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Recent progress in luminescent liquid crystals materials: design, properties and application for linearly polarised emission

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ABSTRACT: Luminescent liquid crystals (LCs) materials have attracted significant interests for organic optoelectronic applications, especially for linearly polarised emission, becaused of their combination of ordered alignment and luminescence property. Since the first polarised organic light-emitting diodes (OLEDs) demonstration in 1995, remarkable progress has been done with polarised electroluminescence because of continuous advances with the design of suitable LC materials. In this *Review*, we summarize luminescent LC materials with representative examples based on fluorescent materials, phosphorescent materials, and lanthanide complexes. The structure-property relationships for polarised emission and, when available, electroluminescence of these materials are presented and discussed, with a focus on phosphorescent metallomesogens. We also present the rational behind the design and development of luminescent LCs materials for high efficiency polarised OLEDs, along with the challenges ahead to achieve efficient devices.

1 Introduction

Because of their unique combination of optophysical and anisotropic fluids properties, luminescent liquid crystals (LCs) are fascinating materials gaining tremendous interest for optoelectronic applications.[1,2] In condensed phases they can organize with crystal-like order leading for example to attractive charge transport properties, while they retain fluidity allowing for self-healing capabilities and dynamic properties. In addition, their anisotropic organization is particularly engaging for applications involving polarised light.

With this in mind, polarised emission based on luminescent LCs has attracted a great deal of interest from both academics and industrials because of possible applications in optoelectronics, such as the light source for liquid crystal displays (LCDs)[3-5] and three-dimensional (3D) imaging systems,[6-8] as well as in the medical field, *e.g.* to relieve chronic pain by near-infrared linearly polarised irradiations.[7] However, to date, the polarisation of light is achieved with a polariser in combination with a non-polarised light source, which wastes ~50% of the produced light by absorption (Figure 1 for LCD as representative example). The direct production of polarised light would result in devices with improved energy efficiency, which is technologically (lower energy consumption of portable
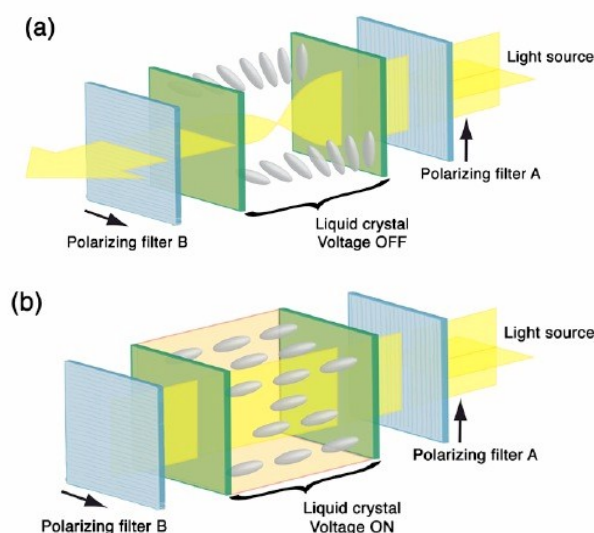

Figure 1. Working principle of LCD: a non-polarised light is polarised vertically by polariser A, passes through the liquid-crystal layer, finally arrives at polariser B. When voltage is OFF, (a), the liquid crystals twist the light, which can pass through B (cell ON). When voltage is ON, (b), the liquid crystals doesn't twist the light, which is absorbed by B (cell OFF). A linearly polarised light source will make polariser A unnecessary.

display devices for smaller batteries and longer autonomy) and economically (energy savings) important.

Since the introduction of the heterojunction by Tang and Van Slyke,[10] organic light emitting diodes (OLEDs) have continuously progressed and are considered to be the "next big thing" in display and lighting applications.[11-16] Their key advantages are high brightness, wide viewing angle, low cost, lighter form factor, and active emission. Therefore, OLEDs are also a great opportunity for the direct production of polarised light by electroluminescence (EL). The first example of linearly

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polarised EL was reported in 1995 by Dyreklev *et al.* using an aligned polymer film.[17] The polarised ratio (or dichroic ratio, R = $E_{\perp}/E_{\parallel}$, the ratio between the brightness of perpendicular and parallel linearly polarised EL emissions) was only 2.4 but demonstrated the principle that OLEDs indeed offer the possibility of a directly polarised light source (polarised OLEDs).[18,19] So far, linearly polarised emission and circular polarised emission have both been successfully proven in OLEDs.[20-22] However, important challenges remain for the linearly polarised OLEDs, which is the focus of this review, to become a commercial product as $R > 40$ is necessary for practical applications in addition to high efficiencies and stability of the device.

Owing to the combination of the optoelectronic characteristics of luminescent materials with the unique properties of anisotropic fluids that can be easily aligned, luminescent LC materials are a particularly enticing family of material for polarised OLEDs.[21-33] Herein we review luminescent LC materials and discuss their LC and emission properties in the context of linearly polarised electroluminescence. First we briefly introduce the main techniques to prepare aligned films, as it is a key requirement for polarised emission. Then, in section 3, we present fluorescent LC materials based on oligomers and small molecules, such as oligofluorenes, oligothiophenes, and diazole derivatives, and highlight important achievements for polarised OLEDs obtained with such materials and, briefly, with polymer fluorescent LC materials. This will set the context of the field as the best polarised OLEDs so far have been obtained with fluorescent materials. In section 4, phosphorescent LC materials based on platinum complexes are discussed, including the design rules and structure-property relationships as well as their potential application for polarised OLEDs. Although these materials have rarely been used for polarised OLEDs, their ability to harvest both singlet and triplets excitons is very attractive for the development of highly efficient polarised electroluminescence. We also highlight typical luminescent LC materials based on lanthanide complexes. Finally, we conclude the *review* and summarize rational concepts for the design and development of luminescent LC materials for high efficiency polarised emission, along with challenges and perspectives of the field.

2 Methods to prepare aligned films for polarised emission

The alignment of the emissive layer in OLEDs plays a critical role to achieve polarised light with a high dichroic ratio. Various methods have been developed to prepare the aligned emitting layer and some excellent reviews about the methods of preparation of aligned film have been published.[16,17]

Originally, a polymer aligned film was achieved by the mechanically stretch method in 1995.[15] The method of mechanically stretch usually draws the films at a certain temperature, e.g. LC temperature. The important parameter is the drawing ratio, which is defined as the ratio between the

length of the film after and before drawing.[34,35] However, this method not only has an intricate film transfer process onto the substrate, but also, to a great extent, depend on the ability of materials to melt and on drawing rates.
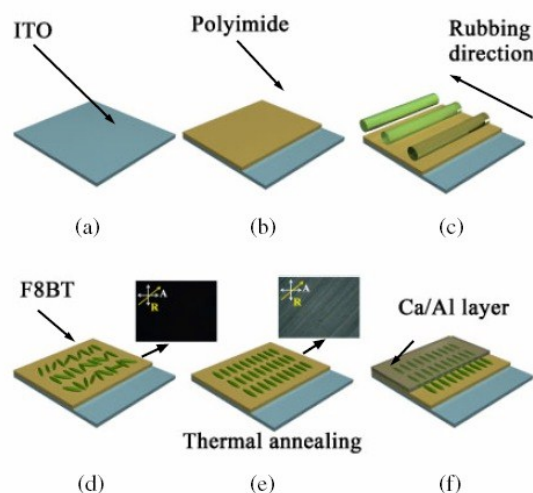

Figure 2. Schematic diagrams of the fabrication of polarised OLED: (a) ITO layer as anode, (b) PI layer as alignment layer, (c) rubbing process, (d) spin coating of the emissive layer (here F8BT), (e) thermal annealing process, and (f) Ca/Al deposition as cathode. Adapted with permission from ref 38. Copyright 2014 The Japan Society of Applied Physics.

Mechanical friction is widely applied to prepare aligned film by rubbing the LC film with cloth or a Teflon rod[36,37] or depositing the LC materials onto a rubbed aligned substrate, *e.g.* polyimide (PI) (Figure 2).[38] In this method, high effective polarised emission can be achieved. Recently, another approach of friction-transfer techniques to aligned films was developed *via* squeezing and drawing the film on a clean surface of metal or glass kept at a controlled temperature in a nitrogen atmosphere.[39] This technique afforded a method for preparing an oriented film without an underlying alignment substrate. To the best of our knowledge, the polarised EL with the highest R up to 53 was obtained via this friction-transfer method.[39]

Langmuir-Blodgett (LB) deposition technique is also popular for achieving alignment film.[40,41] Although LB deposition can precisely control the thickness of films and provides high degree of molecular order, the major drawbacks of the LB technique are the unsatisfactory polarised ratio and small-scale application. Only few polarised OLEDs were explored by this method.

The self-organization properties of liquid-crystal can be effectively harnessed for the preparation of aligned films.[42,43] This method depends on the chemical structure of the molecule and therefore would be considered to be a chemical alignment method. Furthermore, the orientation of LC materials can be improved when deposited onto a rubbed (pre-aligned) under-layer.
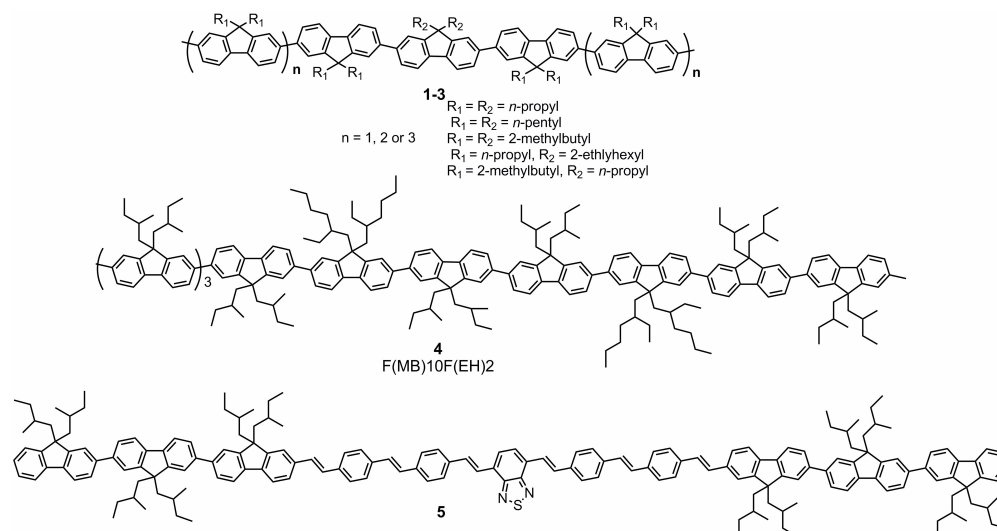
Figure 3. Chemical structures of reported oligofluorenes-based luminescent LC materials.

3 Fluorescent liquid crystals

Over the past few years, small molecule, dendrimers and polymer fluorescent materials have made significant progress for their application in OLEDs.[44-47] In order to enhance the emission efficiency of devices, some investigations have focused on improving the molecular organization and charge mobilities of luminescent materials. On this ground, numerous luminescent LC materials both as small molecules and as polymers have been explored.[48,49,21] Combining the rational design of LC and luminescent materials, the prevailing strategies to achieve luminescent LC materials are to introduce mesogenic moieties onto a rigid fluorescent core. In this section we focus on fluorene, thiophene, and 1,3,4-oxadiazole (OXD) derivatives as representative examples because of their excellent charge transport and favorable self-organization properties. As the state-of-the-art of polymers-based polarised emission has been thoroughly summarized in recent reviews and books,[16,17,65,67] we will only briefly mention these materials.

3.1. Oligofluorene-based luminescent LC materials

Oligofluorenes are one of the most popular families of LC materials due to their rigid quasi-planar structure, high luminescence efficiency, good thermal stability, and suitable charge carrier properties.[50-52] However, low glass transition temperatures (T_g) limit their use in aligned film for polarised emission. To preserve the molecular alignment in the solid state, Chen and coworkers have prepared a series of nematic oligofluorenes with high glass transition temperature by modifying the number of fluorene units and the pendant chains. These oligofluorenes presented efficient polarised emission from blue to red color. As depicted in Figure 3, the first examples of oligofluorenes with a nematic phase, **1-4**, exhibited good thermal stability with T_g up to 150 °C and clearing point (T_c) over 375 °C. The author showed that higher glass transition

temperatures could be obtained by increasing the number of core units and branched aliphatic pendent chains. Additionally, the T_c increased with the number of fluorene units.[53] After annealing at a temperature above T_g for 15-30 min followed by cooling to RT, glassy nematic films were achieved with the uniaxial molecular alignment of the liquid crystalline state. All these glassy nematic films (**1-4**) displayed intense blue emission at about 420 nm with photoluminescence quantum yields (Φ_{lum}) of 43-60%. Polarised absorption and emission with R between 7 and 17 were measured for **1-4** on a PI alignment film. The dichroic ratio gradually increased with increasing the length of the molecule.
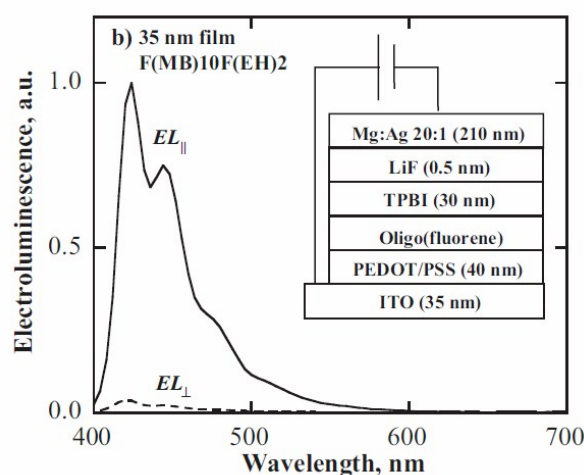
Figure 4. Device structure and polarised EL spectra for an OLED containing a 35 nm thick F(MB)10F(EH)2 (**4**) film at a current density of 20 mA cm^{-2}. Adapted with permission from ref 54. Copyright 2003 Wiley.

Subsequently, polarised OLEDs with the architecture ITO/PEDOT:PSS/oligofluorenes/TPBI/LiF/Mg/Al (Figure 4) were fabricated based on oligofluorenes F(MB)5 (**1**), F(Pr)5F(MB)2 (**2**), and F(MB)10F(EH)2 (**4**).[54] The aligned

emission layer was achieved via spin-casting the oligofluorenes onto a PEDOT/PSS alignment film followed by thermal annealing. The best performing devices were based on F(MB)10F(EH)2 (**4**), which is the oligomer with the highest aspect ratio, and displayed a maximum dichroic ratio $R = 31.2$ at 448 nm and current efficiency up to 1.10 cd A^{-1} (Figure 4). As for the PL, the EL dichroic ratio was also found to increase with the length of the molecule due to the higher degree of uniaxial molecular alignment.

Concurrently, another series of oligofluorene-based thermotropic nematic materials (**OF1-8**) were synthesized by inserting donor or acceptor units (quaterthiophene, benzothiadiazole and benzonitrile, etc.) into derivatives of **1-4**, which modulated the emission from blue to red.[55] All these novel oligomers showed a glass transition temperature between 97 and 127 °C and an isotropisation temperature above 300 °C. The aligned films of **OF1-8** were prepared following similar procedures to aligned films of **1-4**. Linearly polarised emissions with a polarised ratio between 9.4 and 13.7 were obtained. The polarised OLEDs, comprising the aligned films of **OF-1** and **OF-2**, exhibited nearly yellowish green and pure red emission with $R = 18.0$ and 14.4, as well as maximum current efficiency of 5.91 cd A^{-1} and 0.51 cd A^{-1}, respectively.

The first polarised white OLEDs were reported in 2004 by Chen *et al*.[56] The design relied on controlling the energy transfer between an energy acceptor (**5**, red emission) doped into a liquid crystalline energy donor (**F(Pr)5F(MB)2**, blue emission). The donor-acceptor emissive film was aligned with an aligned PEDOT:PSS underlayer and was used as the emissive layer for polarised OLEDs. The Förster energy transfer between donor and acceptor groups resulted in polarised white EL with $R = 16.6$ (integrated polarised ratio) and maximum current efficiency up to 4.5 cd A^{-1} (Figure 5). This result demonstrated a simple and attractive design strategy for polarised white OLEDs.
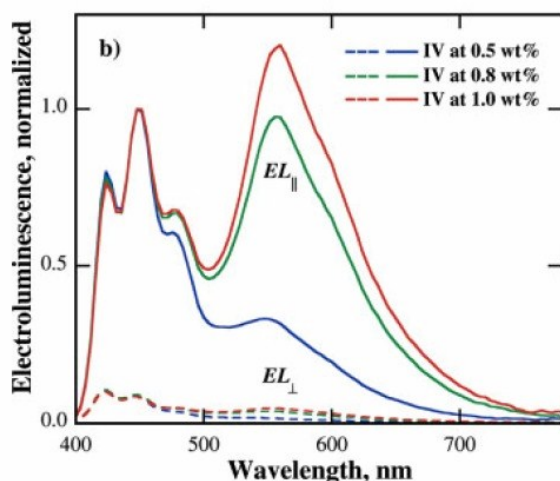
Based on the above results, it is noted that fluorene derivatives are favoured for achieving polarised emission. However, these fluorene-based luminescent LC molecules were almost linearly shaped framework. On the other hand, these fluorene oligomers did show neither good charge mobility nor high efficiency in device. Therefore, high efficiency and good charge mobility still remain a big challenge for fluorene-based polarised devices. To this end, novel luminescent LC molecules with good charge mobility need to be developed and combined with the preparation of aligned film of high quality.
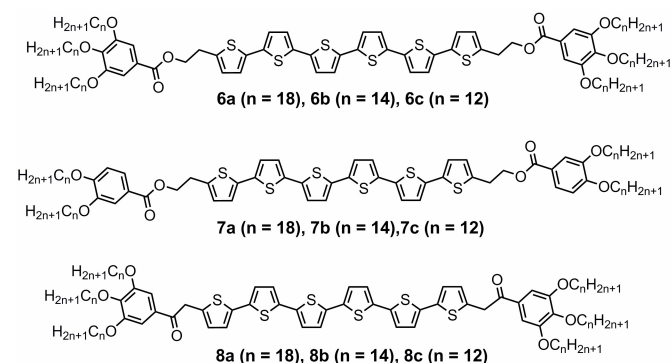

Figure 6. Chemical structures of reported oligothiophenes-based luminescent LC materials.

3.2. Oligothiophene-based luminescent LC materials

Thiophene-based materials are particularly attractive for liquid crystalline and high charge mobility compounds. Indeed thiophene derivatives usually possess a low melting point because of reduced packing efficiency of the molecules compared to the corresponding phenyl unit. Secondly, the thiophene system has a strong lateral dipole, which could favour negative dielectric anisotropy. Finally, the interaction between sulfur atoms (intra-/intermolecular) can have a strong effect on the structure of the mesophases and polarisation of emitted light.[57-59] Yasuda *et al*. reported a series of polycatenar oligothiophenes **6-8** (Figure 6) displaying various LC structures (smectic, columnar, and micellar cubic phases), which depend on the number and length of the attached alkoxy chains.[60] Compounds **6a-c** displayed higher isotropisation temperatures than **8a-c** with the same chain length because the oxyethylene linker in **6a-c** leads to effective space-filling and greater core-core interactions. A smectic LC phase was observed for tetracatenars **7a-c** owing to the calamitic shape and lower number of peripheral alkoxy chains. Both the peripheral flexible chains and the linking units can be used to finely tune the intermolecular interactions and mesomorphic properties. Additionally, the hole mobilities were up to 0.01 $cm^2 V^{-1} S^{-1}$ due to the ordered structures. The aligned film of **8a** in the columnar phase was obtained and displayed a polarised red emission at 610 nm with R of 11, which is one of the few investigations of polarised emission from columnar mesogens.

Figure 5. Polarised EL spectra for acceptor **5** in donor **F(Pr)5F(MB)2** (host) at the specified doping levels. Adapted with permission from ref 56. Copyright 2003 Wiley.

3.3. OXD-based luminescent LC materials

Fluorescent LC materials containing 1,3,4-oxadiazole (OXD) have been developing rapidly because of their rich mesophases, high emission quantum yield, outstanding electron mobility, and good thermal stability.[61] In view of the influence of molecular shape, number of mesogenic units and flexible chains on mesomorphic property, to date, many OXD-based LC materials with linear-/star-shaped have been reported (Figure 7). Linear molecule **9** simply consisting of phenyl-OXD as the rigid central unit and peripheral hexyloxy chains, showed two smectic phases (S_X and S_A) and one nematic phase (N).[62] High electron mobility of **9** up to 0.8×10^{-3} cm^2 V^{-1} s^{-1} was measured in the S_X mesophase. Homogeneously aligned films were achieved via casting compound **9** onto a rubbed (aligned) nylon-66 film. Highly polarised PL was observed in all LC phases, with the order parameters (*S*) of 0.46, 0.44, and 0.78 in
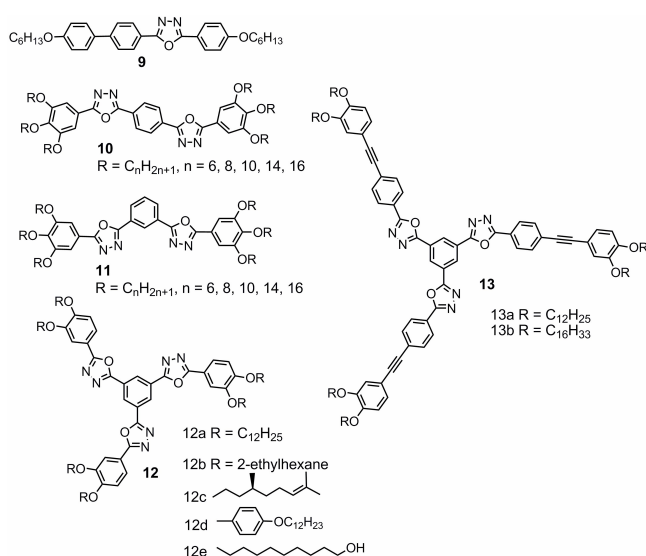

Figure 7. Chemical structures of reported OXD-based luminescent LC materials.

the S_X, S_A, and N phases, respectively. In addition, EL devices with the configuration ITO/CuPc/compound **9**/Alq3/Al were fabricated. The homogeneously aligned film of **9** was obtained on a CuPc film prepared by epitaxial growth. Polarised EL with *S* up to 0.32 was observed from the smectic mesophase. Other linear molecules **10** and **11** incorporating two OXD units exhibited a columnar phase.[63-65] The *meta*-connected compounds **11**[63] showed a lower melting point and broader liquid crystal phase than those of the corresponding *para* substituted compounds **10**[65]. Even though compounds **11** showed an intense blue emission in CH$_2$Cl$_2$ (Φ_{lum} > 73%), the emission in the solid state was not explored. Girotto *et al.* and Kim *et al.* designed a series of star-shaped luminescent LC materials based on 1,3,5-trisubstituted benzenes core bearing three alkyl-functionalized OXD arms (**12**).[66,67] The author demonstrated that the peripheral aliphatic chains played a critical role on the mesomorphic properties in this type of molecules. Star-shaped molecules **12** display strong blue emission both in solution in CHCl$_3$ and as thin films with Φ_{lum} in the region of 0.47-0.63, which makes these star-shaped LC

molecules attractive for application in optoelectronic devices. In order to enhance $\pi-\pi$ intermolecular interaction, Das and coworkers designed two OXD-based star shaped columnar LC molecules (**13**) with alkoxy-substituted phenyl ethynylenes expanding the conjugation.[68] These star-shaped materials showed columnar mesophases and gelating properties. Intense blue emission was detected in solution with the Φ_{lum} of 0.75-0.77. By cooling from the isotropic phase to the LC state, interestingly, a glassy film of **13** with LC order was achieved at room temperature and very stable in air (>one year). This glassy film exhibited a blue emission with Φ_{lum} of 26% and 9% for **13a** and **13b**, respectively.

Although the OXD unit is a promising candidate for luminescent LC materials with high emission efficiency and stable liquid crystalline, the polarised light emission properties of these materials have not yet been studied in details.
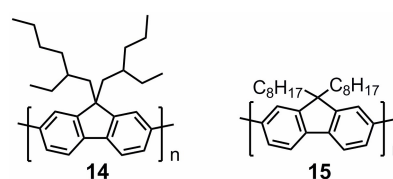

Figure 8. Chemical structures of reported polyfluorenes luminescent LC materials.

3.4. Polymeric Fluorescent LC materials

Compared to the small molecules, a large body of work is available for polymer-based luminescent LC materials. The large amount of literature has been already summarized in several reviews.[16,52,69-71] Herein, two representative fluorene-based luminescent LC materials are shown in Figure 8.

Dyreklev *et al*,[15] reported the first polymer-based polarised EL device using a stretched film of a blend of poly(3-(4-octylphenyl)-2,2′-bithiophene) (PTOPT) and polyethylene (PE) as the aligned emission layer. However, these materials are not mesomorphic and the alignment method is a complicated film transfer process, in which the draw ratio of the stretch film is strongly dependent on the polymer melt. In order to improve the quality of the alignment and polarisation performance of the films, focus has then been on luminescent polymers with LC properties.

Polyfluorenes (PFs) are a particularly attractive family of organic semiconductor materials due to their high emission efficiency OLEDs and possible thermotropic LC properties. In 1997, Grell *et al.* reported poly(dioctylfluorene) (PFO) exhibiting a thermotropic LC phase and prepared the align PFs film on a rubbed PI substrate showing polarised PL with *R* = 10.[72] In order to achieve higher polarisation ratio, the same group synthesized a LC poly(9,9-di(ethylhexyl)fluorene) with branched ethylhexyl alkyl (**14**).[73] The aligned emissive layer was fabricated via spin-coating **14** on a rubbed blend made of PI and ST638 (See abbreviations), followed by thermal annealing at a temperature of 185 °C for 2 h.

Table 1. Liquid crystal and optophysical properties of typical small molecules used for linearly polarised emission.

Compound	Transition [a]	T (°C)	Emission (nm)	Φ_{PL} %	Alignment technique	S_{ab} (λ_{ab}) [g]	Polarisation ratio (R_{PL}) [h]	Polarisation ratio (R_{EL}) [l]	Ref.
1 F(MB)5	Cr-N N-Iso	89 167	415 [c], 448 [c]	54 ± 2	Annealing [e]	0.74 ± 0.01 0.75 [51]	10.8 ± 0.5	11.8 (412) 9.5 (444)	53,54
1 F(MB)4F(Pr)1	Cr-N N-Iso	84 124	410 [b], 440 [b] 420 [c], 448 [c]	47 ± 6	Annealing [e]	0.67 ± 0.01	6.9 ± 0.5	N/A	53
2 F(Pr)5F(MB)2	Cr-N N-Iso	149 366	409 [b], 442 [b] 419 [c], 452 [c]	43 ± 4	Annealing [e]	0.83 ± 0.01 0.80 [51]	14.1 ± 0.2	14.7 (420) 10.5 (448)	53,54
2 F(Pr)5F(EH)2	Cr-N N-Iso	116 319	N/A	56 ± 4	Annealing [e]	0.77 ± 0.01	10.5 ± 0.7	N/A	53
2 F(MB)6F(EH)1	Cr-N N-Iso	100 315	N/A	60 ± 5	Annealing [e]	0.77 ± 0.01	13.1 ± 0.7	N/A	53
3 F(MB)8F(EH)1	Cr-N N-Iso	115 >375	420 [c], 450 [c]	59 ± 4	Annealing [e]	0.81 ± 0.01	13.2 ± 1.5	N/A	53
3 F(MB)7F(EH)2	Cr-N N-Iso	109 >375	420 [c], 451 [c]	54 ± 1	Annealing [e]	0.81 ± 0.01	15.8 ± 0.8	N/A	53
3 F(MB)7F(DMO)2	Cr-N N-Iso	84 273	411 [b], 440 [b] 420 [c], 449 [c]	57 ± 1	Annealing [e]	0.77 ± 0.01	12.2 ± 0.4	N/A	53
4	Cr-N N-Iso	123 >375	422 [c], 448 [c]	49 ± 1	Annealing [e]	0.84 ± 0.01 0.82 [51]	17.2 ± 0.9 20.3 [51]	27.1 (424) 31.2 (448)	53,54
OF-1	Cr-N N-Iso	106 >350	533 [b] 533 [c]	77	Annealing [f]	0.83 (362) 0.87 (430)	12.7 ± 0.8	18.0 ± 0.6 (532)	55
OF-2	Cr-N N-Iso	104 304	635 [b] 643 [c]	68	Annealing [f]	0.77 (374) 0.77 (534)	9.8 ± 0.9	14.4 ± 0.4 (636)	55
OF-3	Cr-N N-Iso	112 342	520 [b], 558 [b] 532 [c], 572 [c]	42	Annealing [f]	0.79 (367)	12.6 (532) 13.3 (572)	N/A	55
OF-5	Cr-N N-Iso	97 >320	461 [b], 493 [b] 479 [c], 512 [c]	82	Annealing [f]	0.82 (427)	9.7 (479) 11.7 (512)	N/A	55
OF-6	Cr-N N-Iso	111 >320	461 [b], 493 [b] 479 [c], 511 [c]	74	Annealing [f]	0.79 (422)	9.4 (479) 11.8 (511)	13.0 ± 0.3 (512)	55
OF-7	Cr-N N-Iso	110 >320	479 [b], 513 [b] 545 [c]	75	Annealing [f]	0.84 (432)	13.7 ± 1.0	N/A	55
5 **(OF-8)**	Cr-N N-Iso	116 >320	576 [b] 632 [c]	47	Annealing [f]	0.79 (400) 0.84 (504)	13.2	N/A	55
5 (1 wt %) **doped into 2**	N/A	N/A	448 [EL] 560 [EL]	N/A	Annealing [f]	N/A	N/A	11.9 (448) 25.6 (560)	56
8a	Cr₁-Cr₂ Cr₂-Col_h Col_h-Iso	85 102 117	574 [b] 615 [c] 625 [d]	N/A	Annealing [e] Mechanical shear force	N/A	11	N/A	60
9	Cr-Sm Sm1-Sm2 Sm2-N N-Iso	314 351 392 444	410 [c]	N/A	Annealing [f]	N/A	0.46 [i] (Sm1) 0.44 [j] (Sm2) 0.78 [k] (N)	0.32 [m] (Sm2)	62

[a] Transition temperatures determined by DSC on heating. Cr: crystalline; N: nematic; Sm: highly ordered smectic; Col_h: hexagonal columnar; Iso: isotropic. [b,c,d] Emission spectra with unpolarised excitation in solution, solid state and liquid crystals phase. [e] Compound coated onto an uniaxially rubbed thin film of a polyimide alignment layer (Nissan SUNEVER). Thermal annealing done in dry argon purged glassware at temperatures 10-20 °C above T_g for 15-30 min. [f] Compound coated onto an uniaxially rubbed PEDOT/PSS film (Baytron P VP AI 4083, Bayer). Thermal annealing was performed in dry argon purged glassware at temperatures 10-20 °C above T_g for 15-30 min. [g] Orientational order parameter, $S_{abs} = (R_{abs} - 1)/(R_{abs} + 2)$. [h,l] Evaluated at the higher-energy emission peak maximum of the two. [i,j,k] The order parameters calculated from the relation of $S_{PL} = (I_{PL//} - I_{PL\perp})/(I_{PL//} + 2I_{PL\perp})$, where $I_{PL//}$ and $I_{PL\perp}$ are the values of the PL intensity parallel and perpendicular to the rubbing direction, respectively. [m] The order parameters calculated from the relation of $S_{EL} = (I_{EL//} - I_{EL\perp})/(I_{EL//} + 2I_{EL\perp})$, where $E_{PL//}$ and $E_{PL\perp}$ are the values of the EL intensity parallel and perpendicular to the rubbing direction, respectively.

The polarised OLEDs with the configuration ITO/(17% ST638/83% PI) rubbed : **14**/ Ca/Al exhibited a blue emission with R up to 15 at 477 nm and brightness of 45 cd m^{-2}. To achieve higher polarised ratio, the same group modified the device structure with the addition of a layer of NPD to improve the hole-injection, inducing polarised EL with $R = 21$.[74]

Misaki and coworkers successfully achieved highly oriented films of PFO (poly(9,9-dioctylfluorene), **15**) in the nematic and β phase with a friction-transfer technique.[39,75,76] The devices based on the oriented films of PFO in β phase exhibited the best polarisation performance. A maximum current efficiency of 2.0 cd A^{-1} and a polarisation ratio of 53 at 466 nm were demonstrated (Figure 9). To date, this is the record for polarised blue OLEDs and the R value would be sufficient for application in LCD backlights.[39]
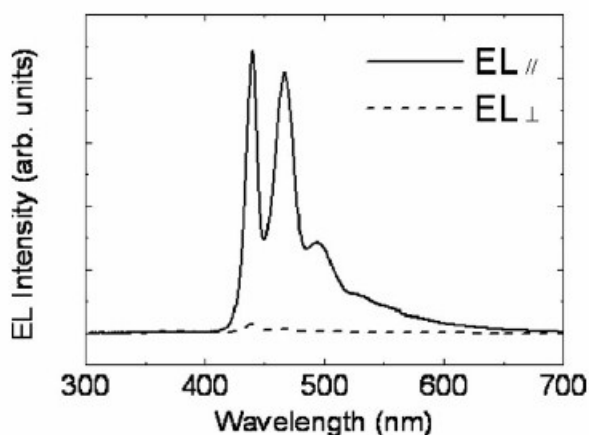

Figure 9. Polarised EL utilizing the oriented film of β-phase PFO. EL$^{//}$ and EL$^{\perp}$ are the EL intensities parallel and perpendicular to the friction direction, respectively. Adapted with permission from ref 39. Copyright 2008 AIP.

Poly(p-phenylenevinylene),[77,78] azobenzene derivatives[79,80] and polyacetylene[81] were also investigated for polarised emission. In addition, in situ formation of polymers from reactive monomeric mesogens was also explored.[82,83] The state-of-the-art in polarised emission with reactive mesogens was summarized by O'Neill and coworkers.[17]

4 Luminescent metallomesogens

In recent years, liquid crystals containing metal ions, namely metallomesogens, have been of great interest due to their outstanding optoelectronic and magnetic characteristics combined with the properties of anisotropic fluids. In particular, within the scope of this review, LC materials based on heavy metal ions are important for OLEDs, as they can achieve 100 % internal quantum efficiency. Therefore, significant progresses have been made with luminescent metallomesogens based on platinum, palladium, iridium, lanthanide, gold, silver, and zinc ions. However, highly efficient luminescent metallomesogens remain a big challenge because of the generally observed decrease of luminescence efficiency in condensed phase. In this section, several representative luminescent metallomesogens

will be described, and their polarised emission properties will be discussed.

4.1. Platinum-based luminescent metallomesogens

Cyclometalated platinum complexes are one of the most attractive candidates for polarised OLEDs due to, first, the possibility of nearly 100 % internal quantum efficiency resulting from harvesting both singlet and triplet excitons,[84-86] and, second, the square-planar geometry and intermolecular Pt…Pt interactions favoring self-organized system, orientated morphologies, and high mobilities. To date, most platinum-based luminescent metallomesogens employed nitrogen-containing heteroaromatic derivatives (2-phenylpyridine/2-phenylpyrimidine) or Schiff-base derivatives as the cyclometalated ligands and acetylacetonate derivatives as the ancillary ligands.[87-104] In these complexes, the cyclometalated ligand, platinum ion and auxiliary ligand constitute the rigid core while the aliphatic chains are regarded as flexible moiety. Generally speaking, the rigid core plays a critical role in the structural order and luminescence while the flexible parts induce the mesogenic properties. However, interplay between the two is often observed and the separation core-emission/chains-phase structure is only a crude simplification.
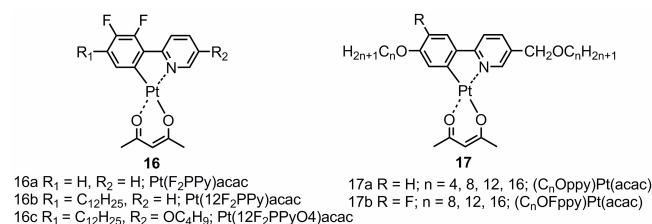

16
16a R_1 = H, R_2 = H; Pt(F$_2$PPy)acac
16b R_1 = C$_{12}$H$_{25}$, R_2 = H; Pt(12F$_2$PPy)acac
16c R_1 = C$_{12}$H$_{25}$, R_2 = OC$_4$H$_9$; Pt(12F$_2$PPyO4)acac

17
17a R = H; n = 4, 8, 12, 16; (C$_n$Oppy)Pt(acac)
17b R = F; n = 8, 12, 16; (C$_n$OFppy)Pt(acac)

Figure 10. Chemical structures of **16** and **17**.

2-Phenylpyridine is an appealing candidate to design luminescent metallomesogens because of simple synthetic routes and extensive application in phosphorescent materials. Recently, two types of platinum-based luminescent metallomesogens, **16** and **17** (Figure 10), were reported with rod-like 2-phenylpyridine terminally substituted by aliphatic chains as the cyclometalated ligand.[89,90] In hexane solution, **16b** exhibited both the monomer and excimer emissions covering 490-650 nm. Unfortunately, POM, DSC, and XRD analysis were not conclusive with respect to the LC properties of these materials. Therefore, compounds **16** were mixed with the nematic LC host MLC-6608 and homogeneous alignment of this blend on a rubbed PI film was achieved. The highest polarisation ratio R = 2.54 was obtained for the blend **16c**/MLC-6608.[89]

Wang *et al.* designed the family of complexes **17**, which is substituted by a hydrogen instead of the larger fluorine on 2-position of the orthometallated phenyl.[90] LC properties are improved with larger temperature range of mesophase, which supports the strategy consisting in decreasing the torsion angle between the two aromatic rings and improving the symmetry of the molecule to favor LC phases. With the increase of the

alkoxy chains length, complexes **17** (n = 12, 16) exhibited enantiotropic mesophase with S_m structure. Notably, complexes **17b** displayed a broader mesophase and higher clearing point than **17a** owing to F…F interactions.[105,106] The electron-withdrawing fluorine in *para* of the metallated position in **17b** leads to the expected red-shifted absorption and emission profiles (ca. 11 nm).[107] No change was detected for the absorption and emission in solution with increasing alkoxy length. Interestingly, **17a** (n = 12) displayed distinctive PL emissions in different phases due to different order in the aggregation. In the investigation of polarised emission at room temperature, the aligned film of **17a** (n = 12) was prepared by annealing its neat film either on a glass substrate or on an aligned PI thin film. As a result, **17a** (n = 12) displayed polarised PL with *R* of 2.7 on glass and 10.5 on the PI film. It is worth noting that a pre-aligned film is crucial to obtain highly polarised emission.
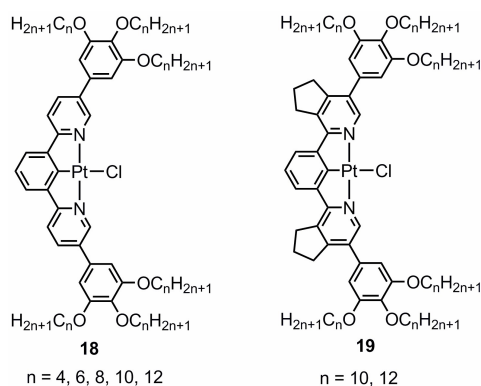

Figure 11. Chemical structures of **18** and **19**.

Considering the popular applications of terdentate N^C^N-coordinated platinum complex in highly efficient OLEDs, the first luminescent metallomesogens based on terdentate platinum complexes bearing 1,3-di(2-pyridyl)benzenes derivatives were reported by Kozhevnikov *et al*.[93] On the one hand, the hexacatenar arms of 3,4,5-trialkoxyphenyl fragments in the half-disc-like complexes **18** and **19** favored the formation of a columnar phase (Figure 11). On the other hand, an excessive number of alkyl chains induced low emission efficiency because of more effective non-radiative deactivation. Φ_{lum} of **18** and **19** were in the region of 0.07-0.12 in CH_2Cl_2 solution. Obviously, proper number and length of aliphatic chains are key to achieve high efficient platinum-based luminescent metallomesogens. Moreover, the luminescence performance in the neat film was drastically dependent on the intermolecular association in the different phase state. For complex **18**, the structured emission from the monomer was observed at 575 nm with a shoulder at 624 nm in crystalline state while only the excimer-like emission at 660 nm was obtained in LC state.
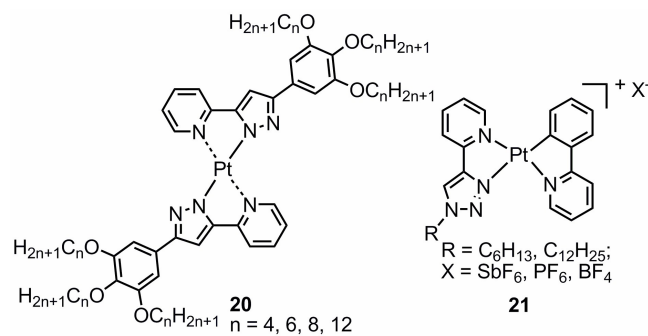

Figure 12. Chemical structures of **20** and **21**.

Liao *et al* developed a series of luminescent metallomesogens based on pyridyl pyrazolate chelates (**20**, Figure 12).[94] Introducing six alkyloxyphenyl groups onto the pyridyl pyrazolate ligand, complexes **20** yielded a columnar mesophase over a wide temperature range (>120 °C). All of these platinum complexes showed green phosphorescence at about 520 nm in CH_2Cl_2 with high Φ_{lum} of 0.6-1.0. In the solid state, red emission at 630-660 nm with low Φ_{lum} of 0.1-0.24 was observed due to the Pt…Pt interactions and dimer or excimer formation.

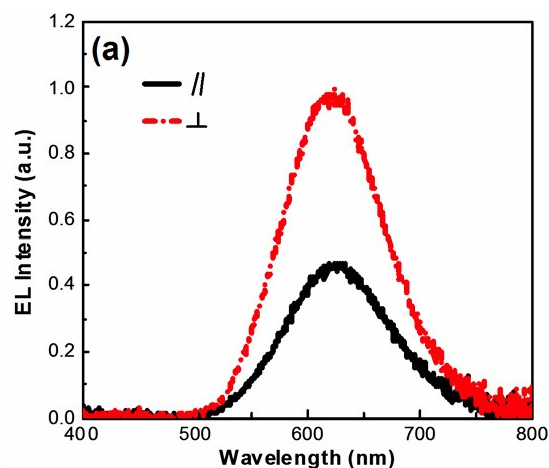**Figure 13**. EL spectra of **20** (n = 6) measured with the polarisation parallel with (//) and perpendicular to (⊥) the rubbing direction. Adapted with permission from ref 95. Copyright 2011 ScienceDirect.

Even though numerous efforts on mesogenic platinum complex have been made, there are only few reports on platinum complex-based polarised OLEDs. Liu *et al*. reported the first example of polarised OLEDs adopting mesogenic platinum complex (**20**, n = 6).[95,96] In this contribution, aligned film of **20** were prepared by directly rubbing the surface of the cast film, followed by thermal annealing at 150 °C. The polarised PL emission of the film was measured at about 660 nm with a dichroic ratio ($PL_\perp/PL_{//}$) of 2. Polarised OLEDs were fabricated with the configuration ITO/rubbed PEDOT:PSS (30 nm)/**F(MB)5**:25wt% **20** (55 nm)/TPBi (45 nm)/LiF (0.5 nm)/Al (150 nm). The emissive layer is a blend of **20** with the mesogenic oligofluorene host **F(MB)5** (Figure 3). The polarised EL spectra exhibited only emission from **20** and an EL dichroic ratio of 2 (Figure 13). Additionally, the polarised

OLEDs presented a maximal luminance of 2000 cd m^{-2} and current efficiency up to 2.4 cd A^{-1}. To the best of our knowledge, this is among the most efficient polarised phosphorescent OLEDs to date.

Recently, Swager *et al* designed a series of cationic platinum complexes-based LC materials (**21,** Figure 12).[97] These cationic platinum complexes exhibited a thermotropic columnar LC phase although they have only a single alkyl chain substituent. It was attributed to the Pt…Pt intermolecular interactions facilitating aggregation. Interestingly, absorption and luminescence varied distinctively from yellow to red on heating or under mechanical processing because of the changing Pt...Pt interactions in the LC phase.

Dinuclear platinum complexes-based luminescent metallomesogens are attractive as a mean to increase the aspect ratio of the molecule, change the LC properties of the materials and possibly to gain control over the Pt…Pt intermolecular interactions and the associated photophysical properties (such as MMCT). Jiang *et al* designed a novel dinuclear platinum complex **22** (Figure 14), in which 1,6-bis((6-(4-(dodecyloxy)phenyl)pyridin-3-yl)oxy)hexane was used as cyclometalated ligand and 1,3-(1-*n*-hexyl,3-*n*-heptadecyl) diketone as ancillary ligand.[98] The two platinum fragments are linked by a non-conjugated flexible hexane-1,6-dioxy unit. This crystalline binuclear platinum complex showed a transition to a smectic phase at relatively low temperature (42 $^{\circ}$C). The aligned film of **22** on a rubbed PI film exhibited a polarised emission at 516 nm with dichroic ratio of 3.1 at room temperature.
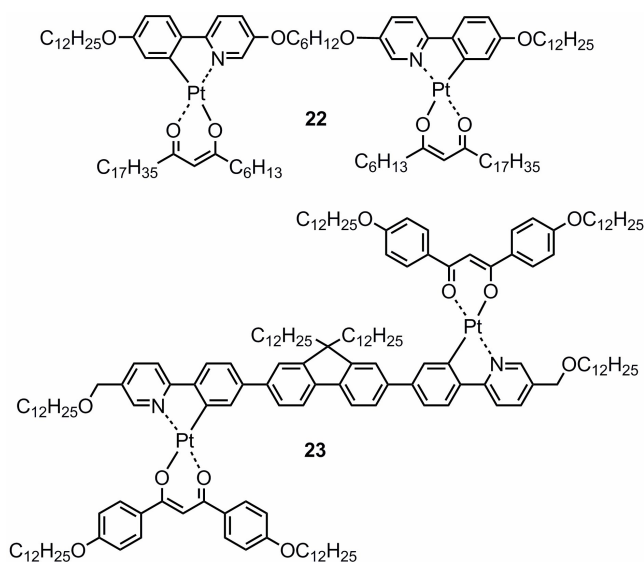

Figure 14. Chemical structures of **22** and **23**.

Concurrently, another dinuclear platinum, complex **23**, was designed with a rigid 9,9-didodecylfluorene bridging unit as the linkage to enhance the emission efficiency.[99] Complex **23** revealed a lamellar structure and a broad emission in the region of 450-700 nm both in CH$_2$Cl$_2$ solution and as neat film. As expected, the aligned film of **23** on an aligned PI substrate possessed a highly polarised emission with *R* = 10.3.

Additionally, complex **23** showed hole mobility of 8.4 × 10^{-4} cm^2 V^{-1} s^{-1}, which is of particular interest for polarised OLEDs.

Considering the advantages of polymer for polarised OLEDs, recently, one main-chain polymer containing mesogenic rod-like cyclometalated palatinate monomer was prepared.[108] This polymer showed smectic phase and a maximum emission at 528 nm. A polarised emission with *R* = 2.5 was achieved by annealing the polymer on a pre-aligned nylon-6,6 film.

Platinum complexes are widely used in the field of luminescent metallomesogens due to their effective emission and planar structure. Nevertheless, poor and red-shifted emission in generally observed for platinum complexes in the solid state and LCs state compared to luminescence in solution. Solving the balance between attractive LC properties and suitable high emission in mesophases of platinum complexes is key to achieving high efficiency polarised emission. On the other hand, polymers have been extensively studied in LC materials and high efficiency OLEDs due to the thermal stability and viscosity. Along these lines, the phosphorescent polymer LCs could be a newly-developing field in luminescent LCs materials.

4.2. Lanthanide-based luminescent metallomesogens

Lanthanide complexes are a popular family of materials to design metallomesogens due to their unique emission spectra, long lifetime at room temperature, and large magnetic anisotropy. Although coordination geometries of lanthanide complexes are adverse to LC properties because of their quasi-spherical shape, a number of luminescent metallomesogens based on lanthanide complexes (named luminescent lanthanidomesogens) have been investigated.[109,110] The general design strategy is to introduce long alkyl chains or flexibly coupled mesogenic units onto the luminescent lanthanide complexes.
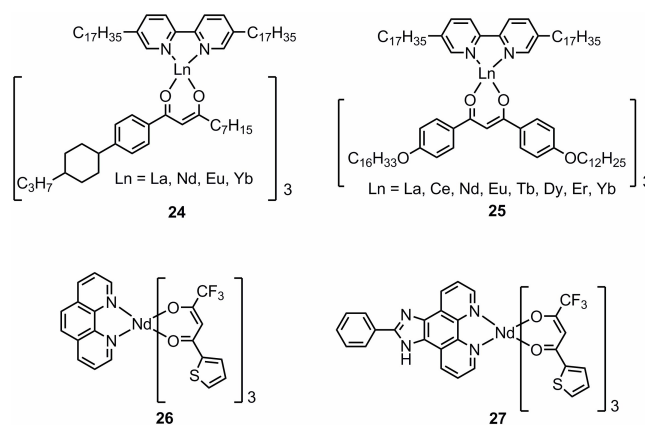

Figure 15. Chemical structures of representative lanthanide-based polarised emission.
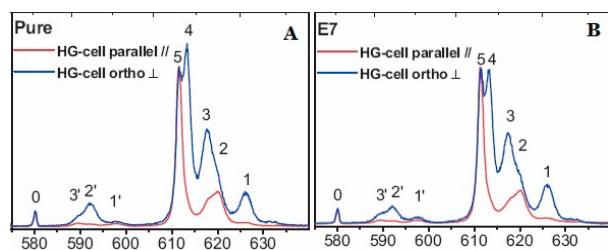
Figure 16. Polarised luminescence spectra of; (A) pure **24** as an aligned supercooled phase in a HG-cell (homogeneous cells with a parallel PI alignment layer for the two surfaces inducing a planar alignment); (B) **24** dissolved in the nematic liquid-crystal mixture E7 aligned in a HG-cell (homogeneous cells inducing a 90°C alignment perpendicular to the surface of the cell). All spectra were measured at room temperature and the excitation wavelength was 350 nm. The intensity was normalized for the transition at 611 nm. The transitions shown in the spectra are the $^5D_0 \rightarrow {^7}F_J$ (J = 0, 1, 2) lines. Adapted with permission from ref 111. Copyright 2008 Wiley.

The lanthanidomesogens **24** (Figure 15) consisted of three β-diketonate derivative ligand and 5,5'-bis(heptadecyl)-2,2'-bipyridine ligand reported by Galyametdinov *et al.*[111]. They displayed S_A and nematic phase. Aligned thin films of **24** (europium ion) both as neat film and doped into a nematic LC host matrix E7 were fabricated via super cooling from the LC phase. As expected, linear polarised luminescence was detected for the aligned films (Figure 16).

The symmetrical luminescent lanthanidomesogens (**25**) were designed with ligands analogous to those of complexes **24**.[112] All complexes **25** exhibited a smectic phase, independently of the lanthanide ions. Among these lanthanidomesogens, complex with Eu ion showed red-emission in the solid state at room temperature. The oriented film of this Eu-based complex was prepared by cooling the LC phase to room temperature in a magnetic field. Interestingly, the transition intensity of $^5D_0$-$^7F_2$ (as non-polarised emission) was enhanced by 25 % in the orientated film compared to that of non-orientated complex due to the uniform orientation of the Eu complex in LC phase.[112]

Recently, another strategy for achieving polarised emission was reported by using a luminescent materials guest and LC materials host system. The aligned film was usually obtained upon alignment of the guest-host mixture in a LC cell with alignment layer.[113-119] Binnemans and his coworkers prepared the guest-host system with luminescent europium complexes (**26**, **27**) and nematic LC host (5CB).[120] The aligned film was obtained from a LC cell, and a polarisation ratio of 1.74 was found for the emission band from the $^5D_0$-$^7F_2$ transition. This result indicated that the europium complexes do not need to exhibit liquid-crystalline behavior themselves, although a structural anisotropy of the complex seems to be necessary to obtain a good alignment in the liquid-crystal host matrix.

5 Conclusions and outlook

Polarised EL is attractive for applications as backlight sources of LCDs, high-contrast OLEDs, optical data storage, optical communication, 3D imaging system, and medical applications. A major challenge is to prepare well aligned emissive layers to obtain high dichroic ratio of electroluminescence. As self-organizing materials suitable for the preparation of aligned films, luminescent liquid crystals are particularly suitable emitters and progress has been made in this field in the recent years. However this field of research is still in its infancy and while many examples of luminescent liquid crystals are reported, only few studies exist on their polarised PL properties and even less on polarised EL from these materials.

In this review we summarized the development of luminescent LC materials based on fluorescent materials and phosphorescent metal complexes and their application for polarised emission.

Fluorescence-based luminescent LC materials have proved to be a promising candidate for application in polarised emission. For the small molecules, most of these fluorescent materials are oligofluorenes, oligothiophenes, and diazole derivatives. The effective design strategy is to employ luminescent planar and rigid units as the core and aliphatic chains as the flexible peripheral units. Polarised EL with dichroic ratio *R* over 30 was achieved for small molecules, which is still below the requirements for commercial applications. On the other hand, the fluorene-based polymers (PFs) have reached polarised EL with *R* > 50. Although fluorescent LC materials are promising in terms of dichroic ratio achieved, mainly due to the high aspect ratio of the molecules, the OLEDs performances are limited by the intrinsic inability to harvest triplet excitons.

Phosphorescent complexes based on heavy metals can harvest both singlet and triplet excitons, potentially achieving polarised OLEDs with 100% internal quantum efficiency. The first challenge is to obtain metallomesogens with good photoluminescence properties in the solid state. There are obvious candidates displaying highly efficient emission in solution; the difficulties are to impart LC properties and to avoid concentration quenching in condensed phases. Besides metals with square planar and linear geometries, the 3D-geometry of most metal complexes is not favorable for mesomorphic properties. Furthermore metals with square planar and linear geometries have tendencies to form metal-metal interactions in solid state, which is generally an advantage for anisotropic organization but result in low energy emission bands problematic for pure monochromatic devices. In addition, within a same family of complexes, the molecular design influences both the LC properties and the luminescence properties and while additional flexible chains on the periphery of the core complex tend to promote LC properties, some examples demonstrate that such additional chains favor non-radiative deactivation of the excited state. It should be emphasized that the molecular designs to date are based on grafting flexible chains directly onto the coordinated ligand. It becomes therefore quasi-impossible to tune the photophysical properties of the complexes without impacting the aggregation properties of the material. The second challenge is the low dichroic ratio achieved by luminescent metallomesogens. Examples of R > 10 are scarce. The best values have been

obtained with dinuclear platinum complexes and are attributed to the higher aspect ratio of these dimers compared to mononuclear materials.

To solve this intricate molecular design problem, two approaches appear promising. The first is to take advantages of aggregation induced emission (AIE) processes. In this case, luminescence is most efficient in the solid state due to restricted geometry changes. The second approach is to use host-guest systems and is arguably the most suitable for OLEDs application due to its similarity with standard OLEDs architecture: a phosphorescent emitter is mixed with an organic host, which can easily form an aligned film. It would allow for the advantageous combination of the high dichroic ratio from fluorescent host with higher efficiencies of phosphorescent emitters. The difficulty will be to control and fix the orientation of the emitter in the host.

One unique point of luminescent liquid crystals, not discussed in details in this perspective, is the possibility to observe different emissions in different phases and induce changes of luminescence with external stimuli.[140] In future, such dynamic behavior will likely be implemented in OLEDs, which would create a range of new dynamic lighting device capable to respond to environmental changes.

Acknowledgements

Notes and references

Notes
The authors declare no competing financial interest

Abbreviations

PL Photoluminescent
EL Electroluminescent
LC Liquid crystals
R   Polarised ratio
PI Polyimide
OLEDs Organic light-emitting diodes
OXD1,3,4-oxadiazole
CuPc copper phthalocyanine
Alq3 tris-(8-hydroxyquinoline)aluminum
ST638 (4,4′,4″-tris(1-naphthyl)-N-phenyl-amino)-triphenyl-amine

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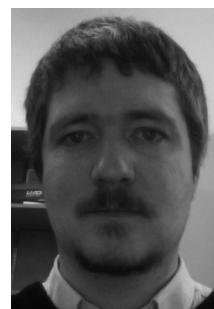
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