



Luminescent metallomesogens based on platinum complex containing triphenylene unit



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ABSTRACT

To explore the influence of mesogenic unit on the liquid crystals and luminescence properties of metal complex, two novel triphenylene-based platinum complexes of TppyPtacac and TppyPtPhacac featuring donor–acceptor framework have been designed and synthesized, in which Tppy is triphenylene–phenylpyridine skeleton and acac/Phacac is pentane-2,4-dione derivative. Differential scanning calorimetry (DSC), polarized optical microscopy (POM) and X-ray diffraction (XRD) techniques demonstrate the complex TppyPtPhacac shows a column mesophase in the region of 55–110 °C. Both platinum complexes exhibit intense emission at about 550 nm in CH₂Cl₂ solution. Compared to the analogous platinum complexes without triphenylene unit, TppyPtacac and TppyPtPhacac display a remarkable red-shifted emission profiles (ca. 50 nm) due to strong intramolecular charge transfer. Furthermore, the hole mobilities up to $2.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $2.99 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ are achieved for the annealed film of TppyPtacac and TppyPtPhacac, respectively, which is one of the highest hole mobility with respect to cyclometalated platinum complexes.

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1. Introduction

Over the past two decades, luminescent liquid crystals (LC) materials have attracted much attention as charming candidates for organic optoelectronics devices, especially for polarized organic light-emitting diodes (OLEDs) owing to the combination of the optoelectronic characteristics of luminescent materials with the unique properties of anisotropic fluids.^{1–3} To date, numerous efforts have been devoted to design luminescent LC materials based on small molecules,^{4,5} polymers^{6,7} and metal complexes.^{8,9} Among these materials, the luminescent LC materials with metal ions (luminescent metallomesogens) are a particularly enticing family due to their outstanding optoelectrical and magnetic characteristics combined with the properties of anisotropic fluids.

To this end, platinum complexes are one of the most attractive candidates for luminescent metallomesogens due to the possibility of nearly 100% internal quantum efficiency, square-planar geometry, strong intermolecular Pt···Pt interaction and diverse charge transfer transition (e.g., metal-metal-to-ligand charge transfer, excimeric ligand-to-ligand charge transfer).^{10–13} To the best of our

knowledge, most platinum-based luminescent metallomesogens employed nitrogen-containing heteroaromatic derivatives (2-phenylpyridine/2-phenylpyrimidines) as the cyclometalated ligands and acetylacetonate derivatives as the ancillary ligands.^{14–20} Tschierske and co-workers prepared a series of platinum-based luminescent metallomesogens containing rod-like 2-phenylpyrimidines/2-phenylpyridines ligand. The effect of the molecular structure on the mesogens (lamellar, nematic and columnar phase) and luminescence properties were systematically investigated.^{14,15} Subsequently, the functionalized bidentate and terdentate platinum complexes have received considerable attention in luminescent metallomesogens. Bruce et al. reported the half-disc *N,C,N*-Pt(II) complexes possessing a column mesogen and phase state-dependent emission spectra.¹⁶ The rod-like, *ortho*-platinated complexes bearing 2,5-diphenylpyrimidines and β-diketone ligands showed a smectic phase and strong luminescence ($\Phi_{\text{em}} > 50\%$), reported by the same group.^{17,18} Recently, we also presented the luminescent metallomesogens based on mononuclear and dinuclear platinum complexes.^{19,20} Both of the mono-/dinuclear platinum complexes possessed green emission in the smectic phase. However, all of these platinum-based luminescent metallomesogens are comprised of rigid cyclometalated ligand and peripheral flexible chains. Few investigations in the platinum complex with a pendant mesogens unit have been explored.²¹

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With this in mind, we focus our attention on the structure–property relationship in mesogenic unit and luminescent metallomesogens. Inspired by a wide application of triphenylene unit in discotic liquid crystals and emission materials,^{21,22} it could be available to favour the liquid crystal and charge mobility by introducing the triphenylene derivative into luminescent metallomesogens. Furthermore, encouraged by our previous work on platinum-based metallomesogens,^{19,20} we designed and synthesized two novel triphenylene-based platinum complexes featuring donor–acceptor (D–A) framework, so-called TppyPtPhacac and TppyPtacac, in which the Tppy is the triphenylene-phenylpyridine skeleton and Phacac/acac is the pentane-2,4-dione derivative (Chart 1). In these molecules, the triphenylene derivative acts as the donor (D) unit while the platinum segment is considered as the acceptor group (A). Both D–A platinum complexes are expected to promote the mesogens and tuning the emission via intramolecular interaction.

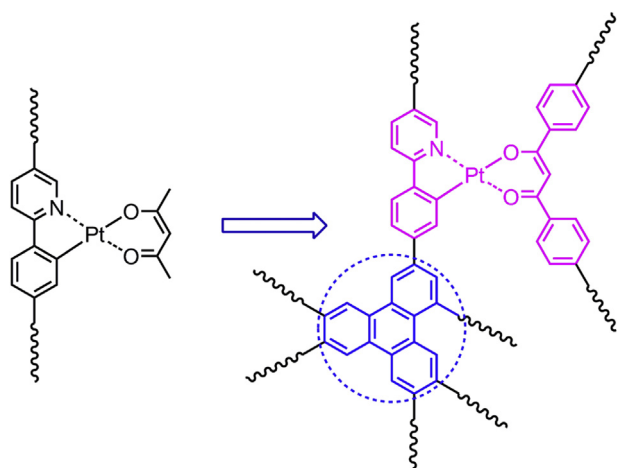


Chart 1. Structural evolution of platinum-based metallomesogens.

Herein, the preparation, liquid crystal and optophysical properties of both platinum complexes are discussed in detail. Complex TppyPtPhacac shows a column mesophase characterized by differential scanning calorimetry (DSC), polarized optical microscopy (POM) and X-ray diffraction (XRD) techniques. The hole mobilities up to $2.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $2.99 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ are achieved for the annealed film of TppyPtacac and TppyPtPhacac, respectively.

2. Results and discussion

2.1. Synthesis

The synthetic routes of platinum complexes are shown in Scheme 1. The key precursor triphenylene derivative **5** was prepared via a four-step reaction starting from pyrocatechol.²⁴ Then, compound **5** was reacted with **6**²⁰ to give the cyclometalated ligand **7** via Suzuki Coupling reaction in a moderate yield of 54.9%. Chloride-bridged dimer was obtained according to the previous procedure and used to the next step without any further purification.¹⁹ Finally, cleavage reaction between chloride-bridged dimer and ancillary ligand (acac or **8**²⁰) was carried out to afford the platinum complexes in 41–50% yield. The cyclometalated ligand and platinum complexes were characterized by ¹H NMR, ¹³C NMR TOF-MS and elemental analysis.

2.2. Liquid crystalline properties

The thermal stability of these platinum complexes was evaluated by thermal gravity analysis (TGA). The decomposition temperatures with 5% weight loss are observed at 162 °C and 192 °C for TppyPtacac and TppyPtPhacac, respectively (Fig. S1). It is noted that TppyPtPhacac exhibits a better thermal stability owing to the additional phenyl units in the ancillary ligand.

On the other hand, the phase transition properties of TppyPtacac and TppyPtPhacac were characterized by DSC and POM. As shown in Fig. S2, only one endothermic peak at 152 °C is observed between the solid and isotropic phase while one exothermic transition at 118 °C is detected on the cooling circle. On contrary, the DSC curve of TppyPtPhacac shows two endothermic peaks at 55 °C and 110 °C, which are corresponding to the melting and clearing transitions. Notably, the melting point decreases with the increasing number of peripheral chains. However, only one peak at 50 °C is detected for TppyPtPhacac during the cooling scan, implying that an undetectable transition from isotropic to liquid crystal phase has occurred.²¹

The POM study revealed that TppyPtacac presents a spherulitic texture (Fig. 1a) and no fluidity upon cooling circle, indicating that TppyPtacac could be a crystal. The complex of TppyPtPhacac exhibits a birefringent texture along with good fluidity during heating and cooling process. Even though no characteristic texture was observed, a distinct colour change from yellow to green is observed on heating process for TppyPtPhacac (Fig. 1b and c). According to these results, complex TppyPtPhacac is tentatively proved to be theomorphic LC property.

To further confirm the LC property, X-ray diffraction (XRD) was carried out for both platinum complexes. As in the case of TppyPtacac, the XRD diffraction pattern reveals a crystal packing with a disorder structure at 100 °C (Fig. S3). For TppyPtPhacac, as shown in Fig. 2, a distinct reflection peak at 17.9 Å and one weak peak at 15.7 Å, with a *d*-spacing ratio of 1/3^{1/2}:2, are obtained, which demonstrates it is a column LC phase. Additionally, a diffuse peak in wide angle region (ca. 4.3 Å) is assigned to the loose ordering of the molten peripheral chains.^{25,26} Compared to the previous work,¹⁹ it is noted that the LC phase was changed from smectic to column via introducing the triphenylene derivative into platinum complex.

2.3. Optophysical properties

The UV–vis absorption and photoluminescent (PL) spectra of both platinum complexes were measured in CH₂Cl₂ solution (10^{-5} M) and as a thin film at rt. As depicted in Fig. 3, similar absorption spectra are observed for both platinum complexes in the solution. The intense absorption bands in the region of 263–350 nm are attributed to the ligand centred ¹(π – π^*) transitions.²⁷ The weak absorption bands from 360 nm to 474 nm are assigned to the metal-to-ligand charge transfer (MLCT) transition. Compared to the reported platinum complexes,¹⁹ it implies that introducing the triphenylene unit into cyclometalated ligand has a strong effect on the absorption of platinum complexes.

Excitation with 450 nm at rt, both platinum complexes exhibit a maximum emission peak at about 550 nm (± 2 nm) and a shoulder at about 592 nm. Compared to the reported 2-phenylpyridine-based metallomesogens,¹⁹ TppyPtacac and TppyPtPhacac present a red-shifted emission (ca. 50 nm) in solution owing to an effective intramolecular charge transfer transition. The neat film of both platinum complexes display a remarkable bathochromic shifts (ca. 70 nm) with a maximum peak located at about 620 nm due to the formation of nonemission excimer or excimer-like adducts.²¹ However, a monomer emission from TppyPtacac is observed in the neat film, which implies that the TppyPtPhacac has a more tendency to aggregation in the film.

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