest recorded for a platinum-based metallomesogen.

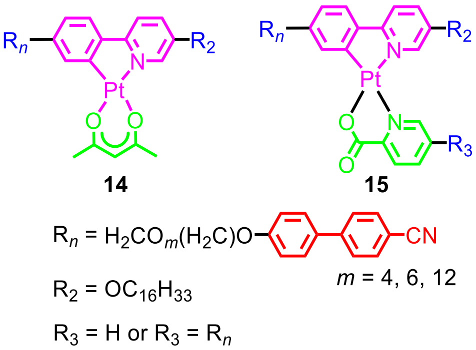


Figure 9. Chemical structure of complexes **14** and **15**. Adapted from ref. 59, copyright 2017, Taylor & Francis LTD.

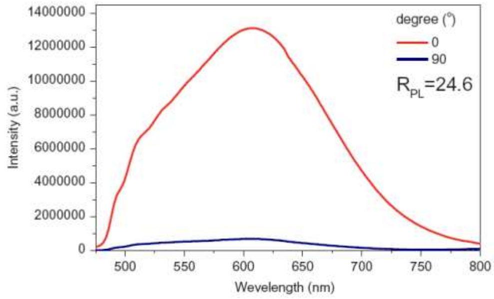


Figure 10. Polarised PL spectra for complex **15** ($R_3 = Rn$, m = 12) on the aligned polyimide film in liquid crystalline phase state. Adapted from ref. 59, copyright 2017, Taylor & Francis LTD.

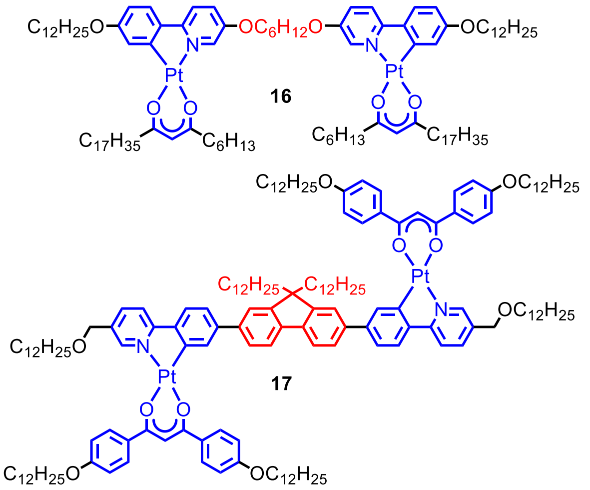


Figure 11. Chemical structures of **16** and **17**. Adapted from ref. 60 (**16**), copyright 2015, Elsevier Science. Adapted from ref. 61 (**17**), copyright 2012, American Chemical Society.

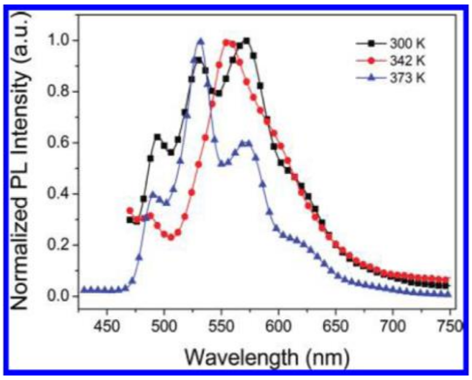


Figure 12. Emission spectra of complex **17** in its neat film at 300, 342, and 373 K. Adapted from ref. 61, copyright 2012, American Chemical Society.

Compared to the mononuclear platinum complex, luminescent dinuclear platinum metallomesogens are still scarce. Jiang *et al.* used a non-conjugated, flexible 1,6-dioxahexylene unit as a bridge to link two platinum skeletons to prepare complex **16** (**Figure 11**),[60] which was reported to show a smectic mesophase and polarised emission. However, the published texture is not immediately consistent with the reported liquid crystal behaviour. Wang *et al.* also reported a dinuclear platinum complex, in this case employing a conjugated fluorene moiety as the linking group (**17**, **Figure 11**).[61] This complex presented a smectic mesophase with relatively low transition temperature owing to the presence and relative orientation of the flexible chains. Complex **17** revealed a broad emission in the region of 450-700 nm both in CH_2Cl_2 solution and the neat film, which demonstrated that there was a strong intermolecular interaction leading to long-wavelength emission. Additionally, the PL profiles of **17** were strongly temperature dependent in different states (amorphous, mesophase and isotropic state, **Figure 12**) because of different molecular aggregation. It is noted that the aligned complex **17** on polyimide film possessed a highly polarised emission with polarised ratio of 10.3, which implies that this dinuclear complex has a potential application for polarised OLEDs.

Cyclometallated platinum complexes based on 2-phenylpyridine ligands are, therefore, promising candidates for luminescent metallomesogens, but the materials require much more detailed investigations before their potential can properly be assessed.

Finally, the preparation of some luminescent LC Schiff base complexes of Pd and Pt by Cîrcu and co-workers is noted, although there was no detail concerning the nature of the excited states neither the efficiency of emission.[62-66]

Pt complexes with bidentate N^N ligands

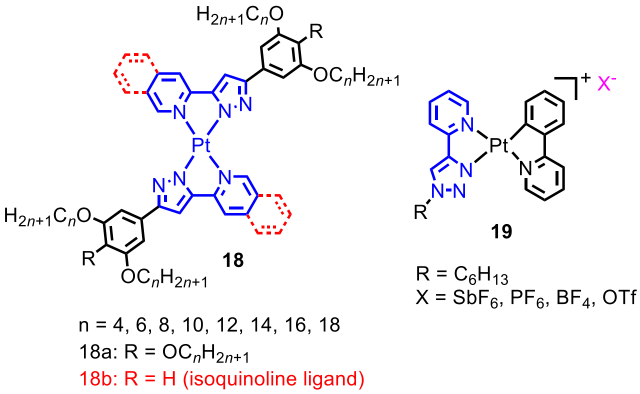


Figure 13. Chemical structures of **18** and **19**. Adapted from ref. 68, 74 and 75 (**18**), copyright 2011 (ref. 68 and 74) and 2016 (ref. 75), Wiley-VCH (ref. 68 and 75) and Elsevier Science (ref. 74). Adapted from ref. 76 (**19**), copyright 2014, American Chemical Society.

Bidentate, anionic N^N ligands derived from, for example, 2-(pyrazol-3-yl)pyridines or 2-(1,2,3-triazol-4-yl)pyridine, can lead to highly luminescent cyclometallated platinum complexes,[67] with the azido nitrogen increasing the ligand field by virtue of being a strong σ-donor. Pyrazolyl-functionalised pyridines turn out to be especially popular,[68-75] so that complex **18a** (**Figure 13**) with tris(alkoxy)phenyl groups, prepared by Hsu *et al.*,[68] exhibited columnar mesophases with very wide temperature ranges. The melting point had an obvious dependence on chain length whereas the clearing temperature did not. Intense green emission (520 nm) with near unit emission efficiency was obtained in solution, while a unique, much longer-wavelength emission band at 630-660 nm was observed in the neat film due to the Pt–Pt interactions and the formation of a MMLCT state. The luminescence of the platinum complex showed drastic temperature dependence, being blue-shifted on heating from room temperature to 250 °C, and then back to the green phosphorescence of the monomer when further heating to the isotropic state.

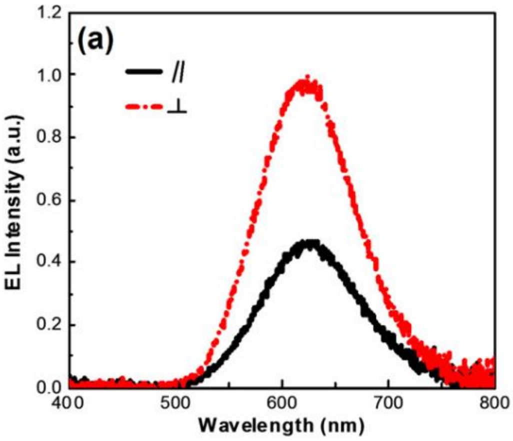


Figure 14. EL spectra of **18a** (R = OC_nH_{2n+1}, n = 6) measured with the polarisation parallel with (//) and perpendicular to (∞) the rubbing direction. Adapted from ref 74. Copyright 2011, Elsevier Science.

Studies of the molecular alignment of **18a** (*n* = 6) for polarised emission revealed[74] that effective alignment was achieved by spin-coating the active layer onto an aligned substrate, namely rubbed, conducting polymer poly(3,4-ethylenedioxy-thiophene):poly(styrenesulfonate) (PEDOT:PSS). With this preparation, polarised red photoluminescence (PL) and electroluminescence (EL) were demonstrated with a dichroic ratio of 2, a maximal brightness exceeding 2000 cd m^{-2} and a maximum current efficiency up to 2.4 cd A^{-1} (**Figure 14**).

Lodeiro and *co*-workers recently published several papers about the synthesis, mesomorphism and photophysical properties of complex **18b** (R = H, isoquinoline ligand).[75] Similar to complex **18a**, a columnar mesophase was observed (**Figure 15**) and it was found that the complexes were sensitive to a variety of external stimuli, such as temperature, mechanical grinding, pressure, solvents and vapours (**Figure 16**).This allowed fabrication of active films of **18b** in a polymeric matrix which were used as temperature sensors and chemosensors.

Triazolyl complexes **19** were reported by Swager and co-workers[76] and showed columnar mesophases whose stabilisation was attributed to significant Pt-Pt interactions. This is significant as in these molecules there is a single alkyl chain. The complexes exhibited solid-state phosphorescence as well as distinct colour and luminescence changes upon heating or grinding, which can be explained by the flexibility of the intermolecular Pt···Pt interactions.

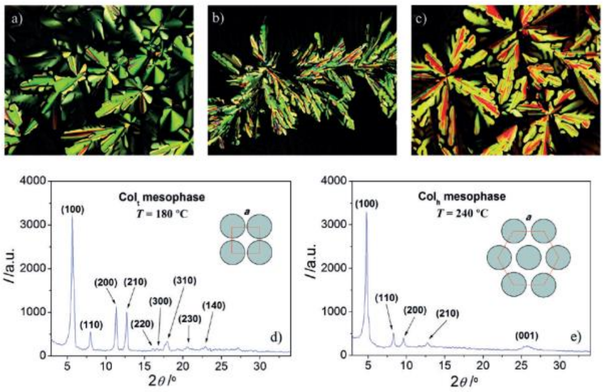


Figure 15. Characterisation of the liquid-crystalline phases of **18b**: polarised light optical microphotographs of the Col$_h$ mesophases observed on cooling process: (a) **18b** (*n* = 10) at 244 ºC and (b,c) 18b (*n* = 12) at 244 ºC at 348 and 306 ºC, respectively. Powder X-Ray diffraction pattern of **18b** (*n* = 4) at 244 ºC at (d) 180 ºC and (e) 240 ºC. Adapted from ref. 75, copyright 2016, Wiley-VCH.

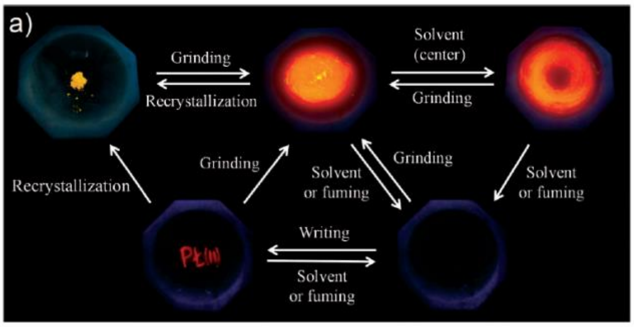


Figure 16. Reversible mechanochromic behavior of complex **18b** (n =4). The images were obtained under UV radiation (λ_{exc}=365 nm). Adapted from ref. 75, copyright 2016, Wiley-VCH.

To date, luminescent metallomesogens based on cyclometallated platinum complexes with bidentate N^N ligand is rare, but their photophysical properties are very charming, such as mechanochromic response and chemosensors. On the other side of the coin, the square-planar complexes comprised of two bidentate ligands, Pt(N^N)$_2$, are usually unstable with respect to a D_{2d} distortion, which is facile to form a tetrahedral conformation because of a twisting of the plane of one ligand relative to that of the other. Therefore, such distortion can facilitate non-radiative decay, leading to low emission efficiency.

Pt complexes with terdentate N^C^N ligand

Theoretical analysis of complexes of the general type [Pt(N^C^N)X] show that they have a high degree of rigidity, with little geometrical reorganisation in the excited state.[77] Such rigidity supports the formation of liquid crystal mesophases and can lead to enhancement of the emission efficiency. Thus, there are studies that show many [Pt(N^C^N)X] complexes (*e.g.* X = Cl)with exceptionally high luminescence quantum yields of up to 0.85 in solution at room temperature.[78] To this end, Kozhevnikov *et al.* designed platinum-based, luminescent metallomesogens **20-23** (**Figure 17**) based on NCN ligands.[79,80] Most of the complexes reported contained a 3,4,5-trialkoxyphenyl fragment, some also with a fused cyclopentylene ring, which was found to affect the mesophase shown and the mesophase stability so that complex **20** showed a Col$_r$ phase, while **21** showed a Col$_h$ phase with a higher clearing point.[79] The complexes had relatively low emission efficiencies (0.07 and 0.12, respectively), but an interesting observation was that the emission wavelength for complexes **20** depended on thermal and mechanical history (**Figure 18**). Thus, fast cooling led to red emission from an MMLCT state in an excimer, while slow cooling led to orange emission from a monomer. Interestingly, preparation of spin-coated films led to the excimer-like red emission, but when heated to 120 °C, the excimer was disrupted and the orange-emitting monomer state was formed. Mechanical disturbance of the monomer then led back to the excimer revealing a read-write process.

In order to further explore the structure-property relationship, the same group introduced fluorines into the central phenyl ring (**22**) and then by using trialkoxybenzoyl esters to introduce the terminal chains (**23**).[80] Although they are analogous structurally with **20** and **21**, both the mesophase and emission properties were different. Thus, complex **22** showed a mesophase that had a monoclinic space group in the lower-temperature phase while a *P*6/*mm* lattice was observed in the higher-temperature phase. For the mesophase in complex **23**, it was possible to index the phase precisely as the rhombohedral *R*3*m* (**Figure 19**). Both complexes **22** and **23** were

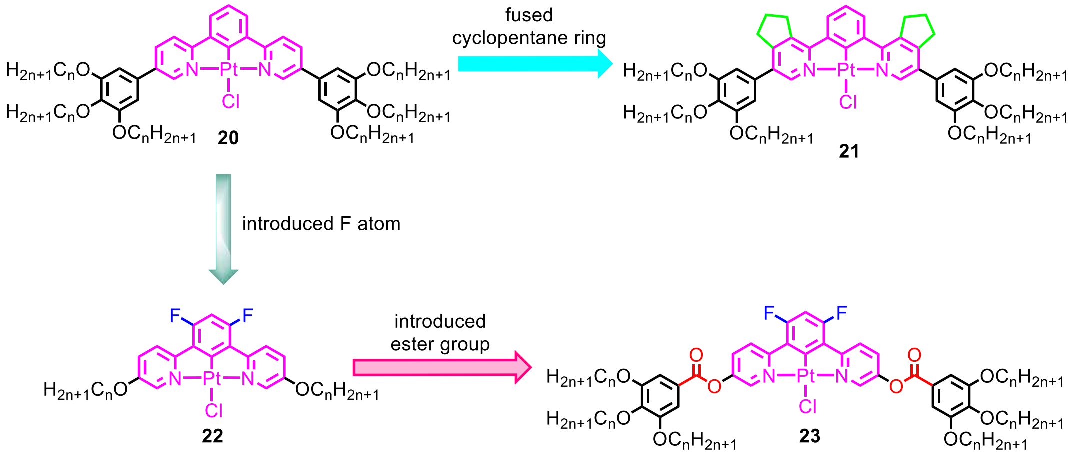


Figure 17. Chemical structure of **20-23** (**20**: n = 4, 6, 8, 10, 12; **21**: n = 10 and 12; **22** and **23**: n =16). Adapted from ref. 79 (**20** and **21**), copyright 2008, Wiley-VCH. Adapted from ref. 80 (**22** and **23**), copyright 2015, Royal Society of Chemistry.

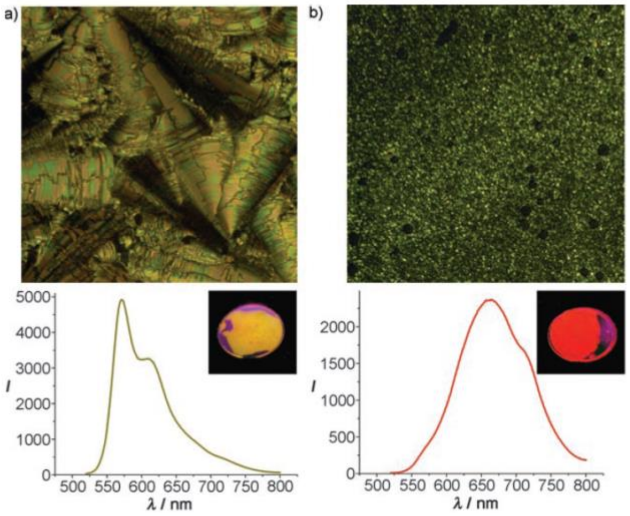


Figure 18. **20** (n = 6) at room temperature, Top: Photomicrographs (taken between crossed polarisers), Bottom: emission spectra ($\lambda_{excitation}$=420 nm.), Inset: real samples of pure films sandwiched between glass slides; a) fast cooled from the LC phase after the texture is fully developed, b) fast cooled direct from the isotropic phase. Adapted from ref. 79, copyright 2008, Wiley-VCH.

intensely phosphorescence (lifetime *ca* 1 *μs*) in solution (Φ_{lum}: **22**: 0.54; **23**: 0.72) and in the solid state, although neither showed any temperature-dependent variation in emission properties. Complex **23** (479 nm) showed a blue-shifted emission spectrum when compared to complex **22** (497 nm) attributed to the alkoxy groups directly appended at the pyridyl 5-positions in **22**, which are strongly electron-donating and have a greater destabilising influence on the HOMO rather than the LUMO leading to a lower excited state energy.

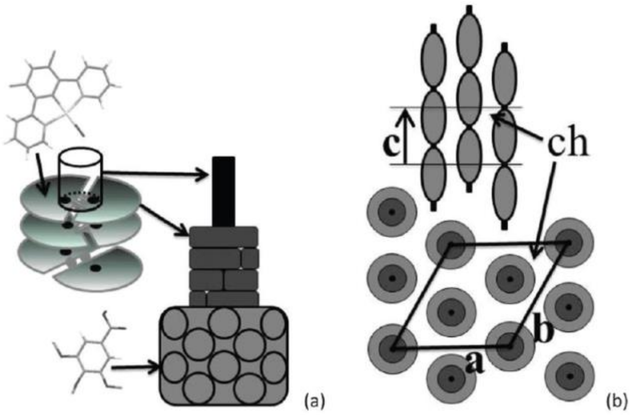


Figure 19. Schematic view of the packing in the three-dimensional mesophase of **23**: (a) core of columns constituted by the assembly of two complexes stacks (dark grey) with Pt-containing zones in the centre (black); shell of gallate fragments (light grey); peripheral chains (ch) not represented; (b) columns with disruption zones arranged in a R3*m* lattice (hexagonal axes). Adapted from ref. 80, copyright 2015, Royal Society of Chemistry.

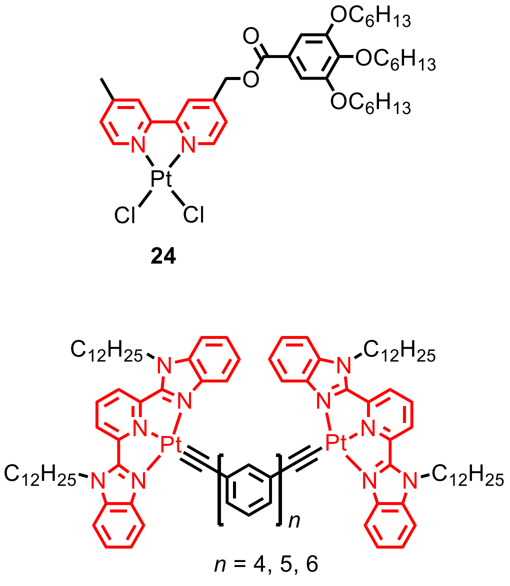


Figure 20. Chemical structure of **24** and **25**. Adapted from ref. 81 (**24**), copyright 2011, Wiley-VCH. Adapted from ref. 82 (**25**), copyright 2017, American Chemical Society.

Eventually, it has to point out that a series of platinum complex containing bipyridine/terpyridine/N^C^N/or N^C^N terdentate ligand showed outstanding both self-assemble and luminescence property reported by Yam and co-workers.[81,82] For example, complex **24** (**Figure 20**) bearing bipyridine unit was shown to be capable of forming metallogels in organic solvents (decalin).[81] Complex **24** displayed a lamellar liquid crystal behaviour in the range of 50°C□170°C. However, very weak emission (550 nm) was detected in solution for complex **24**. Recently, ’the same group reported a series of dinuclear alkynylplatinum (II) metallofoldamers containing 2,6-bis(*N*-dodecylbenzimidazole-2’-yl)pyridine pincer ligand (**25**) which exhibited gelation/self-assembly behaviour *via* noncovalent Pt…Pt and π-π stacking interactions.[82] In this research, the effect of the chain lengths of the complexes on the gelation behaviour, conformations and morphologies have been investigated. These platinum complexes focused on the relationship between Pt-Pt/π-π interaction and luminescence property, which could bring some novel strategies into the platinum-based metallomesogens.

Despite the popularity of cyclometallated platinum complex in the field of liquid crystalline OLED material, they still present several issues such as: tend to aggregate in concentrated solution and solid state which can lead to emission quenching; the absence of detailed study of photophysical properties in the liquid crystal state and good examples of polarised emission; iii) liquid crystal transition temperatures, which can be rather. As such, there remains much potential for the further development of platinum-based luminescent metallomesogens.

3. Iridium complex-based luminescent metallomesogens

By far the most widely studied phosphorescent materials for OLEDs applications are cyclometallated complexes of iridium(III) due to their high stability, emission efficiency both in solution and neat film, and short triplet state lifetime.[48,83-86] As this is a well-studied material that has been used in commercial mixtures, the design and preparation of derivatives with liquid-crystalline properties is of great potential interest. However, there is still a significant challenge in that the octahedral geometry is not conducive to the formation of the anisotropic materials necessary for liquid crystal formation. Consequently, rather few iridium-based phosphorescent metallomesogens have been reported to date.[87-93]

Neutral iridium complex based metallomesogens

In considering the popular chromophoric unit of bis(2-phenylpyridine)iridium, Santoro *et al.* demonstrated iridium-based metallomesogens by modification of the cyclometalating ligand.[88] Thus, as shown in Figure **21**, several flexible chains were introduced into the periphery of a rigid 2,5-diphenylpyridine ligand. Complex **26** possessed both lamellar and columnar rectangular phases with an emission maximum at 580 nm, although it has a very low emission efficiency (Φ_{lum} = 0.5%) and proved unstable over time. Conversely, use of a hexacatenar 2-phenylpyridine as a cyclometalating ligand and acetylacetonate as the ancillary ligand gave complex **27** with a Col$_h$ phase between 31 and 66 °C, and a luminescence quantum yield, Φ_{lum} of 9.1% at 582 nm. An interesting observation was that a precursor di-*μ*-chloro dimer (**28**) also proved to be liquid crystalline and with weak luminescence. This work clearly revealed that the mesogenic property was a function of the number and disposition of terminal alkoxy chains on the cyclometalating ligand. To the best of our knowledge, this is the first example of a liquid crystalline in the neutral heteroleptic cyclometallated iridium complex, which paves a novel strategy for design luminescent metallomesogens.

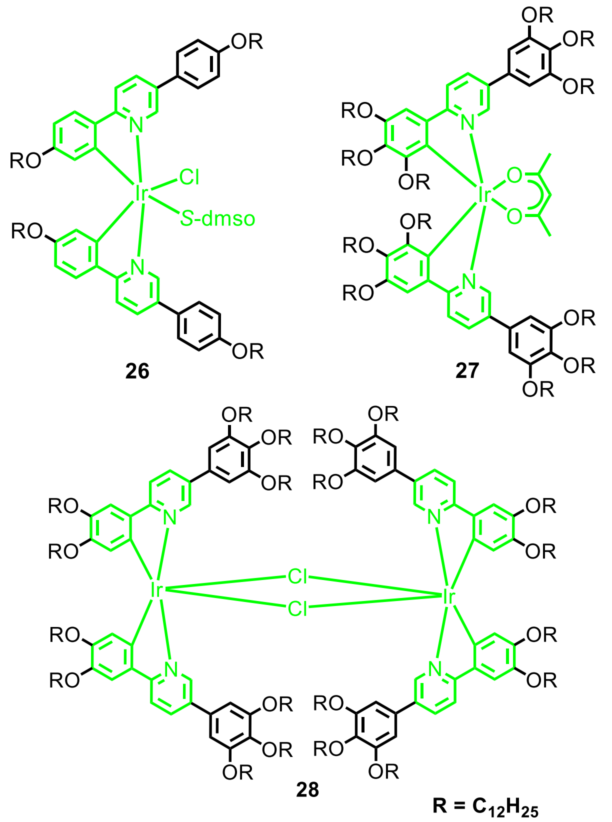


Figure 21. Chemical structure of **26-28**. Adapted from ref. 82, copyright 2011, American Chemical Society.

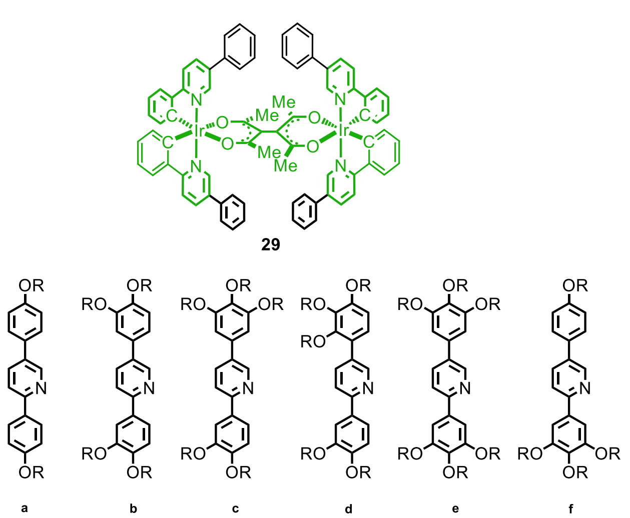


Figure 22 *Meso* form (Δ, Λ) of phosphorescent, liquid-crystalline, dinuclear iridium(III) complexes – peripheral alkoxy chains removed for clarity; 2,5-phenylpyridine ligands used in the study (R = $C_{12}H_{25}$–). (Needs copyright permission). Adapted from ref. 89, copyright 2012, Wiley-VCH.

Prokhorov *et al.* then reported[89] related dimeric iridium(III) complexes (**29**, **Figure 22**) in which the dinucleating ligand was a dimeric ‘back-to-back’ acac ligand – 1,1,2,2-tetraacetylethane (tae) – which had been reported previously by Ma *et al.* for the preparation of dinuclear platinum(II) emitters.[94] The dimers formed as *meso* and racemic variants which, in the case of complexes prepared with ligands **a** and **d**, were separable: the two forms of the complex with **d** had different liquid crystal transition temperatures, although the nature of the isomer did not affect emission quantum yields. Complexes of ligands **a** and **c** were not liquid crystals, but the others were, all showing Col$_h$ phases with emission efficiencies between 38 and 58%.

Using the tae ligand, it was also possible to realise mixed iridium(III)/platinum(II) heterodimers. None of them was a liquid crystal and at room temperature, Pt-to-Ir energy transfer les to observable emission only from the latter luminophore, although emission from both metal-based units was observed at 77 K.

Recently, Wang *et al*. introduced the use of acac ligands that had been modified with a mesogenic unit based on a 4-alkylcyclohexyldifluorobiphenyl (**Figure 23**), which led to the formation of a series of blue and green phosphorescent, liquid-crystalline iridium(III) complexes (**30-35**) with high emission efficiency.[90] In these complexes, the number of mesogenic units attached to the acac had a negligible effect on the physical properties. and all complexes except the 2-(naphthalen-1-yl)pyridine-containing complexes (**32** and **35**) showed a SmA phase (**Figure 24**). All complexes displayed strong phosphorescence in solution and in the solid state ($\mathit{\Phi}_{\mathrm{lum}}$: 0.1-0.6, lifetime: ca. 1□2 μs) from the sky-blue to the red region (**Figure 24**). Interestingly, very high hole mobilities – up to 0.004 cm^2 V^{-1}s^{-1} – were achieved for the annealed film of iridium-based metallomesogens, which is among the highest hole mobilities known for iridium complexes.

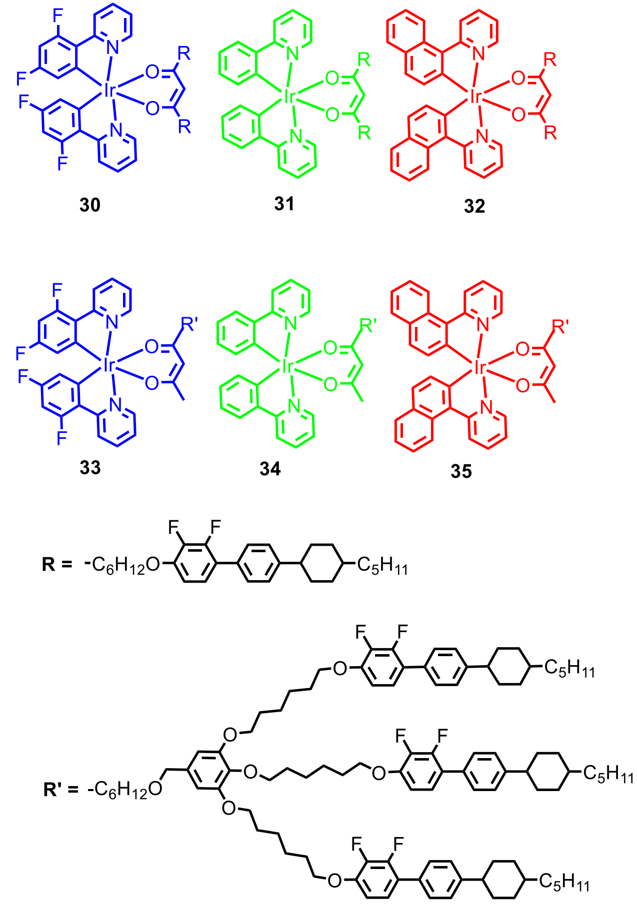


Figure 23. Chemical structure of **30**-**35**. Adapted from ref. 90, copyright 2016, Wiley-VCH.

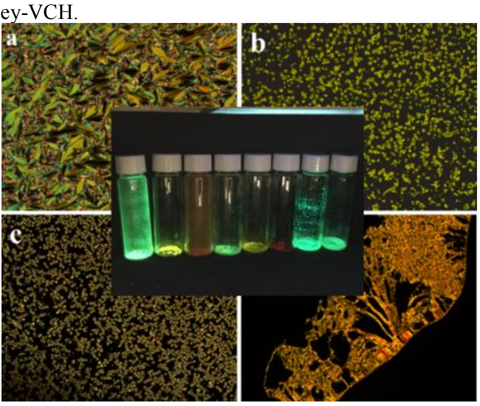


Figure 24. POM images on cooling (a: 31; b: 30; c: 33; d: 34) and the emission images under UV light at room temperature. Adapted from ref. 90, copyright 2016, Wiley-VCH.

Ionic iridium complex based metallomesogens

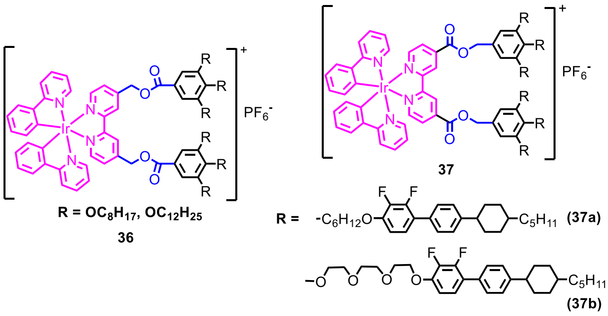


Figure 25. Chemical structure of **36** and **37**. Adapted from ref. 91 and 92 (**36**), copyright 2010 and 2012, Wiley-VCH (ref. 91) and Royal Society of Chemistry (ref. 92). Adapted from ref. 93 (**37**), copyright 2018, Royal Society of Chemistry.

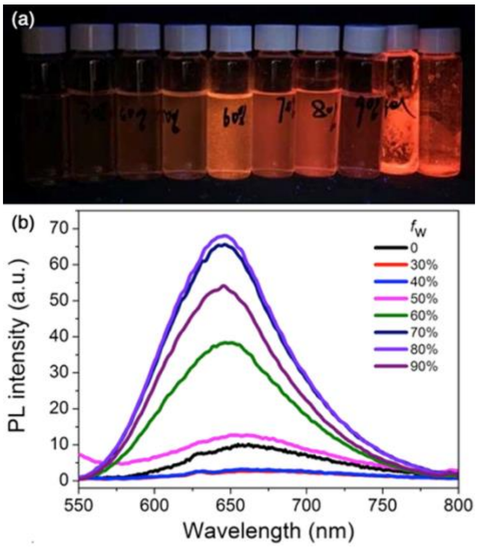


Figure 26. (a) Photograph of **37a** (*R* is alkyl chain) 10^{-5} M in THF-water mixtures with different vol% values (from left to right (f_w): 0 %, 30 %, 40 %, 50 %, 60 %, 70 %, 80 %, 90 % and solid) taken under UV illumination at 365 nm; (b) Emission spectra of **37a** in THF-water mixtures. Adapted from ref. 93, copyright 2018, Royal Society of Chemistry.

The first mesomorphic, luminescent iridium-based complexes were reported in 2010 by Szerb *et al.*[91,92] The strategy used a bis(2-phenylpyridinato)iridium skeleton as the emission core, with liquid crystallinity induced with a hexacatenar 2,2'-bipyridine (**36**) (**Figure 25**). As expected, cationic complex **36** displayed a columnar mesophase obtained only when the sample is cooled rapidly (> 10 °C min^{-1}) and different phosphorescence emission were detected for complex **36** in different state. Thus, a progressive blue shift of the emission maximum with a strong enhancement of the emission efficiency was observed on changing from solution ($\mathit{\Phi}_{\mathrm{lum}}$ = 0.12) to the liquid-crystalline state ($\mathit{\Phi}_{\mathrm{lum}}$ = 0.39) and finally to the crystalline solid ($\mathit{\Phi}_{\mathrm{lum}}$ = 0.48). Additionally, **36** experienced a reversible colour change under surface stress and heating procedures.[92]

Very recently, Wu *et al.* reported two ionic iridium complexes with different aliphatic chains substituents attached once more to a 2,2'-bipyridine (**Figure 25**).[93] Complex **37** showed a lamellar mesophase with deep-red emission being observed in solution and in the solid state. Unexpectedly however, complex **37a** presented obvious aggregation-induced

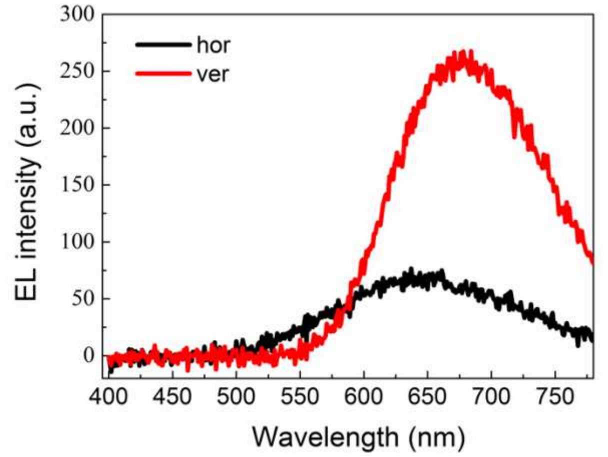


Figure 27. Polarised EL spectra of **37a** in device. Adapted from ref. 93, copyright 2018, Royal Society of Chemistry.

emission (AIE) behaviour in THF-water mixture (**Figure 26**). Non-doped polarised organic light-emitting diodes (OLEDs) employing complex **37a** as emitter were fabricated by rubbing and annealing procedures and a linearly polarised electroluminescence with a dichroic ratio of 4 was achieved (**Figure 27**), which is the highest ratio reported for metallomesogenic, phosphorescent OLEDs. Clearly, the choice of linker between the core complex and mesogenic pendent groups is key to achieve distinctive polarisation of electroluminescence and aggregation induced emission (AIE) as no similar behaviour was found for **37b**. The significance of this research suggested that iridium-based phosphorescent OLEDs could be able to efficiently produce polarised electroluminescence.

5. CONCLUSIONS AND OUTLOOK

Luminescent liquid crystals provide an entry into new classes of liquid crystal materials due to their combination of charming optical and liquid crystal properties. These novel materials have a potential application in the field of display backlighting in replacing the solid-state LEDs used currently. Over the past few decades, various strategies were therefore developed to construct luminescent liquid crystals containing small molecules, polymers, oligomers and metal centres However, metal-containing, luminescent liquid crystals still lag somewhat behind.

To this end, the development of luminescent metallomesogens is advancing rapidly and the prospect of theoretical emission efficiencies of unity where there is efficient spin-orbit coupling is an enticing prospect. Carefully molecular design has then led to remarkable progresses in the creation of various luminescent metallomesogens bearing Au, Pd, Pt, Ir, Cu, Ag and lanthanide elements, but many of these materials lack the efficient emission in the liquid crystal state and solid state. Nonetheless, there has been a good measure of progress in compounds based on complexes with a d^8 or d^{10} configuration and, while the design of octahedral d^6 complexes presents a much greater challenge, some impressive solution emission efficiencies and hole mobilities have been reported.

However, while the concept of luminescent metallomesogens is now quite well established, challenges remain if the materials are to have a serious chance of being applied. For example, there needs to be great control over both phase type and transition temperatures, which comes from a profound understanding of liquid crystals and, occasionally, a little bit of luck. AIE is a potentially useful effect and so the possibility of engineering in this property requires investigation. Similarly, polarised triplet emission could be of significant value and understanding how this may be controlled, not least in high coordination number complexes, is challenging. Thus, there is still some way to go before luminescent metallomesogens can take off for practical applications.

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Notes

The authors declare no competing financial interest

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Professor Duncan W. Bruce, obtained his BSc (1981) and PhD (1985, supervisor David Cole-Hamilton) at the University of Liverpool before taking up a series of appointments at the University of Sheffield (Temporary Lecturer, Royal Society Warren Research Fellow, Lecturer and Senior Lecturer). In 1995, he was appointed full professor of inorganic chemistry at the University of Exeter and then moved to the University of York as Professor of Materials Chemistry in 2005, where he is currently Head of Department. He has held visiting position at a number of universities and his work has been recognised by various awards, including the Corday Morgan and Tilden Prizes of the Royal Society of Chemistry.

Professor Weiguo Zhu, born in 1964, obtained his PhD in 2000 from College of Chemistry at Sichuan University under supervision of Professor Minggui Xie. From 2000 to 2002, he was a Postdoc researcher associated with Professor Yong Cao at South China University of Technology. Since he returned to Xiangtan University (XTU) in 2002, he has been a full Professor in XTU. From 2006 to 2007, he was a visiting scholar in The University of Sheffield associate with Dr Ahmed Iraqi. In 2016, he moved to Changzhou University. His current research interests include design, synthesis and application of organic and polymeric optoelectronic materials in organic light-emitting diodes and organic solar cells.

Dr Yafei Wang, born in 1983, received his PhD degree from the College of Chemistry, Xiangtan University, in 2011. Since then, he has been working at this University. From 2012 to 2013, he was a Postdoc research associate with Professor Klaus Müllen at Max-Planck Institute for Polymer Research. In 2014, He moved to the University of Birmingham with Dr Etienne Baranoff as a Marie Curie Fellow. In 2014, he became an associate Professor at the College of Chemistry, Xiangtan University. In 2016, he promoted a full professor at the School of Materials Science & Engineering, Changzhou University. His research interest mainly focuses on the design and synthesis of novel organic luminescent materials for OLEDs.

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