**Chiral Platinum-based Metallomesogens with Highly Efficient Circularly Polarized Electroluminescence** **in Solution-Processed Organic Light-Emitting Diodes**

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((Optional Dedication))

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Circularly polarized luminescence (CPL) is of interest due to its wide potential application in semiconductors. To balance the emission efficiency and luminescence dissymmetry factor (*g*PL) of a CPL emitter, in this context, two chiral, phosphorescent and liquid-crystalline cyclometalated platinum complexes, abbreviated *R*-Pt and *S*-Pt, were prepared. The complexes, which showed an intense green emission at 504 nm both in solution and in the solid state, contain a simple, *ortho*-metallated 2-phenylpyridine unit functionalised with a chiral 2-octanol chain, with liquid crystallinity being induced by modifying the *β*-diketonato ligand with mesogenic groups. Interestingly, both the chiral smectic (SmA\*) and nematic (N\*) phases were found by a combination of polarized optical microscopy, differential scanning calorimetry and small-angle X-ray scattering. By annealing, distinct CPL emission is achieved in the solid state with a *g*PL around 0.02. Employing the chiral platinum complexes as the dopant, solution-processable organic light-emitting diodes present an external quantum efficiency of 11.3% and strong, circularly polarized electroluminescence (CPEL) with an extremely high luminescence dissymmetryvalue (*g*EL) of 0.06 after annealing at 100oC. This work opens an avenue for designing CPL-active emitters with high emission efficiency and high dissymmetry factor.

**1. Introduction**

Circularly polarized luminescence (CPL) has attracted much attention in recent years due to its potential applications in optical data storage, three-dimensional (3D) displays and bioresponsive imaging[1]. CPL refers to differential spontaneous emission of left- (*L*) or right (*R*)-handed circularly polarized light upon photo- or electro-excitation[2]. Generally, an outstanding CPL-active material needs to possess high luminescence dissymmetry factor (*g*PL) (defined as 2(*I*L – *I*R)/(*I*L + *I*R) where *I* is the emission intensity), which takes a value between –2 to +2[3]. In addition, good emission efficiency is clearly important, especially in the condensed state. Over the past decades, several strategies to realise efficient CPL-active materials have been developed[4] and much work has concentrated on determining the most efficient method of introducing a chiral centre into the emissive material[5]. To date, various kinds of chiral materials, including polymers and small molecules[6], have been developed for CPL.

However, most of the reported CPL-active emitters are fluorescent materials which therefore have an intrinsic internal quantum efficiency (IQE) of 25%[7], leading to a limitation in the device. To enhance the IQE of the CPL emitter, various complexes with different transition metals were explored recently as they offer the prospect of quantitative IQE[8]. For these circularly polarized organic light-emitting diodes (CP-OLEDs), device performance and the luminescence dissymmetry factor (*g*EL) of circularly polarized electroluminescence (CPEL) were two mainly aspects to evaluate the level of device[9]. To date, few examples have been reported with both high emission efficiency in solution-processable CP-OLED and a large luminescence dissymmetry factor. For example, Di Bari *et al*. reported a CP-OLED based on chiral Eu-complexes and its highest *g*EL value could reach -1.0[10]. Nevertheless, the device eﬃciency and brightness were unsatisfactory. Yan *et al*. reported a series of chiral iridium complexes containing the enantiopure 1-(2-hydroxynaphthalen-1-yl)naphthalen-2-ol (BINOL) fragment. Although CP-OLEDs fabricated by vacuum deposition using this chiral iridium complex showed an EQE of 23.6%, the *g*EL was very low (*ca* 10-4)[11]. Brandt *et al*. prepared a phosphorescent platinahelicene complex with a high *g*EL factor, but unfortunately, the performance of the CP-OLED (luminance of 374 cd m-2 and current efficiency of 0.40 cd A-1) was not so good[12]. Alternatively, thermally activated delayed fluorescence (TADF) materials can also harvest both singlet and triplet excitons to achieve a theoretical 100% IQE[13] and, to this end, there is interest in CPL emission from such materials[14]. For example, Feuillastre *et al*. integrated the 1,1′-binaphthyl moiety into the donor-acceptor molecule, realising the first TADF material exhibiting CPL emission via chiral perturbation. This novel molecular architecture exhibited high solution-phase emission quantum yield (PLQY) of 74% and the luminescence dissymmetry factor (*g*PL) from photoluminescence process was 0.0013, although *g*EL data were not reported[15]. Following this work, Wu *et al*. reported chiral octahydrobinaphthol-based (OBN-Cz) TADF emitters, with a very high PLQY (up to 92%), both CPL and CPEL showed intense emission with *g*PL and *g*EL was 0.002, as well as maximum EQE of 32.6%[16]. However, these CP-OLEDs were fabricated through vacuum deposition which has complicated procedures and high cost. Accordingly, to achieve the high *g*EL value and efficiency of CP-OLEDs concurrently, it is necessary to develop the CPL emitters with novel molecular structure.

Liquid-crystalline materials exhibit long-range order, which can lead to high carrier mobilities in the condensed state, playing a key role in OLEDs. Recently, we demonstrated that a dispersion of a triplet donor and an emitter in a nematic liquid crystal led to effective enhancement of the observed luminescence dissymmetry factor through chiral induction.[17] Encouraged by this observation, we set about looking for liquid crystals exhibiting CPL emission, not least as our previous work had shown that the platinum-based metallomesogens exhibited good emission efficiency in the condensed state.[18] Therefore, it is timely to focus on materials that are phosphorescent liquid crystals and also exhibit CPL. However, to the best of our knowledge, chiral phosphorescent metallomesogens are little investigated and no results regarding CPL have been reported. To this end, we introduced a chiral centre into a phosphorescent metallomesogen to generate a single, chiral material that is phosphorescent, liquid crystalline and has a good CPL emission with a large dissymmetry factor.

In this contribution, the cyclometallated platinum complex was employed as the emissive unit and the cyclohexyldifluorobiphenyl derivative as the mesogenic unit, with a chiral centre introduced *via* a terminal, flexible chain to realise a chiral phosphorescent metallomesogen. With this in mind, two platinum complexes, designated ***R*/*S*-Pt** (Figure 1), were prepared and characterised, and their liquid crystal and chiroptical properties were explored systematically. It is worth noting that annealing procedure played an important role on the chiroptical properties. Employing both ***R*/*S*-Pt** complexes as the dopant, solution-processable organic light-emitting diodes were fabricated and showed highly efficient circularly polarized electroluminescence with the *g*EL value of 0.06, which is one of the highest values for the reported CP-OLED materials (Figure 1).



**Figure 1.** Molecular structure of platinum complexes of ***R*/*S*-Pt** composed of liquid crystalline moiety and chiral moiety. Using ***R*/*S*-Pt** complexes as the dopant, solution-processable organic light-emitting diodes were fabricated. Enhanced circularly polarized electroluminescence with the *g*EL value of 0.06 were obtained through annealing.

**2. Results and Discussion**

**2.1. Thermal Behaviour**

The synthetic route to the platinum complexes is depicted in Figure S1, and the detailed procedures are shown in the Supporting Information; ***R-*Pt** is taken as an example to describe the synthesis. Starting from commercial octan-2-ol, compound **2** was prepared *via* nucleophilic substitution in the presence of PPh3 and NBS in dichloromethane. The etherification reaction between compound **2** and 6-bromopyridin-3-ol afforded compound **3**, treatment of which with phenylboronic acid provided the cyclometallating ligand **4** under typical Suzuki-Miyaura coupling conditions. Ancillary ligand **5** and the final cyclometallated platinum complexes were prepared according to our previous report.[18c, 19] The chiral platinum complexes were purified with HPLC and then characterised using 1H and 13C NMR spectroscopy, and TOF-MS.

Thermogravimetric analysis (TGA) showed satisfied thermal stability of both platinum complexes with a decomposition temperature of 294 °C for ***R*-Pt** and 298 °C for ***S*-Pt** at 5% weight loss (Figure S2, Supporting Information). The mesomorphism of the platinum complexes were explored by differential scanning calorimetry (DSC, Figure 2) and polarized optical microscopy (POM, Figure 2) and, in addition, temperature-dependent small-angle X-ray scattering (SAXS) was used to characterise the mesophase further. The DSC trace of complex ***R*-Pt** (as an example) on first heating (Figure S3) showed a melting point at 79 °C followed by a complex series of three endothermic events between 105 and 122 °C and then a clearing point at 141 °C. On cooling, exothermic events were observed at 143 °C and 77 °C, but the compound did not crystallise (at least by 25 °C under the conditions of this experiment) and neither was their evidence for glass formation. However, subsequent re-heating and cooling cycles were very reproducible showing the two events at ca. 77 and 141 °C. Then observing the complex under the polarising microscope, it is found that the transition at 141 °C is from the isotropic liquid to the chiral nematic phase (N\*) as evidenced by the planar, Grandjean texture shown in Figure 2d. Then at 77 °C this gives way to the focal conic fan texture of the SmA\* phase (Figure 2c). This behaviour was mirrored by the *S*-enantiomer (Figure S4, Supporting Information). To further probe the mesomorphism, complex ***R*-Pt** was studied *via* temperature-dependent small-angle X-ray scattering (SAXS). The SAXS pattern in the N\* phase provides no useful information, but on entering the SmA\* phase, three orders of lamellar reflection were observed, with a lamellar spacing of 40.1 Å calculated from the *d*(001) reflection at 2** = 2.42°. Compared with the calculated molecular length of about 51 Å, which assumes fully extended, all-*trans* chains, the observed layer spacing suggests some sort of interdigitated arrangement within the SmA phase. This is unsurprising given the need to fill space and the structure of ***R*-Pt**.



**Figure 2. a)** DSC curves of ***R*-Pt** with the rate of 10 °C min-1 under N2 atmosphere. The endothermic peaks at about 80 °C and 146 °C are assigned to SmA\*-N\* and N\*-Iso transitions, respectively. The exothermic peaks could be also observed at the similar temperatures on the cooling process. b) SAXS pattern of complex *R*-Pt on cooling process at 55 °C. Three reflection peaks could be observed and the ratio of their reciprocal *d* spacing was 3:2:1. Optical texture of ***R*-Pt** on cooling process at (c) 60 °C (SmA\*) and (d) 126 °C (N\*).

**2.2. Photoluminescence and Circularly Polarized Luminescence of the Platinum-based Chiral Metallomesogens**

***R*-Pt** was chosen as an example for exploring their photophysical properties and its absorption and emission spectra in solution at room temperature are shown in Figure 3a, revealing three main absorption bands between 200 and 450 nm. The absorption band at 254 nm arises from a ligand π-π\* transition, while those in the range 300-375 nm are assigned to singlet metal-to-ligand charge transfer transitions (MLCT). The bands between 370 and 450 nm were then ascribed to the triplet MLCT transitions. At ambient temperature, intense emissions with maxima at 504 nm and 538 nm and a shoulder at 576 nm were observed in solution with a slight hypsochromic shift in the emission in the neat films. It should be noted that, due to the rigidochromic effect[20], a characteristic hypsochromic shift emission with more structured emissive shape was detected in frozen solution at 77 K. The photoluminescent quantum yields of *R*/*S*-Pt were obtained to be 75 and 44% in dichloromethane, respectively. Subsequently, we explored thoroughly the temperature-dependent emission of ***R*-Pt** while exciting at 360 nm. As shown in Figure 3b, increasing the temperature at which the measurement is made will obviously quench the emission. There was no obvious change of emission peak shape in the testing temperature of mesophase (100-120°C). However, after transferring to isotropic state (140 oC), the process of non-radiative transitions would be enhanced, suppressing the triplet emission of *R*-Pt.

To further explore the chiroptical properties of the metallomesogens, we have measured the circular dichroism (CD) and circular polarisation luminescence (CPL) spectra of ***R*-Pt**and ***S*-Pt** both in solution and as films. In dilute solution (dichloromethane), neither a CD nor a CPL signal could be observed (Figure S5, Supporting Information), whereas in the cast film, mirror-imaged CD spectra could be obtained on recording data for the two enantiomers (Figure 3c). However, there was no CPL signal evident in the pristine film (Figure 3d). Keen to exploit the liquid-crystallinity of the materials, we therefore measured the CPL spectra of ***R*/*S*-Pt** complexes in neat films with annealing because of the higher-order orientation in the annealed film, especially in liquid crystal state[21]. Thus, when the neat film of ***R*-Pt** was annealed at 100 °C (at which temperature the complex is in the N\* phase), an intense CPL spectrum was observed with a large *g*lum value up to 0.02 (Figure 3d and 3e). *S*-Pt showed the similar CPL spectra and its corresponding *g*lum was 0.01 (Figure S6, Supporting Information), which could be ascribed to the ***S*-Pt** has a lesser optical purity. The temperature-dependent CPL emission of a film of ***R*-Pt** was also explored and it was found that when the complex was in the isotropic phase (150 °C), the CPL response fell off very steeply (Figure S7, Supporting Information), consistent with the results of emission spectra. Subsequently, the lifetime of ***R*-Pt** was confirmed by time-resolved emission. As shown in Figure 3f, the emission of ***R*-Pt** in solution at 540 nm shows the single exponential decay with lifetime of 13.2 μs. However, in the cast film, the emission of the *R*-Pt at 550 nm exhibits biexponential decay with an average lifetime of 4.5 μs, in which *τ*1 = 12.7 μs (1.3%) and *τ*2 = 4.4 μs (98.7%). Thus, the majority of emitting centres now show a shorter excited state lifetime, which would be consistent with the close approach of complex molecules in the condensed phase and some degree of self-quenching.



**Figure 3.** a) Normalised absorption (dash line) and emission spectra (solid line) of ***R*-Pt**. The concentration is about 1.0 × 10-5 mol dm–3. *λ*ex = 360 nm. b) Emission spectra of ***R*-Pt** film under different temperature. *λ*ex = 360 nm. c) CD spectra of ***R*-Pt** and ***S*-Pt** in the neat film. d) CPL spectra of ***R*-Pt** film before and after the annealing process. *λ*ex = 360 nm. e) The *g*lum value of CPL versus wavelength. f) Time-resolved emission of the***R*-Pt** in solution (red) at 540 nm, in pristine film (green) at 550 nm and the pristine film after annealing treatment (blue) at 550 nm. The magenta square represented the instrument response function. *λ*ex = 370 nm.

**2.3. Device Performance**

In order to determine the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of the complex, cyclic voltammetry (CV) experiments were undertaken in CH3CN. As shown in Figure S9, both platinum complexes show almost identical CV curves in the range of –1.5 to 2.0 V. Irreversible oxidation potentials are detected at 1.23 V and 1.2 V (*vs* Fc/Fc+, *E*oxFc/Fc+ = 0.48 V and below) for complexes ***R*-Pt** and ***S*-Pt**, respectively, while the reduction potentials are observed at –1.23 V (*R*-Pt) and –1.27 V (*S*-Pt). According to the empirical formula *E*HOMO = –(*E*ox + 4.8) eV and *E*LUMO = –(*E*red + 4.8) eV, the HOMO and LUMO levels are calculated to be –6.03 eV/–3.57 and –6.0 eV/–3.53 for complexes ***R*-Pt** and ***S*-Pt**, respectively (Figure 5a).

Solution-processable OLEDs were then fabricated with a configuration of ITO/PEDOT:PSS (35 nm)/emitter (50-55 nm)/TmPyPB(50 nm)/CsF(1.2 nm)/Al(120 nm), with poly(3,4‐ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) as the hole-injection layer. The emitter consists of the host matrix of PVK:OXD-7 (7:3) and the guest of platinum complex, while 1,3,5-tri(*m*-pyrid-3-yl-phenyl)benzene (TmPyPB) is the electron-transporting layer with CsF and Al used as the composite cathode. ***R*-Pt** is again selected as the example to illustrate the electroluminescent property in detail, and the corresponding parameters are tabulated in Table S1. It is noted that the electroluminescence (EL) spectra of the ***R*-Pt** are similar to its PL spectra, suggesting that complete energy transfer occurs between host and guest. While the EL spectra are invariant with increased dopant concentration between 10 wt% and 80 wt% (Figure 4a), the device performances firstly increase and then decrease with dopant concentration as shown in Figure 4b. All the devices exhibit relatively low turn-on voltages (*V*on, at 1 cd m-2) in the range 3.2～4.0 V (Figure 4c and Table S1) and show CIE coordinates at about (0.37, 0.57). At 40 wt% dopant concentration, the device showed its optimum performance with an external quantum efficiency (EQE) of 11.3%, a luminance of 7150 cd m-2 and a current efficiency of 37.1 cd A-1 (Figure 4c). The corresponding EL data for ***S*-Pt** are shown in Figure S8.



**Figure 4.** Characteristics of ***R*-Pt** devices with different dopant concentrations. a) EL spectra; b) *EQE* curves; c)Current density-voltage-luminance curves. The inset picture showed the photo of the devices emission.

**2.4. Circularly Polarized Electroluminescence**

Then the circularly polarized electroluminescence (CPEL) characteristics of the devices based on *R*/*S*-Pt complexes were investigated systematically at 40 wt% dopant concentration under an applied potential of 6 V (Figure 5b and Figure S10, Supporting Information). In common with the CPL data from photoluminescence, both CP-OLEDs made from complexes ***R*-Pt** and ***S*-Pt** display negligible CPEL signals at ambient temperature. Thus, the influence of temperature on the CPEL property of the devices was explored by annealing at 60 °C and 100 °C. As shown in Figure 5b, the CPEL signals is too weak to detect after annealing at 60 °C, but when the device was annealed at 100 °C, a strong CPEL signal with the corresponding *g*EL value of 0.06 was detected (data for ***S*-Pt** are found in in Figure S10). According to the previous report[21], this phenomenon can be ascribed to the fact that ***R*-Pt** possesses a more order structure in the mesophase when annealed in the LC temperature (in this case at 100oC). It should be noted that *g*EL is larger than the *g*PL for both two enantiomers, which could be attributed to the effect of thickness of emitters on the CPL emission. To best of our knowledge, it was the highest value among the reported CPEL property based on metallomesogens. In addition, the sign of CPEL signal was consistent with the CPL after annealing treatment, which indicated that the CPL emission followed the chirality of chiral platinum complexes. We also carefully checked the *g*EL value of devices with diﬀerent dopant concentration. As shown in Figure. 5d, when the dopant concentration was 40 wt%, the *g*EL showed the highest value, which indicated that liquid crystal molecules presented best ordered orientation after annealing treatment.



**Figure 5.** a) Configuration and energy level of *R*-Pt device. b) CPEL spectra of *R*-Pt film before and after the annealing process. The CPEL signal was consistent with the CPL after annealing treatment. c) The *g*EL value of CPEL versus wavelength. The *g*EL value of CPEL was increased from 0.004 to 0.06 after annealing. d) The *g*EL value of devices with diﬀerent dopant concentration.

**3. Conclusion**

In summary, two platinum-based chiral metallomesogens *R*/*S*-Pt were synthesised and characterized and were found to show an enantiotropic N\* phase and a SmA\* phase that is just monotropic. Though intense emission with a maximum emission at 504 nm was achieved, circularly polarized luminescence is absent in solution and pristine state. However, after annealing, a distinct CPL signal with a maximum *g*PL value of 0.02 was detected. The solution-processable OLEDs based on *R*/*S*-Pt exhibited highly efficient CPEL and satisfactory device performance with a maximum *g*EL value around 0.06 and EQE about 11.3%. To the best of our knowledge, this report is the highest *g*EL value among the reported chiral metallomesogens. This research not only open a novel way for designing efficient chiroptical materials but also provide a method for enhancing luminescence dissymmetry factor of chiral luminescent materials.

**4. Experimental Section**

Materials

(*R*)-Octanol is commercial from D&B Biological Technology Company Ltd. S-2-Octanol are commercial from Energy Chemical Company Ltd. Other reagents were purchased from Energy Chemical Company Ltd. All reactions were carried out under N2 atmosphere.

Characterisation

1H NMR and 13C NMR spectra were acquired using a Bruker Dex-300/400 NMR instrument using CDCl3 as a solvent. Mass spectra (MS) were recorded on a Bruker Autoflex MALDI-TOF instrument using dithranol as a matrix. UV-vis absorption spectra were recorded using a SHIMADZU UV-1650PC. Steady-state photoluminescence (PL) spectra were obtained with a PTI QuantaMaster 40 spectrofluorometer at room temperature and absolute PL quantum yields (PLQY) were recorded via HAMAMASTU C9920-02G. Low temperature photoluminescence spectra were measured using a Jasco FP-6500 at 77 K. Photoluminescence decay traces were obtained through the time correlated single photon counting (TCSPC) techniques by using a PicoQuant, FluoTime 250 instrument (PicoQuant, Germany). A 377 nm pulsed laser was used as an excitation source and data analyses were performed using exponential fitting models by FluoFit software. The PLQYs was carried out via FLS920 equipment in dichloromethane with the excitation wavelength of 350 nm. Thermogravimetric analysis (TGA) was carried out with a NETZSCH STA449 from 25°C to 600°C at a 20°C/min heating rate under N2 atmosphere. Cyclic voltammetry measurements were performed using a 273A (Princeton Applied Research). Electrochemical property was evaluated by cyclic voltammetry with three typical electrodes in degassed CH3CN solution with a rate of 100 mV/s. The CV system employed Bu4NPF6 as electrolyte. Platinum disk is used as the working electrode, platinum wire is regarded as the counter electrode and silver wire is used as the reference electrode. Ferrocenium/ferrocene (Fc/Fc+) was used as the external standard compound. Each oxidation potential was calibrated using ferrocene as a reference. Differential scanning calorimetry (DSC) was measured at the phase transition temperature with a rate of 20 °C min–1 on the first heating circle and 10 °C min–1 on the first cooling and second heating process. Polarized optical microscopy (POM) was carried out using an Olympus BX50 Optical Microscope equipped with a Linkam Scientific LTS350 heating stage, Linkam LNP2 cooling pump and Linkam TMS92 controller. X-ray diffraction was measured by Bruker D8 Discover diffractometer with a 2D Vantec detector. Sample is mounted in a capillary in a bespoke heating environment-a hollow graphite furnace-with temperature control via a Eurotherm controller. CD spectra were measured on a JASCO J-1500 spectrophotometer. CPL and CPEL spectra were measured on a JASCO CPL-200 spectrophotometer under ambient conditions and the detector was perpendicular to the sample surface.

Synthesis of (S)-2-bromooctane

To a dichloromethane solution (200 mL) of (*S*)-octan-2-ol (7.0 g, 53.8 mmol), PPh3 (21.10 g, 80.7 mmol) and NBS (12.40 g, 69.9 mmol) was added slowly at 0 oC. Then protect it from light and stir it at room temperature for 24 hours. After that, the solution was poured into water and washed for three times (3 × 200 mL). The combined organic layers were dried over anhydrous MgSO4 and evaporated to dryness. The residue was purified by chromatography on silica gel column eluting with PE/ DCM (*v*:*v* = 4:1) to afford a light yellow liquid (7.20 g, 69 %). 1H NMR (300 MHz, CDCl3) δ 4.14 (q, *J* = 6.6 Hz, 1H), 1.94-1.73 (m, 2H), 1.71 (d, *J* = 6.6 Hz, 3H), 1.53-1.35 (m, 2H), 1.35-1.24 (m, 6H), 0.89 (t, *J* = 6.7 Hz, 3H).

Synthesis of (S)-2-bromo-5-(octan-2-yloxy)pyridine

A solution of (S)-2-bromooctane (7.20 g, 37.5 mmol), 6-bromopyridin-3-ol (5.40 g, 31.2 mmol), K2CO3 (21.60 g, 15.6 mmol), KI (1.03 g, 6.24 mmol) and acetone (200 mL) was heated to reflux and stirred for 24 h under N2. The mixture was cooled to room temperature and then poured into water (100 mL), extracted with dichloromethane (3 × 100 mL). The combined organic layers were washed with water, dried over anhydrous MgSO4 and evaporated to dryness. The residue was purified by chromatography on silica gel column eluting with PE/ DCM (*v*:*v* = 4:1) to afford a light yellow liquid (3.80 g, 43 %). 1H NMR (400 MHz, CDCl3) δ 8.03 (s, 1H), 7.35 (d, *J* = 8.7 Hz, 1H), 7.07 (dd, *J* = 8.7, 3.1 Hz, 1H), 4.34 (dd, *J* = 12.1, 6.1 Hz, 1H), 1.79-1.67 (m, 1H), 1.62-1.53 (m, 1H), 1.48-1.34 (m, 2H), 1.34-1.23 (m, 9H), 0.88 (t, *J* = 6.7 Hz, 3H).

Synthesis of (S)-5-(octan-2-yloxy)-2-phenylpyridine

A solution of (S)-2-bromo-5-(octan-2-yloxy)pyridine (3.00 g, 10.5 mmol), phenylboronic acid (1.54 g, 12.6 mmol), Pd(PPh3)4 (0.24 g, 0.50 mmol), 2M K2CO3 (30 mL), ethanol (30 mL), toluene (90 mL) was heated to 80oC and stirred for 24 h under N2. After cooling to room temperature, the solution was poured into water and extracted with dichloromethane (3 × 150 mL). The combined organic layers were washed with water, dried over anhydrous MgSO4 and evaporated to dryness. The residue was purified by chromatography on silica gel column eluting with PE/ DCM (*v*:*v* = 1:1) to afford a colourless liquid (2.30 g, 76 %). 1H NMR (400 MHz, CDCl3) δ 8.36 (d, *J* = 2.9 Hz, 1H), 7.92 (d, *J* = 7.3 Hz, 2H), 7.65 (d, *J* = 8.7 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.24 (d, *J* = 2.9 Hz, 1H), 4.42 (t, *J* = 9.1 Hz, 1H), 1.78 (ddd, *J* = 16.4, 11.0, 5.9 Hz, 1H), 1.66-1.56 (m, 2H), 1.52-1.37 (m, 2H), 1.37-1.24 (m, 9H), 0.88 (t, *J* = 6.7 Hz, 3H).

Synthesis of (S)-Chiral platinum complex

To a mixture of K2PtCl4 (0.72 g, 1.72 mmol) and water (30 mL) was added a solution of (S)-5-(octan-2-yloxy)-2-phenylpyridine (1.00 g, 3.50 mmol) and 2-ethoxyethanol (90 mL). The mixture was stirred at 80°C for 24 h under N2. After cooling to room temperature, the precipitate was collected and washed with water and hexane. The solid was used to the next step without any further purification. A mixture of the dimer solid (335 mg, 0.33 mmol), ancillary ligand (0.60 g, 0.61 mmol) and K2CO3 (0.85 g, 6.12 mmol) was stirred in THF (60 mL) and methanol (20 mL) at 80°C for 24 h under N2. After cooling to room temperature, the mixture was evaporated to dryness, poured into water and extracted with dichloromethane (3 × 100 mL). The combined organic layers were washed with water, dried over anhydrous MgSO4 and evaporated to dryness. The residue was purified by chromatography on silica gel column eluting with PE/ DCM (*v*:*v* = 1:1) to afford a light yellow solid (0.31 g, 35 %). 1H NMR (300 MHz, CDCl3) δ 8.71 (d, *J* = 2.6 Hz, 1H), 7.58 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.48 (d, *J* = 8.9 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 4H), 7.36 (d, *J* = 2.6 Hz, 1H), 7.33 (dd, *J* = 3.1, 1.9 Hz, 1H), 7.31-7.27 (m, 3H), 7.25 (s, 1H), 7.15 (td, *J* = 7.4, 1.3 Hz, 1H), 7.05 (ddd, *J* = 9.8, 8.1, 1.8 Hz, 3H), 6.75 (ddd, *J* = 9.6, 4.1, 2.1 Hz, 2H), 5.46 (s, 1H), 4.40 (dd, *J* = 12.1, 6.1 Hz, 1H), 4.04 (td, *J* = 6.5, 4.0 Hz, 4H), 2.50 (tt, *J* = 12.1, 3.0 Hz, 2H), 2.27 (t, *J* = 7.4 Hz, 4H), 2.07-1.98 (m, 1H), 1.97-1.70 (m, 17H), 1.69-1.61 (m, 3H), 1.55-1.39 (m, 19H), 1.38-1.17 (m, 37H), 1.06 (qd, *J* = 13.9, 3.4 Hz, 5H), 0.94-0.82 (m, 10H). 13C NMR (75 MHz, CDCl3) δ 135.46, 128.62, 127.03, 123.5, 109.58, 75.72, 69.88, 44.37, 37.37, 36.31, 34.32, 33.61, 32.23, 31.77, 29.70, 29.23, 29.21, 29.16, 29.14, 29.09, 26.66, 26.35, 26.08, 25.83, 25.70, 25.60, 25.41, 22.58, 19.52, 14.08, 1.02. (MALDI-TOFMS) m/z: calcd. For C82H107F4NO5Pt, 1456.77; found 1458.23.

(R)-2-bromooctane was prepared using the same synthetic process as for compound (S)-2-bromooctane. The yield of the product was 62 %. 1H NMR (400 MHz, CDCl3) δ 4.13 (dq, *J* = 13.2, 6.6 Hz, 1H), 1.88-1.73 (m, 2H), 1.70 (d, *J* = 6.6 Hz, 3H), 1.54-1.35 (m, 2H), 1.35-1.21 (m, 6H), 0.88 (t, *J* = 6.7 Hz, 3H).

(R)-2-bromo-5-(octan-2-yloxy) pyridine was prepared using the same synthetic process as for compound (S)-2-bromo-5-(octan-2-yloxy) pyridine. The yield of the product was 41 %. 1H NMR (400 MHz, CDCl3) δ 8.03 (d, *J* = 3.1 Hz, 1H), 7.35 (d, *J* = 8.7 Hz, 1H), 7.07 (dd, *J* = 8.7, 3.1 Hz, 1H), 4.34 (h, *J* = 6.1 Hz, 1H), 1.78-1.67 (m, 1H), 1.64-1.52 (m, 1H), 1.40 (ddd, *J* = 16.5, 11.8, 5.9 Hz, 2H), 1.33-1.23 (m, 9H), 0.88 (t, *J* = 6.7 Hz, 3H).

(R)-5-(octan-2-yloxy)-2-phenylpyridine was prepared using the same synthetic process as for compound (S)-5-(octan-2-yloxy)-2-phenylpyridine. The yield of the product was 81 %. 1H NMR (400 MHz, CDCl3) δ 8.36 (d, *J* = 2.8 Hz, 1H), 7.92 (d, *J* = 7.3 Hz, 2H), 7.65 (d, *J* = 8.7 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.26-7.22 (m, 1H), 4.47-4.37 (m, 1H), 1.83-1.72 (m, 1H), 1.66-1.56 (m, 2H), 1.52-1.37 (m, 2H), 1.32 (dd, *J* = 14.8, 6.8 Hz, 9H), 0.88 (t, *J* = 6.8 Hz, 3H).

(R)-Chiral platinum complex was prepared using the same synthetic process as for compound (S)-Chiral platinum complex. The yield of the yellow product was 39 %. 1H NMR (300 MHz, CDCl3) δ 8.71 (d, *J* = 2.6 Hz, 1H), 7.61-7.56 (m, 1H), 7.48 (d, *J* = 8.9 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 4H), 7.36 (d, *J* = 2.7 Hz, 1H), 7.34-7.31 (m, 1H), 7.30-7.26 (m, 3H), 7.25 (s, 1H), 7.14 (td, *J* = 7.4, 1.3 Hz, 1H), 7.05 (ddd, *J* = 9.8, 8.1, 1.8 Hz, 3H), 6.74 (ddd, *J* = 9.6, 4.2, 2.1 Hz, 2H), 5.46 (s, 1H), 4.40 (h, *J* = 5.8 Hz, 1H), 4.04 (td, *J* = 6.5, 4.1 Hz, 4H), 2.50 (tt, *J* = 11.9, 2.9 Hz, 2H), 2.27 (t, *J* = 7.3 Hz, 4H), 1.97-1.69 (m, 17H), 1.66-1.58 (m, 1H), 1.53-1.39 (m, 17H), 1.29 (dt, *J* = 23.3, 10.4 Hz, 32H), 1.14-0.98 (m, 5H), 0.89 (q, *J* = 6.9 Hz, 10H). 13C NMR (75 MHz, CDCl3) δ 152.76, 147.39, 144.97, 143.35, 135.42, 128.63, 128.05, 127.04, 123.54, 118.77, 109.57, 75.70, 69.83, 44.37, 41.18, 40.33, 37.37, 36.30, 34.32, 33.61, 32.24, 31.78, 29.44, 29.21, 29.16, 29.10, 26.67, 26.08, 25.83, 25.71, 25.42, 22.67, 19.52, 14.14. (MALDI-TOFMS) m/z: calcd. For C82H107F4NO5Pt, 1456.77; found 1458.57.

Fabrication of pristine and annealed film

Firstly, *R*-Pt (1 mg) was added into a 1 mL centrifuge tube and dissolved in dichloromethane (1 mL). Then, the resulting solution was sonicated for about 1 min to obtain a good solution. The sample used to investigate the CD, and CPL was fabricated by adding mixture dropwise on a clean quartz glass substrate. The pristine film was obtained after being dried. The annealed film was prepared through slow annealing of the pristine film on the heat stage. To explore the emission spectra at different temperatures, the solution mixture was transferred on the slide and then the solvent was evaporated slowly using a hot stage. Finally, the heating mixture was loaded into the liquid crystal cell by capillary action. The sample employed to investigate the lifetime was fabricated by transferring the solution mixture into a quartz cell and then evaporating slowly using a vacuum pump. The thin film was generated in the inner face of the quartz cell and kept under deaerated conditions.

Device fabrication and Measurement

The patterned ITO substrates were rinsed with acetone and isopropyl alcohol using sonication for 15 min, followed by 15 min UV-ozone-treatment. After surface treatment, the PEDOT:PSS layer was spin-coated onto the ITO substrate as the hole-injecting layer, and then annealed at 150 oC for 15 min. The emissive layers were prepared by spin-coating onto the PEDOT:PSS and then annealed at 100 oC for 15 min. The melting point and clearing point of ***R*-Pt** are at 79 °C and 141 °C, respectively. Thus, ***R*-Pt** has an ordered structure in the mesogenic state and preformed intense CPEL emission. Therefore, the annealing temperature was selected at 100 °C, where ***R*-Pt** could transfer to the liquid crystal phase completely. The hole blocking layer, electron-transporting and the cathode materials were thermally evaporated onto the emitter layer in a vacuum chamber. The thermally evaporated deposition rates are 0.6-1 Å s-1 for organic layers, 0.1 Å s-1 for CsF and 1.5-1.8 Å s-1 for Al electrode, respectively. The current-voltage-luminance (*J-V-L*) characteristics and the electroluminescence spectra of the devices were simultaneously obtained by using a spectroradiometer (PR735) and Keithley 2400 sourcemeter unit under ambient atmosphere at room temperature. In the devices, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) serves as the hole injection layer, while 1,3,5-tri(m-pyrid-3-yl-phenyl)benzene (TmPyPB) act as the electron-transport layers.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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Two platinum-based chiroptical metallomesogens were synthesised and characterised. Both of enantiomers showed circularly polarized luminescence in the film after annealing treatment with maximum *g*PL value up to 0.02. The solution-processable OLEDs exhibited highly efficient circularly polarized electroluminescence, with EQE about 11.3 % and *g*EL reaching 0.06.

Keywords: ((circularly polarized luminescence, OLED, chiral liquid crystal, platinum complex, phosphorescence)

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**Chiral Platinum-based Metallomesogens with Highly Efficient Circularly Polarized Electroluminescence in Solution-Processed Organic Light-Emitting Diodes**

