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Tetradentate complex, **Pt**<sub>12</sub>, with six alkoxyl chains on the periphery can form columnar mesophase. The carrier mobility in mesogenic state is two orders of magnitudes greater than that in the amorphous state, showing ordering packing in liquid crystlline phase can facilitate the charge transport.

# Tetradentate platinum(II) complexes: Synthesis, photophysical properties, liquid crystalline characteristics and charge transport behaviour

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#### Abstract

Three new tetradentate phosphorescent Pt(II) complexes (Pt<sub>6</sub>, Pt<sub>12</sub> and Pt<sub>16</sub>) with half-disc molecule structure were designed and synthesized, which are based on tetradentate ligands with six alkoxyl chains on the periphery, (6,6'-bis((3',4',5'-alkoxy-[1,1'-biphenyl]-4-yl)oxy)-2,2'-bipyridine). All complexes show red phosphorescence in dichloromethane solution ( $\lambda_{em} \approx 640$  nm) with quantum yields in range of 4.3 % - 6.7 % and phosphorescent lifetimes in range of 0.46 – 0.55  $\mu$ s in degassed dichloromethane solution. Among these complexes, the complex, Pt12, with 12 carbons chain lengths shows columnar mesophase with liquid crystal temperature range of - 22.0 °C to 77.8 °C, which was confirmed via polarized optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The complex, Pt<sub>12</sub>, exhibits ambipolar carrier transport behaviors, which has been confirmed by the space charge limited current (SCLC) measurement. Moreover, the carrier mobility in mesogenic state is two orders of magnitudes greater than that in the amorphous state, showing ordering packing in liquid crystalline phase can facilitate the charge transport.

Keywords: Metallomesogens; Photoluminescence; Tetradentate platinum complexes; Ambipolar carrier mobility

#### 1. Introduction

In recent years, transition-metal complexes, especially iridium(III) and platinum(II) complexes, have received consistent attention for their wide application in the field of organic light-emitting diodes (OLEDs) due to their high efficiency and stable device performance.[1-15] For organic electronic devices, such as OLEDs, organic field-effect transistor (OFETs) and organic photovoltaic devices (OPVs), the carrier mobility in these devices is one of the crucial parameters to achieve high device performances.[16-28] However, finding organic semiconductors with high charge mobility remains challenging, because the carrier mobility of organic semiconductors is much lower than that of inorganic semiconductors. The carrier mobility of organic semiconductors mainly depends on their packing model and degree of order. The carrier mobility in the well-oriented crystalline thin film of organic semiconductors is much higher than that in polycrystalline thin film in which carrier mobility is interrupted by grain boundaries or in amorphous thin film in which disordered molecular arrangement impedes the transfer of carrier.[16] For example, the carrier mobility in the polycrystalline thin film of pentacene is six orders of magnitudes lower than that in single crystal thin film. The carrier transport is further deteriorated in the amorphous thin film of pentacene, the charge mobility is only 10<sup>-9</sup>

cm<sup>2</sup>·V<sup>-1</sup>·s<sup>-1</sup>.[29-33] Although single crystal thin films have high charge carrier mobility, large area single crystal thin films are not easy to be made in large-scale industrial applications. The order of liquid crystal is between crystal state (perfectly order) and amorphous state (pretty disordered), and it is easy to form large homogeneous order film, so liquid crystals is a promising charge transport materials.[34-43] Recently, metal-containing liquid crystals (metallomesogens) have caused great interest due to their potential applications in polarized emission and carrier-transporting.[44-55] Platinum(II)-containing liquid crystalline complexes, as multifunctional organic semiconductors, are widely studied. There are two reasons for this, one is that, like other heavy metal complexes, the strong spin-orbit coupling effect from platinum(II) ion allows the efficient mixture of the excited single and triplet states, resulting in phosphorescent emission with high quantum yield and microsecond lifetime, and the other is that, the square-planar geometry of platinum(II) complexes is suitable platform from which metallomesogens can be obtained by connecting flexible carbon chains at periphery of the center moiety of the complexes. The diversity of platinum(II) liquid crystalline complexes is related to the shape, anisotropy, dipolar properties and intermolecular interactions. Most of the metal platinum liquid crystal complexes are formed by bidentate and tridentate ligands. Very recently, tetradentate platinum(II)

complexes are promising platinum(II) complexes, because tetradentate platinum(II) complexes have rigid cyclic geometry which helps to reduce non-radiative decay and to improve quantum efficiency.[56,58-67] Not long ago we synthesized a new type of phosphorescent tetradentate platinum complexes by using tetradentate C\*N^N\*C ligands (where C\*N^N\*C is tetradentate ligand. 6,6'-bis(4-(alkoxy)phenoxy)-2,2'-bipyridine). By adjusting the length of peripheral alkoxyl chains, the tetradentate liquid crystal complexes with smectic phase were obtained.[68] We noticed that larger rigid structure of the tetradentate complexes is likely to form columnar liquid crystals by carefully adjusting the number and length of the peripheral alkoxyl chains. Considering that columnar liquid crystals can form one-dimensional superstructures of  $\pi$  conjugated organic molecules that facilitates unidirectional carrier transport along the column, [34, 35, 40, 42, 43, 45] in this article, we designed and synthesized a series of new platinum complexes that are based on tetradentate ligands with six peripheral alkoxyl chains. 6,6'-bis((3',4',5'-alkoxy-[1,1'-biphenyl]-4-yl)oxy)-2,2'-bipyridin e. By carefully adjusting alkoxyl chains length, we obtain a new tetradentate platinum(II) liquid crystal with columnar

phase, **Pt**<sub>12</sub>. The photophysical properties of these tetradentate complexes are systematically researched. Moreover, carrier mobility was tested by the space charge limited current (SCLC) measurement. The experimental results show that tetradentate platinum(II) complex (**Pt**<sub>12</sub>) has ambipolar carrier transport properties. Furthermore, we find that the carrier mobility in the liquid crystal state is two orders of magnitude greater than that in the amorphous state.

#### 2. Synthesis of the complexes

The synthesis of the tetradentate platinum(II) complexes was shown in Scheme 1. The compound **a** obtained from demethylation of 5-bromo-1,2,3-trimethoxybenzene was used to etherify with 1-bromoalkanes with different carbon chain length to get **b**<sub>n</sub>. The ligand precursors, **c**<sub>n</sub>, were obtained by Suzuki coupling reaction of **b**<sub>n</sub> with (4-hydroxyphenyI)boronic acid. The ligands, **L**<sub>n</sub>, were produced by Williamson ether reaction. The complexes, **Pt**<sub>n</sub>, were synthesized by complexation of **L**<sub>n</sub> and K<sub>2</sub>PtCl<sub>4</sub> in acetic acid solution.



Scheme 1 Synthesis of the complexes **Pt**<sub>n</sub> (n = 6, 12, 16). Conditions: (I) BBr<sub>3</sub>, DCM, - 70 °C, overnight, Ar; (II) 1-bromoalkane, K<sub>2</sub>CO<sub>3</sub>, DMF, 70 °C, 24 h, Ar; (III) (4-hydroxyphenyl)boronic acid, K<sub>2</sub>CO<sub>3</sub>, THF, H<sub>2</sub>O, Pd(PPh<sub>3</sub>)<sub>4</sub>, reflux, 24 h, Ar; (IV) 6,6'-dibromo-2,2'-bipyridine, 1-methylimidazole, K<sub>2</sub>CO<sub>3</sub>, Cul, toluene, 120 °C, 48 h, Ar; (V) K<sub>2</sub>PtCl<sub>4</sub>, AcOH, reflux, 48 h, Ar.

#### 3. Results and Discussions

#### 3.1. Absorption and emission spectra

The primary data of absorption and photoluminescence (PL)

spectra in degassed dichloromethane (DCM) solution and in the solid states for the complexes  $Pt_n$  are exhibited in Table 1. As shown in Fig.1, strong absorptions of all complexes occur below 300 nm with molar extinction coefficients ( $\epsilon$ ) value of  $6.6 - 8.6 \times 10^4$  dm<sup>3</sup>·mol<sup>-1</sup>·cm<sup>-1</sup>, which are similar to that of

corresponding ligand. Hence strong absorption between 200 and 300 nm are attributed to the absorption of spin-allowed ligand centered charge-transfer (<sup>1</sup>LC). There are two weak lower-energy absorption bands at about 416 nm ( $\epsilon = 5 \times 10^{3} \cdot \text{dm}^{3} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ) and 470 nm ( $\epsilon = 2 \times 10^{3} \cdot \text{dm}^{3} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ), respectively. In terms of time-dependent density functional theory (TD-DFT) calculations (vide infra) and previous reports<sup>1,2,8</sup>, weak absorption band at 416 nm with  $\epsilon$  value of 5  $\times 10^{3} \cdot \text{dm}^{3} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$  are assigned to the spin-allowed metal-to-ligand charge transfer (<sup>1</sup>MLCT) transitions. Weaker bands at about 470 nm with  $\epsilon$  value of 2  $\times 10^{3} \cdot \text{dm}^{3} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ are attributed to the spin-forbidden metal-to-ligand charge transfer (<sup>3</sup>MLCT) transitions. Fig.2 is the lower energy <sup>1</sup>MLCT absorption bands (350 - 500 nm) of  $Pt_{12}$  in the different solvents. Absorption spectra of  $Pt_{12}$  in the range of 200-500 nm in the different solvent can be found in Fig.S1 in support information. The shoulder peaks for the lower energy <sup>1</sup>MLCT bands in toluene, DCM, tetrahydrofura (THF) and N,N-dimethylformamide (DMF) solutions are centred at 432, 416, 396 and 387 nm, respectively. These bands are blue-shifted with the increase of solvent polarity. Weak negative solvatochromic absorption in different polar solvent shows that polarity of the complex at the ground states is slightly larger than that at the excited states and is in agreement with MLCT absorption characteristics.[57,69–71]

				•••• P ••• ••• P ••							
Ptn	<sup>a</sup> λ <sub>abs</sub> /nm	<sup>b</sup> λ <sub>em</sub> /nm				×	<sup>ь</sup> τ/μs	<sup>b</sup> φ	${}^{f}\phi_{s}$	<sup>g</sup> K <sub>r</sub> /	<sup>g</sup> K <sub>nr</sub> /
-	(ε/10 <sup>3.</sup> dm <sup>3.</sup> mol <sup>-1.</sup> c	298 K	77 K	<sup>c</sup> Liquid	<sup>d</sup> Solid	<sup>e</sup> Ground				s <sup>-1</sup>	s <sup>-1</sup>
	m⁻¹)			crystal film	film	solid					
Pt <sub>6</sub>	231 (86), 282 (84),	635	593	_	621	622	0.51	6.7 %	1.0 %	1313	1829
	327 (20), 416 (6),									73	412
	474 (3)					χ´					
Pt <sub>12</sub>	230 (82), 283 (78),	641	606	626	624	622	0.55	5.1 %	1.2 %	9272	1725
	328 (19), 416 (5),									7	455
	474 (2)										
Pt <sub>16</sub>	228 (83), 283 (66),	641	594	-	613	616	0.46	4.3 %	0.9 %	9347	2080
	330 (19), 418 (5),									8	435
	465 (2)										

Table 1 Absor	ption and	photoluminescence	spectra of F	۲ <sub>n</sub> .

<sup>a</sup> Measured in dichloromethane solution at room temperature. <sup>b</sup> Measured in degassed dichloromethane solution at room temperature, quantum efficiencies ( $\varphi$ ) were estimated in degassed dichloromethane solution relative to [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> in degassed H<sub>2</sub>O solution ( $\lambda_{ex}$  = 436 nm). <sup>c</sup> Liquid crystalline film was prepared by heating the samples on glass slide into isotropic phase then cooling to liquid crystalline state and finally quenching to room temperature. <sup>d</sup> Solid films were prepared by placing the solid powder between two quartz glasses. <sup>e</sup> Samples were ground by pestle. <sup>f</sup> The absolute quantum efficiencies from solid samples (5%) doped in polymethyl methacrylate (PMMA) . <sup>g</sup> Radiative decay rate, k<sub>r</sub> (k<sub>r</sub> =  $\varphi/\tau$ ) and nonradiative decay rate, k<sub>nr</sub> ((1 -  $\varphi)/\tau$ ) was estimated from the measured quantum yields and lifetimes in DMC solution, assuming that the emissive state is formed with unitary efficiency upon excitation.



Fig.1 UV-visible absorption spectra of  $L_{12}$  and  $Pt_n$  (n = 6,12 and 16) in DCM solution (c  $\approx 10^{-5}$  mol·dm<sup>-3</sup>) at 298 K.



Fig.2 Absorption spectra (350 - 500 nm) of  $Pt_{12}$  in DCM, DMF, THF and toluene solutions (c  $\approx 10^{-5}$  mol·dm<sup>-3</sup>) at 298 K.

The PL spectra of all complexes are measured in degassed DCM solution at room temperature and 77 K (Fig.3). At room temperature in DCM solution, all complexes show the maximum emission peak-value at about 640 nm, indicating that the peripheral alkoxyl chain length of the tetradentate platinum(II) complexes has only a very little affect on photophysical properties. At 77 K, the PL spectra present some little structured emission and are blue-shifted about 40 nm, the maximum PL spectra are at about 600 nm with the shoulder peak at 630 nm. The structureless PL spectra at room temperature indicate that the emission at room temperature predominately comes from <sup>3</sup>MLCT excited stats, while the slightly vibronic structured emission at 77 K suggests that the emission mainly originates from <sup>3</sup>MLCT excited stats with some contribution from excited state of spin-forbidded ligand centered (<sup>3</sup>LC).[2,72–74] The quantum efficiencies of Pt<sub>6</sub>, Pt<sub>12</sub> and Pt<sub>16</sub> in degassed DCM solution are estimated at 6.7 %, 5.1 % and 4.3 %, respectively. The phosphorescence lifetimes of the complexes in degassed DCM solution are 0.51, 0.55 and 0.46 µs, respectively.

Generally, for square-planar platinum(II) complexes the optical properties are usually associated with the aggregated states of the solid and external stimulation. [9,52,53,75] In order to investigate the optical properties in the different solid states, taken  $Pt_{12}$  as an example, we tested the PL spectra in the solid film, ground solid and mesogenic phase (support information Fig.S2). All solid samples show the rigidochromic effect in the different condensed states. The PL spectra of the complexes in the different condensed states are basically identical with the maximum PL peak at about 620 nm (Table.1) and blue shifted about 20 nm compared with PL spectra in dilute DCM solution, indicating that there are no  $\pi$ - $\pi$  and Pt-Pt intermolecular interactions in these tetradentate complexes in the different solid states due to the spacial-hindrance effect (see theoretical calculation section below), because the intermolecular interactions in the solid states will inevitably lead to red-shifted emission compared to dilute DCM solution.[9] Moreover, when the concentration of DCM solution increases from 10<sup>-5</sup> to 10<sup>-3</sup> mol<sup>-dm<sup>-3</sup></sup> the PL spectra of the complex Pt12 remains consistent (support information Fig.S3), suggesting that the emission of the complexes in the solution comes from the monomer and further confirming there are no intermolecular interactions in the complexes.



Fig.3 PL spectra of  $Pt_n$  (n = 6, 12 and 16) in degassed DCM solution (c  $\approx$  10<sup>-5</sup> mol·dm<sup>-3</sup>) at 298 K and 77 K ( $\lambda_{ex}$  = 450 nm).

#### 3.2. Liquid crystal properties

To research the mesomorphic properties of the complexes, polarized optical microscopy (POM) and differential scanning calorimetry (DSC) at a scan rate of 10 °C/min under nitrogen atmosphere were done. For  $Pt_6$  with six carbon chain length and Pt16 with sixteen carbon chains, no liquid crystalline textures were observed during heating and cooling processes by POM measurement. DCS profile of Pt<sub>6</sub> show the transition from glassy state to isotropic state with little enthalpy change values ( $\Delta H = 0.04 \text{ KJ} \cdot \text{mol}^{-1}$ ) in heating process and from isotropic state to glassy state in cooling process (support information Fig.S5). For Pt16, DCS curves exhibit a little complex, Pt<sub>16</sub> changes from the crystal to glassy state in heating process and transforms into isotropic state in further heating process, the opposite transition occurs in the cooling process (support information Fig.S6). Conversely, for Pt12, liquid crystalline textures were clearly observed through POM in heating and cooling processes. When cooling from the isotropic liquid to 89 °C, pseudo focal-conic fan-shaped textures were gradually come out (Fig.4). As depicted in Fig.5, DSC profile of Pt12 in the cooling process shows the isotropic state translates into mesogenic phase at 77.8 °C, which are turned into crystalline state at - 22.0 °C. There is similar phase transition process in the heating process. The range of liquid crystal temperature for Pt12 is - 22.0 to 77.8 °C for heating process and - 34.8 to 87.2 °C for cooling process, showing that the complex has the characteristics of enantiotropic room-temperature metallomesogens. Complex Pt<sub>16</sub>, which have the longer alkyl chains than Pt12, should be liquid crystal complex, but it doesn't have liquid crystal properties. It is rare that the increase of alkyl chain length reduces the liquid crystallinity of the complex, but similar phenomena have been observed in the some literature.[52,76] The detailed thermal data on the phase transition of Pt<sub>6</sub>, Pt<sub>12</sub> and Pt<sub>16</sub> were listed in support information Table S1.



Fig.4 POM texture of  $\mathbf{Pt_{12}}$  on cooling slowly from the isotropic liquid to 88



Fig.5 DSC curve of **Pt<sub>12</sub>**. (Cr = crystal; Col = columnar mesophases; Iso = isotropic liquid).

X-ray diffraction (Fig.6) was conducted to further confirm the mesophase structure of Pt12. The sample was heated to isotropic phase and then cooled to 25 °C at rate of 2 °C/min. X-ray diffraction was executed at 25 °C. There is one intense peak at 34.0 Å and two weak peaks at 19.8 Å and 16.7 Å in the low angle region, which are indexed as  $d_{10}$ ,  $d_{11}$  and  $d_{20}$ reflections. The reciprocal d-spacing ratio value of  $1:\sqrt{3}:2$ complex self-assembles indicates that the into two-dimensional hexagonal column phase. Moreover, the diffuse halo centered at about 4.13 Å should result from the peripheral alkoxyl chains. No obvious diffraction peak at about 3.5 Å is found, showing that there are weaker  $\pi$ - $\pi$  and metal-metal intermolecular interactions and the complexes should be loosely stacked within the columnar structure. Considering half-disc molecular shape of Pt12, we suppose that the neighboring half-disc molecules with alternatively antiparallel fashion stack into one-dimensional column and finally form two-dimensional hexagonal column phase.[77-81] The schematic self-assembly process is shown

in Fig.7. From the result of theoretical calculation, the radius of half-disc molecule is about 25 Å, which is greater than half of the lattice constant a (39.2 Å, obtained from the X-ray diffraction). Hence, we assume that the molecules are packed by intersect antiparallel pattern.



Fig.6 XRD profile of  $Pt_{12}$  at 25 °C. The sample was prepared by cooling from the isotropic phase to 25°C at rate of 2 °C/min.



Fig.7 Hypothetical model diagram of molecules, Pt12, in haxagonal column phase.

#### 3.3. Electrochemical Character

Cyclic voltammetry (CV) was used to investigate the electrochemical properties of the tetradentate complexes. The CV curves measured by at the scan rate of 100 mV<sup>-</sup>S<sup>-1</sup> in anhydrous and degassed DCM solution and detail redox data are given in support information (Table S2). The complexes have the very similar redox properties because the complexes possess the same structure characteristic except for the difference in the carbon chain length. All complexes undergo irreversible oxidation process with peak potential at about 1.0 V (vs Fc /  $Fc^{+}$ ). According to previous reports for the platinum(II) complexes, the oxidation process of the complexes is assigned to oxidation of the center platinum(II) ion, with the substantial contribution from the tetradentate ligand, which is supported by the density function theory (DFT) calculation (vide infra). On the other hand, the reduction process shows two quasi-reversible waves at about -0.9 V and 1.4 V (VS Fc / Fc<sup>+</sup>), respectively, which is

presumably attributed to reduction on tetradentate ligand moiety. Based on the DFT calculations, the first reduction wave mainly occurs in 2,2'-bipyridine segments with the better  $\pi$  electron-acceptor properties, and the second reduction wave is localized on in one of two symmetrical moieties of tetradentate ligand with 2,2'-bipyridine as the center (see discussion part of theoretical calculation).

#### 3.4. Ambipolar carrier mobility

Carrier mobility plays an important role in organic semiconductor applications. The space charge limited current (SCLC) method was used to investigate carrier transport properties of  $Pt_6$  and  $Pt_{12}$  in amorphous state and mesomorphic phase. The hole-only devices (device structure: ITO/PEDOT:PSS/ $Pt_{12}$  (109 nm)/MoO3/AI) and electron-only devices (device structure: ITO/ZnO/ $Pt_{12}$  (109 nm)/Ca/AI) were prepared to estimate hole and electron carrier mobility. In order to investigate the difference of carrier mobility in the

amorphous state and liquid crystal state, the devices based on the amorphous Pt<sub>6</sub> active layer and the devices based on the mesogenic phase of Pt<sub>12</sub> active layer were fabricated. The detailed methods for device manufacture are shown in experimental section. For the devices based on mesogenic active-layer of  $Pt_{12}$ , the unoptimized hole mobility and the electron mobility are  $4.72 \times 10^{-4}$  cm<sup>2</sup>·V<sup>-1</sup>·s<sup>-1</sup> and  $3.08 \times 10^{-4}$  $cm^2 \cdot V^{-1} \cdot s^{-1}$ , respectively. Although carrier mobility is lower than that of the reported metal complexes, we note that the hole and electron mobility are basically the same, suggesting that these tetradentate platinum(II) complexes have ambipolar carrier transport behaviour. There have been some reports about hole transport of metal complexes, but few reports about electron transport for metal complexes.[44,45,55] The property of hole transport is assigned to metal centre of the complexes.[81] taking into consideration of electron affinity of pyridine rings and oxygen atoms in tetradentate ligand, we tentatively attribute the electron transport ability to the tetradentate ligand segment that is assumed to have sever as an electron acceptor. Moreover, carrier mobility are much lower in the devices from the amorphous active-layer of  $Pt_6$ , amorphous state. The hole mobility and the electron mobility are  $6.80 \times 10^{-5}$  $\text{cm}^2 \cdot \text{V}^{\text{-1}} \cdot \text{s}^{\text{-1}}$ , 4.80  $\times$  10  $^{\text{-6}}$   $\text{cm}^2 \cdot \text{V}^{\text{-1}} \cdot \text{s}^{\text{-1}}$ , respectively. The carrier mobility in the amorphous state is two orders of magnitudes smaller than that in mesogenic state. The results are not unexpected, the compared with the devices from mesogenic active-layer of  $Pt_{12}$ , the disordered packing of  $Pt_6$  in amorphous active-layer severely impedes the carrier hopping between neighboring molecules which is considered the key to determining carrier mobility.





Fig.8 Current density vs voltage under pulsed conditions for the device of **Pt<sub>12</sub>** at 298 K: (a) the electron mobility (device structure: ITO/ZnO/**Pt<sub>12</sub>** (109 nm)/Ca/AI) ; (b) the hole mobility (device structure: ITO/PEDOT:PSS/**Pt<sub>12</sub>** (109 nm)/MoO3/AI).

#### 3.5 Theoretical calculation

In order to investigate the molecular structure and electronic properties of these new tetradentate platinum(II) complexes, we design an analogous tetradentate platinum(II) complex, Pt<sub>1</sub>, in which the methoxy groups are substituted for long alkoxyl chains on the periphery of complexes. The molecular structure on the ground state was optimized by using the density functional theory (DFT). The simulated molecular structure for  $Pt_1$  has distorted square planar geometry (Fig.9). The lengths of metal-ligand bond and the chelate angles around platinum atom are in the range of 2.01-2.09 Å and in the range of 79.5-97.7<sup>0</sup>, respectively. The dihedral angles between coordinated benzene rings and pyridine rings are in the range of 15.0-17.2<sup>0</sup>. The two peripheral trimethoxybenzene rings are seriously tilted by about  $40^{\circ}$  with respect to the center moiety of the complex, suggesting that the complexes should be loosely packed during solid and liquid crystal state, which has been confirmed by the solid PL and mesomorphic properties of the complexes discussed above. The time-dependent DFT (TD-DFT) was used to calculate the excited states. As shown in Fig.10, the electron density of HOMO is mainly contributed by central platinum atom with considerable contribution from the two coordinated benzene rings of ligand and little from peripheral uncoordinated phenyl rings. For LUMO, all electron density is mainly located on 2,2'-bipyridine segments. Further, LUMO+1 and LUMO+2 orbits have the similar

electron density contribution. If tetradentate is just divided into two symmetrical moieties through the centre of 2,2'-bipyridine, the electron density of LUMO+1 and LUMO+2 orbits are alternately distributed in one of two symmetrical moieties. Moreover, the results of theorical calculation indicate that the peripheral alkoxy chains have almost no contribution to either HOMOs or LUMOs orbits, which is supported by almost invariable photophysical and electrochemical properties for these complexes.



Fig.9 Simulated molecular structure of Pt1.



Fig.10 Orbital density calculated by DFT for HOMO (a), LUMO (b), LUMO + 1 (c) and LUMO + 2 (d) in DCM solution of  ${\bf Pt_1}$ .

#### 4. Experimental Section

4.1. Instrument

All starting materials were purchased from Adamas and used directly without further purification. Solvent in any reaction was dried prior to use. Polarized optical microscopy (POM) was observed through OPLYMUS BX41. Differential scanning calorimetry (DSC) was carried out on TA Discovery DSC. X-ray diffraction (XRD) was performed on Rigaku SmartLab. <sup>1</sup>H NMR and <sup>13</sup>C NMR were tested by Varian INOVA-400 MHz and 100 MHz spectrometers respectively. Finnigan-LCQDECA Mass spectrometer and Euro Vector EA300 element analyzer were used to gain mass spectrum and elemental analysis data. UV-Vis absorption spectra got from Perkin Elmer Lambda 950 spectrophotometer at room temperature. Photoluminescence spectra and phosphorescence lifetime were both fetched from Horiba Fluorolog-4 spectrophotometer, and the solutions were degassed carefully by more than three freeze-pump-thaw cycles before measuring. Absorption and photoluminescence spectra both measured in degassed dichloromethane solution. There is an equation for calculating the relative quantum efficiency, which is  $\varphi_s = \varphi_r (A_r/A_s)(n_s/n_r)^2(I_s/I_r)$ . In the equation, r stand for the reference substance  $[Ru(bpy)_3]Cl_2$  (in degassed aqueous solutions,  $\phi_r = 0.042$ ), and s stand for the samples. A is the absorbance of sample. n is the refractive index of solvent ( $n_s = 1.4244$ ,  $n_r = 1.3325$ , 298K). *I* is the integral area of emission. Horiba Fluorolog-4 spectrophotometer equipped with a 150-W ozone-free xenon arc-lamp, monochromator and Quanta- $\phi$  HORIBA Scientific integrating sphere, and FluorEssence<sup>™</sup> software was employed to measure the absolute quantum efficiencies. NANOLED 370 ( $\lambda$  = 370 nm), was used as the excitation source for testing of the excited state lifetime and time-correlated single photo counts (TCSPC) method was used to collect photos.

Density function theory (DFT) calculations for an analogous complex,  $Pt_1$ , were performed in dichloromethane solution. The ground state geometry of  $Pt_1$  was optimized by mean of DFT employed the exchange correlation hybrid functional B3LYP-D3, using 6-311G(d,p) basis set for all non-metallic elements and Stuttgart-Dresden (SDD) effective core potential for platinum. The excited states of  $Pt_1$  were calculated by method of time-dependent DFT (TD-DFT) with the optimized ground state structure, using 6-311G(d,p) ++ basis set for all non-metallic elements and Stuttgart-Dresden (SDD) effective core potential for platinum atom.

Cyclic voltammograms were drawn from the result of tests by Autolab PGSTAT302 voltammetric analyser. A method of three-electrode cell was used to research the electrochemical performance of complexes. A platinum wire and Ag/AgNO<sub>3</sub> electrode (0.001 mol<sup>-3</sup> in degassed anhydrous acetonitrile) are used as counter-electrode and reference electrode respectively. The glassy carbon electrode was the working electrode, and was polished by 0.5 µm Al<sub>2</sub>O<sub>3</sub> powder prior to use. Tetrabutylammonium hexafluorophosphate was added to the sample with a concentration of 0.001 mol<sup>-dm<sup>-3</sup></sup> as a supporting electrolyte at a scan rate of 100 mV's<sup>-1</sup>. Dichloromethane solution was strictly dehydrated and degassed by more than three freeze-pump-thaw cycles. The whole system was purified by argon gas to remove traces oxygen before scanning. All of the electrochemical data reported here were relative to an external ferrocene / ferrocenium reference (Fc / Fc+).

Carrier mobility was measured by space charge limited current (SCLC) method. The device structure: ITO/PEDOT:PSS/Pt<sub>6</sub>(Pt<sub>12</sub>)(109 nm)/MoO3/Al for hole transport and ITO/ZnO/Pt<sub>6</sub>(Pt<sub>12</sub>)(109 nm)/Ca/Al for electron transport. Indium tin oxide (ITO) substrates were cleaned by ultrasonication with soap water, deionized water, acetone, and isopropanol alcohol in sequence. The clean substrates were dried for 4 hours at 80 °C in a vacuum oven and then modified by a UV-ozone treatment for 20 min. Hole-only devices were fabricated as follows, poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) was first filtrated through a 0.45 µm nylon filter and then spin coated on the ITO substrates with a spin speed of 5000 rpm for 60 s to form a thin layer (35 nm). The substrates were baked on a hot plate at 140 °C for 15 min and transferred into the glove box. The active-layer of Pt<sub>6</sub> and Pt<sub>12</sub> are prepared by spin-coated (1200 rpm, 1 min) on top of the PEDOT: PSS from the solution of  $CH_2CI_2$  (20 mg mL<sup>-1</sup>), and the spin-coated Pt<sub>6</sub> and Pt<sub>12</sub> films were heated to 120 °C for 5 min and then cooled to room temperature at rate of 5 °C/min to form active-layer of amorphous phase and that of mesogenic phase, finally, a 10 nm of MoO<sub>3</sub> layer and Al was evaporated onto the surface of the active layer in turn. The electron-only devices were produced as follows, the ITO substates coated ZnO were prepared by thermal evaporation, the amorphous phase active-layer of Pt<sub>6</sub> and the mesogenic phase active-layer Pt12 of were prepared according to the process mentioned above, finally, Ca and AI electrode were prepared by the thermal evaporation on to top of the active layers in turn. The equation  $J = (9 / 8) \varepsilon_0 \varepsilon_r \mu (V^2/d^3) (\varepsilon_0 = 8.85 \times 10^{-12}$ F/m,  $\varepsilon_r = 3$ ) was used to calculate the mobility. In the equation, J stand for current density,  $\varepsilon_0$  stand for the permittivity of vacuum,  $\varepsilon_r$  stand for the dielectric constant,  $\mu$ stand for mobility, and d stand for the thickness of samples.

#### 4.2 Synthesis

#### 4.2.1. 5-Bromobenzene-1,2,3-triol (a)

The solution of 5-bromo-1,2,3-trimethoxybenzene (1.00 g, 4.05 mmol) in anhydrous dichloromethane (15 ml) was stirred for half an hour at - 70 °C, and boron tribromide (3.35 g, 13.36 mmol) dissolved in DCM (10 ml) was dropwise added. After stirred overnight with slow natural warmup to room temperature, water of zero degrees Celsius was dropwise added to quench the superfluous BBr<sub>3</sub>. The mixture was extraction with ethyl acetate (3 × 50 ml) and water. The organic phase was dried over anhydrous magnesium sulfate. After filtration, the solvent was removed by reduced pressure evaporation to obtain compound **a** as gray-yellow solid (0.821 g, 99 %). This compound applied to the next reaction directly without further purification.

#### 4.2.2. 5-Bromo-1,2,3-tris(hexyloxy)benzene (b<sub>6</sub>).

5-Bromobenzene-1,2,3-triol (a) (1.00 g, 4.88 mmol), bromohexane (2.66 g, 16.10 mmol) and potassium carbonate (4.04 g, 29.27 mmol) were added to a dry Schlenk flask with N,N-dimethylformamide (30 ml). The mixture was stirred and heated to 80 °C for 48 hours, under nitrogen atmosphere. After cooling to room temperature, the mixture was extracted with DCM (3 × 30 ml). The organic layer was washed by water for another 3 times to remove the residual DMF, and dried with magnesium sulfate. The filtrate was rotary evaporated to get rid of solvent. The residue was purified by column chromatography, which is filled with silica gel, to gain light white liquid (1.49 g, 67 %). The eluent was PE:EA = 30:1 (V:V) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  = 6.67 (2H s), 3.92 (6H dd, J = 8.2, 4.7 Hz), 1.91 – 1.66 (6H m), 1.47 (6H d, J = 6.6 Hz), 1.42 – 1.24 (12H m), 0.90 (9H t, J = 6.8 Hz).

#### 4.2.3. 5-bromo-1,2,3-tris(dodecyloxy)benzene (**b**<sub>12</sub>).

The synthetic method of the substance is the same as  $\mathbf{b}_{6}$ .

The yield of yellow solid was 69 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  = 7.41 (2H d, *J* = 8.5 Hz), 6.88 (2H d, *J* = 8.6 Hz), 6.69 (2H s), 4.12 - 3.84 (6H m), 1.94 - 1.65 (6H m), 1.56 - 1.41 (6H m), 1.41 - 1.14 (48H m), 0.88 (9H t, *J* = 6.7 Hz).

#### 4.2.4. 5-bromo-1,2,3-tris(hexadecyloxy)benzene (**b**<sub>16</sub>).

The synthetic method of the substance is the same as **b**<sub>6</sub>. The yield of yellow solid was 68 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  = 7.40 (2H d, *J* = 8.6 Hz), 6.87 (2H d, *J* = 8.5 Hz), 6.69 (2H s), 4.01 (12H dd, *J* = 12.2, 5.9 Hz), 1.92 – 1.64 (12H m), 1.47 (12H d, *J* = 7.0 Hz), 1.28 (144H d, *J* = 16.5 Hz), 0.88 (18H t, *J* = 6.6 Hz).

#### 4.2.5. 3',4',5'-tris(hexyloxy)-[1,1'-biphenyl]-4-ol (c<sub>6</sub>).

A mixture of 5-Bromo-1,2,3-tris(hexyloxy)benzene (**b**<sub>6</sub>) (0.80 g, 1.75 mmol), (4-hydroxyphenyl)boronic acid (0.29 g, 2.10 mmol), potassium carbonate (0.48 g, 3.50 mmol), tetrakis(triphenylphosphine)palladium (0.40 g, 0.35 mmol), tetrahydrofuran (10 ml) and water (5 ml) was added to a Schlenk tube. The mixture was stirred and refluxed under nitrogen for 48 hours. On cooling to room temperature, the mixture was extracted with DCM (3 × 30 ml). The organic layer was dried over magnesium sulfate and filtered. After removing the solvent, column chromatography was used to get pale yellow liquid (0.44 g, 53 %), and PE:EA = 6:1 (V:V) was used as eluent. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  = 7.37 (2H d, J = 8.4 Hz), 6.89 (2H d, J = 8.5 Hz), 6.69 (2H s), 4.12 – 3.95 (6H m), 1.88 – 1.74 (6H m), 1.58 – 1.45 (6H m), 1.40 – 1.22 (12H m), 0.89 (9H t, J = 6.5 Hz).

#### 4.2.6. 3',4',5'-tris(dodecyloxy)-[1,1'-biphenyl]-4-ol (c<sub>12</sub>).

The synthetic method of the substance is the same as  $c_6$ . The yield of yellow solid was 52 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  = 7.41 (2H d, J = 8.5 Hz), 6.88 (2H d, J = 8.6 Hz), 6.69 (2H s), 4.12 - 3.84 (6H m), 1.94 - 1.65 (6H m), 1.56 - 1.41 (6H m), 1.41 - 1.14 (48H m), 0.88 (9H t, J = 6.7 Hz).

#### 4.2.7. 3',4',5'-tris(hexadecyloxy)-[1,1'-biphenyl]-4-ol (**c**<sub>16</sub>).

The synthetic method of the substance is the same as  $c_6$ . The yield of yellow solid was 52 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$  = 7.40 (2H d, *J* = 8.6 Hz), 6.87 (2H d, *J* = 8.5 Hz), 6.69 (2H s), 4.01 (12H dd, *J* = 12.2, 5.9 Hz), 1.92 – 1.64 (12H m), 1.47 (12H d, *J* = 7.0 Hz), 1.28 (144H d, *J* = 16.5 Hz), 0.88 (18H t, *J* = 6.6 Hz).

#### 4.2.8.

## 6,6'-bis((3',4',5'-tris(hexyloxy)-[1,1'-biphenyl]-4-yl)oxy)-2,2'-bi pyridine $(L_6)$ .

A mixture of 3',4',5'-tris(hexyloxy)-[1,1'-biphenyl]-4-ol ( $c_6$ ) (0.50 g, 1.06 mmol), 6,6'-dibromo-2,2'-bipyridine (0.13 g, 0.42 mmol), 1-methylimidazole (0.03 g, 0.42 mmol), potassium carbonate (0.23 g, 1.70 mmol), cuprous iodide (0.02 g, 0.08 mmol) and anhydrous toluene (10 ml) was added to a dry Schlenk tube. The mixture was stirred and heated to 120 °C under nitrogen for 48 hours. After cooling to room temperature, extracted and dried, the mixture was purified by column chromatography (PE:EA = 10:1) to gain yellow liquid (0.20 g, 42 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  = 7.90 (2H dd, J = 13.3, 7.1 Hz), 7.70 (2H dd, J = 9.6, 6.3 Hz), 7.59 (4H d, J = 8.5 Hz), 7.26 (4H d, J = 8.6 Hz), 7.20 (2H d, J = 7.8 Hz), 6.87 (2H d, J = 8.1 Hz), 6.80 (4H s), 4.04 (12H dt, J = 17.1, 6.5 Hz), 1.96 – 1.65 (12H m), 1.51 (12H d, J = 4.7 Hz), 1.35 (24H d, J = 3.2 Hz), 1.00 – 0.78 (18H m).

## 4.2.9.

### 6,6'-bis((3',4',5'-tris(dodecyloxy)-[1,1'-biphenyl]-4-yl)oxy)-2,2'bipyridine (**L**<sub>12</sub>).

The synthetic method of the substance is the same as L<sub>6</sub>. The yield of brown solid was 44 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  = 7.92 (2H d, *J* = 7.5 Hz), 7.72 (2H t, *J* = 7.9 Hz), 7.59 (2H d, *J* = 8.7 Hz), 7.26 (4H t, *J* = 4.3 Hz), 6.88 (2H d, *J* = 8.2 Hz), 6.79 (2H s), 4.01 (12H ddd, *J* = 21.8, 14.0, 6.6 Hz), 1.95 – 1.69 (12H m), 1.49 (12H d, *J* = 5.6 Hz), 1.26 (96H s), 0.95 – 0.77 (18H m).

#### 4.2.10.

### 6,6'-bis((3',4',5'-tris(hexadecyloxy)-[1,1'-biphenyl]-4-yl)oxy)-2, 2'-bipyridine (**L**<sub>16</sub>).

The synthetic method of the substance is the same as L<sub>6</sub>. The yield of brown solid was 41 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  = 8.05 (2H s), 7.91 (2H d, *J* = 7.5 Hz), 7.71 (2H t, *J* = 7.8 Hz), 7.59 (2H d, *J* = 8.5 Hz), 7.34 – 7.21 (4H m), 6.87 (2H d, *J* = 8.1 Hz), 6.79 (4H s), 4.07 (12H tt, *J* = 20.8, 6.7 Hz), 1.83 (12H d, *J* = 7.6 Hz), 1.49 (12H d, *J* = 5.0 Hz), 1.26 (144H s), 0.94 – 0.79 (18H m).

#### 4.2.11.

Pt-6,6'-bis((3',4',5'-tris(hexyloxy)-[1,1'-biphenyl]-4-yl)oxy)-2,2'bipyridine (**Pt**<sub>6</sub>).

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6,6'-bis((3',4',5'-tris(hexyloxy)-[1,1'-biphenyl]-4-yl)oxy)-2,2'-bi pyridine (L<sub>6</sub>) (0.2g, 0.18 mmol), K<sub>2</sub>PtCl<sub>4</sub> (0.09 g, 0.22 mmol) and glacial acetic acid (10 ml) was sealed in a Schlenk tube and refluxed under nitrogen for 48 hours. After extracted, dried and filtrated, the filtrate was reduced pressure evaporated to remove solvent. The pure viscous orange liquid (0.17 g, 73 %) was got from column chromatography (PE:EA = 1.5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  = 8.15 (2H s), 7.97 (2H q, J = 8.2 Hz), 7.66 (2H d, J = 7.6 Hz), 7.39 (4H d, J = 8.3 Hz), 7.33 -7.27 (2H m), 6.84 (4H d, J = 9.8 Hz), 4.10 -3.71 (12H m), 1.92 - 1.63 (12H m), 1.42 - 1.18 (36H m), 0.89 (18H t, J = 6.7 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm): 155.6, 153.3, 153.2, 153.1, 152.4, 140.0, 138.3, 137.2, 136.0, 136.5, 126.1, 122.1, 117.0, 115.6, 105.6, 105.0, 77.4, 77.0, 76.7, 73.4, 69.1, 31.7, 30.3, 29.7, 25.8, 22.7, 14.1. HRMS (ESI+) cacld for [M + Na]<sup>+</sup>: 1308.6556; found: m/z = 1308.6556. Elem. Anal. Cacld for  $C_{70}H_{94}N_2O_8Pt$  (1285.6658): C 65.35, H 7.36, N 2.18; found C 65.27, H 7.21, N 2.12.

#### 4.2.12.

Pt-6,6'-bis((3',4',5'-tris(dodecyloxy)-[1,1'-biphenyl]-4-yl)oxy)-2, 2'-bipyridine (**Pt**<sub>12</sub>).

The synthetic method of the substance is the same as Pt<sub>6</sub>. The yield of orange solid was 71 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  = 8.14 (2H s), 7.88 (2H t, *J* = 7.9 Hz), 7.53 (2H d, *J* = 7.6 Hz), 7.40 (2H d, *J* = 8.4 Hz), 7.32 (2H d, *J* = 8.4 Hz), 7.27 (2H d, *J* = 4.4 Hz), 6.83 (4H s), 3.87 (12H dd, *J* = 29.4, 22.9 Hz), 1.79 – 1.56 (12H m), 1.31 (108H d, *J* = 35.4 Hz), 0.98 – 0.75 (18H m). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 156.0, 153.6, 153.3, 153.1, 152.4, 140.0, 138.3, 137.2, 136.0, 135.7, 126.0, 122.3, 116.7, 115.9, 115.6, 105.0, 77.3, 77.0, 76.7, 73.4, 68.9, 37.1, 31.9, 30.4, 29.7, 29.5, 27.1, 26.2, 22.7, 19.7, 14.1. HRMS (ESI+) cacld for [M + Na]<sup>+</sup>: 1813.2190; found: m/z = 1813.2190. Elem. Anal. Cacld for C<sub>106</sub>H<sub>166</sub>N<sub>2</sub>O<sub>8</sub>Pt (1790.2292): C 71.06, H 9.34, N 1.56; found C 71.01, H 9.22, N 1.51.

#### 4.2.13.

Pt-6,6'-bis((3',4',5'-tris(hexadecyloxy)-[1,1'-biphenyl]-4-yl)oxy) -2,2'-bipyridine (**Pt**<sub>16</sub>).

The synthetic method of the substance is the same as  $Pt_6$ . The yield of orange solid was 74 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$  = 8.16 (2H s), 8.04 (2H t, *J* = 7.9 Hz), 7.73 (2H d, *J* = 7.7 Hz), 7.43 (2H d, *J* = 8.5 Hz), 7.39 (2H d, *J* = 8.4 Hz), 7.29 (2H d, *J* = 8.2 Hz), 6.81 (4H s), 3.86 (12H dd, J = 29.3, 22.8 Hz), 1.79 – 1.58 (12H m), 1.26 (156H s), 0.88 (18H t, J = 6.7 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 155.7, 155.7, 153.4, 153.3, 153.1, 152.4, 140.0, 138.3, 137.2, 136.00, 126.1, 122.2, 122.1, 122.1, 115.6, 105.0, 77.3, 77.2, 77.0, 76.7, 73.4, 68.9, 32.0, 30.4, 30.0, 30.0, 29.8, 29.8, 29.7, 29.6, 29.5, 29.4, 26.2, 22.7, 14.2. HRMS (ESI+) cacld for [M + Na]<sup>+</sup>: 2149.5946; found: m/z = 2149.5952. Elem. Anal. Cacld for C<sub>130</sub>H<sub>214</sub>N<sub>2</sub>O<sub>8</sub>Pt (2126.6048): C 73.37, H 10.14, N 1.32; found C 73.30, H 10.02, N 1.27.

#### **5** Conclusion

A new kind of tetradentate platinum(II) complexes were synthesized. The columnar metallomesogen based on the tetradentate ligand was obtained by carefully balancing the number and length of alkoxyl chains around platinum(II) complex. The complex shows ambipolar carrier transport property in columnar mesogenic phase. Our results provide a possible access to achieving ambipolar carrier transport in the single material.

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