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# New phosphorescent platinum(II) complexes with tetradentate C\*N^N\*C ligands: liquid crystallinity and polarized emission<sup>†</sup>

Shilin Zhang, Kaijun Luo,\* Hao Geng, Hailiang Ni, Haifeng Wang\* and Quan Li\*

New phosphorescent, liquid crystalline cyclometalated tetradentate platinum complexes ( $Pt-L^{16}$ ,  $Pt-L^{12}$  and  $Pt-L^6$ ) based on the tetradentate C\*N^N\*C ligands (C\*N^N\*C = 6,6'-bis(4-(alkoxy)-phenoxy)-2,2'-bipyridine) are designed and synthesized. Their crystal structure, and photophysical, electrochemical and liquid crystal characteristics were investigated. The X-ray structure of  $Pt-L^{12}$  shows a severe distortion of this complex towards a tetrahedral geometry. All complexes are emissive both in degassed solution and in the solid state at room temperature with emission maxima in the red region of the spectrum.  $Pt-L^{16}$  and  $Pt-L^{12}$  show monotropic smectic liquid crystal characteristics. Moreover, these liquid crystal complexes can be aligned on a rubbed nylon-6 glass substrate and produce polarized emission with a dichroic ratio of 5.1.

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## Introduction

Cyclometalated platinum(II) complexes (ionic or neutral) have received a great deal of attention in the past two decades because of their numerous potential applications in biological sensing and imaging,<sup>1</sup> photocatalysis,<sup>2</sup> cation recognition,<sup>3</sup> as well as pH sensing.<sup>4</sup> In particular, the cyclometalated complexes of platinum as highly efficient phosphorescent materials in organic light-emitting diodes (OLEDs)<sup>5</sup> have always been extensively investigated because these materials are capable of harvesting both singlet and triplet excitons arising from the strong spin-orbital coupling. In general, there are three main coordination patterns for such cyclometalated platinum complexes: bidentate,<sup>6</sup> tridentate<sup>7</sup> and tetradentate.<sup>8</sup> Very recently, rigid tetradentate platinum(II) complexes have drawn much attention.8 The tetradentate complexes have obvious merits compared with the bidentate and tridentate platinum(II) complexes. The rigid cyclic configuration of tetradentate platinum(II) complexes in which the vibrational deformation of the platinum(II) center and coordinated atoms is confined can improve the thermal stability and decrease the non-radiative vibrational pathways, resulting in a high photoluminescent quantum yield (PLQY).5,9 OLEDs fabricated by using tetradentate plantinum(II) complexes as a triplet dopant

5 Jingan Road, Chengdu 610068, China. E-mail: Luo-k-j007@163.com

usually have higher device efficiency than those using bidentate or tridentate platinum(II) complexes as an emitter.<sup>5,8,10</sup> Additionally, the intermolecular  $\pi \cdots \pi$  and Pt $\cdots$ Pt interactions in the square planar platinum(II) complexes facilitate the formation of metal-containing liquid crystals (metallomesogens) which probably are able to conjugate the luminescence properties with the mesomorphic behavior depending on the judicious combination of metals and ligands.<sup>6,7,11</sup> Particularly, platinum-based luminescent metallomesogens with the polarized phosphorescence property have been widely investigated due to their significant advantages and possible applications in optoelectronics.<sup>12</sup> However, all of them are generally based on bidentate or tridentate cyclometalated platinum(II) complexes. Kinoshita et al.13 designed a tetradentate cycloplatinated complex, N,N'-bis(4-n-decyloxy-salicyl-aldehydo)ethylenediaminateplatinum(II)complex(Pt(4-decyloxy)salen), which did not show liquid crystal characteristics in spite of bearing two peripheral alkoxy chains. Nevertheless, a polarized emission was obtained by doping it in a liquid crystal polymer with a dichroic ratio  $(R_{\rm PL})$  of 1.7. As we know, there are no reports about metallomesogens based on tetradentate cyclometalated platinum(II) complexes to date. In this context, here we firstly report a new class of phosphorescent, liquid crystalline cyclometalated platinum complexes containing tetradentate C\*N^N\*C ligands (Pt-L<sup>16</sup>, Pt-L<sup>12</sup>, Pt-L<sup>6</sup>), where C\*N^N\*C is 6,6'-bis(4-(alkoxy)-phenoxy)-2,2'-bipyridine. By introducing two flexible alkoxy chains on the phenoxide moiety connected to the 2,2'-bipyridine fragment, these complexes display thermotropic liquid crystallinity and the range of the transition temperature of metallomesogens can be affected by the length of the

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College of Chemistry and Materials Science, Sichuan Normal University,

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peripheral alkoxy chains. In addition, these tetradentate platinum(II) complexes show a polarized emission in the aligned nylon-6 film at room temperature.

## **Results and discussion**

#### Synthesis

The synthesis of the ligands and the Pt(II) complexes is depicted in Fig. 1. The ligand precursors,  $\mathbf{P}^n$ , were obtained by etherification of excess hydroquinone with 1-bromoalkane under Williamson ether conditions. Another modified Williamson reaction<sup>5</sup> was used to give the ligands,  $\mathbf{L}^n$ . The final platinum(II) complexes, **Pt-L**<sup>*n*</sup>, were prepared by the complexation of  $\mathbf{L}^n$  with K<sub>2</sub>PtCl<sub>4</sub> in glacial acetic acid under reflux.

#### Crystallographic analysis of Pt-L<sup>12</sup>

The crystal structure of Pt-L<sup>12</sup> was determined by single-crystal X-ray diffraction analysis. The detailed crystallographic data and structure refinement parameters are summarized in Table S1 (ESI<sup>†</sup>). The Pt(01)-C(008) (2.005(4) Å), Pt(01)-C(00A) (1.999(4) Å), Pt(01)–N(003) (2.053(3) Å), and Pt(01)–N(002) (2.058(3) Å) bond lengths are similar to the analogous tetradentate platinum complexes.<sup>14</sup> The bond angles of C(00A)-Pt(01)-C(008) and N(003)-Pt(01)-N(002) are 97.95(15)° and 79.59(12)°, respectively. The angles between the plane of the bipyridyl group and the planes of the two benzene rings are 32.43° and 18.37°, respectively, indicating that the molecular structure deviates greatly from the square planar geometry (Fig. 2 top). The molecules arrange as head-to-tail dimers, which are approximately superimposed when viewed from perpendicular to the ac plane. The distance of Pt...Pt in each dimer is 5.101 Å and 5.566 Å between adjacent dimers, which excludes any intermolecular Pt ... Pt interactions. Moreover, the distance between the planes of the proximal molecules is about 3.625 Å, suggesting weak intermolecular  $\pi \cdots \pi$  interactions. Furthermore, the molecules pack in the interdigitation mode of alkoxy chains between two molecules and form a layered structure (Fig. 2 bottom). The interlayer spacing is 27.1 Å, which is equal to the length of the *c* axis in a unit cell.<sup>15</sup>

#### **Photophysical properties**

The primary photophysical data obtained for all  $platinum(\pi)$  complexes are listed in Table 1. Fig. 3 shows UV-visible absorp-



**Fig. 1** Synthesis of tetradentate Pt(ii) complexes. Conditions: (i) 1-bromoalkane, anhydrous alcohol, K<sub>2</sub>CO<sub>3</sub>, 90 °C, 24 h. (ii) 6,6'-Dibromo-2,2'bipyridine, 1-methylimidazole, K<sub>2</sub>CO<sub>3</sub>, Cul, toluene, 120 °C, 2 days. (iii) K<sub>2</sub>PtCl<sub>4</sub>, AcOH, reflux, 2 days.



**Fig. 2** Molecular structure and atomic labeling scheme (50% probability thermal ellipsoids) of  $Pt-L^{12}$  (top) and the crystal packing of  $Pt-L^{12}$  (bottom), viewed from perpendicular to the *ac* plane. The hydrogen atoms are omitted for clarity.

tion and emission spectra of Pt-L<sup>16</sup> in dichloromethane (DCM) solution. The absorption of all complexes follows Beer's law with the complex concentrations ranging from  $10^{-4}$  to 10<sup>-5</sup> mol dm<sup>-3</sup>. The intense absorption bands below 350 nm are assigned to spin-allowed ligand-centered (<sup>1</sup>LC) transitions, which are similar to those from free ligands. In the visible region (360-470 nm), there are weak absorption bands with  $\varepsilon$  values of 2.74–5.08 × 10<sup>3</sup> dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>, which are absent in the corresponding ligands. As depicted in Fig. 4 (left), Table S2 (ESI<sup>†</sup>), these absorption bands display a solvatochromic shift on changing the solvent from DCM to toluene, THF, DMF and benzonitrile, evidencing a charge transfer nature. Furthermore, in terms of molecular orbital analysis based on time-dependent density functional theory (TD-DFT) calculations of Pt-L<sup>16</sup> (discussion below), we tentatively assign these weak bands to the metal-ligand charge-transfer (<sup>1</sup>MLCT), to a certain extent, mixed with a phenoxide moiety ( $\pi$ ) to the bipyridyl group ( $\pi^*$ ) chargetransfer transition, which is also similar to the analogous tetradentate platinum complexes.<sup>5,16</sup> As is the case for most cyclometalated  $Pt(\pi)$  complexes that bear peripheral flexible chains,<sup>6,12,14,16</sup> the length of the alkoxy chains has little influence on the UV-vis absorption and photoluminescence spectra.

All three complexes are luminescent in degassed solution and in the solid state with emission quantum yields in the range of 4.4%-6.5% (in DCM solution) and emission lifetimes ( $\tau$ ) in the range of 0.9–1.4 µs (Table 1). The low quantum yield may be attributed to the fact that the severe distortion of the molecular structure described by the X-ray structure of Pt-L<sup>12</sup>, to a certain extent, gives rise to the deformation of the geometric configuration in the excited state, which could accelerate non-radiative decay.<sup>17</sup> The emission spectrum of Pt-L<sup>16</sup> at room temperature in DCM shows a broad and structureless red emission band centered at 622 nm. Similar to the absorption data, the solvent effect on the emission of Pt-L<sup>16</sup> was also observed (e.g.,  $\lambda_{max}$  of **Pt-L**<sup>16</sup> in benzonitrile at 618 nm is redshifted to 624 nm in toluene) (Fig. 4 right). We tentatively assign the emissions to mixed MLCT (<sup>1</sup>MLCT + <sup>3</sup>MLCT) and ligand centered triplet (<sup>3</sup>LC) excited states.<sup>16</sup>

Table 1 Photophysical data of the platinum(II) complexes

Complex	$\frac{\lambda_{\rm abs}/\rm nm}{(\epsilon/10^3 \rm \ dm^3 \ \rm mol^{-1} \ \rm cm^{-1})^a}$	$\lambda_{ m em}^{\ \ d}/ m nm$					
		298 K <sup>b</sup>	77 K <sup>b</sup>	Solid	Film <sup>c</sup>	$ au^b/\mu { m s}$	$\phi_{_{ m PL}}{}^{e}$
Pt-L <sup>16</sup> Pt-L <sup>12</sup> Pt-L <sup>6</sup>	226 (38.7), 242 (39.0), 278 (29.2), 336 (7.90), 412 (4.34), 470 (2.74) 224 (29.1), 244 (28.1), 278 (19.9), 334 (6.94), 412 (3.92), 470 (2.63) 224 (36.3), 246 (35.0), 276 (25.2), 334 (8.56), 412 (4.92), 472 (3.27)	622 623 626	596 584 578	594 579 558	586 566 579	$0.9 \\ 1.1 \\ 1.4$	4.4% 4.8% 6.5%

<sup>*a*</sup> Measurements were carried out in dichloromethane solution. <sup>*b*</sup> Measured in degassed dichloromethane solution. <sup>*c*</sup> Prepared by 5% doped in PMMA. <sup>*d*</sup> The excitation wavelength of 412 nm was used for all complexes. <sup>*e*</sup> Measured in degassed dichloromethane solution relative to [Ru (bpy)<sub>3</sub>]Cl<sub>2</sub> (excitation wavelength = 436 nm,  $\phi_{lum} = 0.042$ ).



Fig. 3 UV-visible absorption and emission spectra of Pt-L<sup>16</sup> in degassed CH<sub>2</sub>Cl<sub>2</sub> ( $\approx$ 1.2 × 10<sup>-5</sup> mol dm<sup>-3</sup>) at 298 K and 77 K ( $\lambda_{ex}$  = 412 nm).



Fig. 4 UV-visible absorption (left) and emission spectra (right) of Pt-L<sup>16</sup> in different air-equilibrated solvents at 298 K ( $\approx 10^{-5}$  mol dm<sup>-3</sup>,  $\lambda_{ex} = 412$  nm).

For complex Pt-L<sup>16</sup>, independent of the applied concentration ( $\approx 1.2 \times 10^{-6}$ - $10^{-3}$  mol dm<sup>-3</sup>), a unique phosphorescence band at about 622 nm was observed in DCM solution (Fig. S3, ESI<sup>†</sup>), indicating that the emissions of Pt-L<sup>16</sup> in solution clearly originate from the monomer. This is likely owing to the considerable distortion from the planarity induced by the phenoxide fragment, which prevents the intermolecular interactions necessary for excimer formation.<sup>5</sup> Furthermore, these tetradentate complexes show a rigidochromic blue shift of 26-48 nm when a solution sample was cooled to 77 K (Fig. S4, ESI<sup>†</sup>). We note that unlike most bidentate platinum(II) complexes with a square planar geometry, these tetradentate complexes exhibit the rigidochromic effect in the concentrated phases, such as a solid film and a 5% doped PMMA film (Fig. S5, ESI<sup>†</sup>). Comparing their emission peak at about 622 nm in solution, the maximum emission bands show 28–68 nm blue shifts in the solid state and 36–57 nm in the 5% doped PMMA films, respectively. Obviously, the blue-shifted emission in the concentrated state shows monomer emission characteristics, indicating very weak intermolecular interactions in the concentrated phases, which is coincident with the crystal-packing characteristics of the complex **Pt-L**<sup>12</sup> discussed above.

#### **TD-DFT calculations**

Time-dependent density functional theory (TD-DFT) calculations were performed on all complexes Pt-L<sup>16</sup>, Pt-L<sup>12</sup> and Pt-L<sup>6</sup>. The quantum mechanical computer software program BHANDHLYP and B3LYP exchange-correlation functional were used to perform all calculations. The HOMO and LUMO orbitals of Pt-L<sup>16</sup> are shown in Fig. 5, and the rest of the selected molecular orbitals are provided in Fig. S10 (ESI<sup>†</sup>). The results clearly indicate that the HOMO has dominant contributions from the platinum center and the phenoxide groups. The LUMO is almost localized on the bipyridyl moiety. Moreover, neither the HOMO nor the LOMO orbital density is localized on the terminal alkoxy chains, implying that the two peripheral alkoxy chains on phenoxide fragments do not participate in the composition of the frontier molecular orbitals. The calculated absorption spectra are shown in Fig. S2 (ESI<sup>†</sup>) and are generally well consistent with the experimentally measured spectra of three complexes.

#### **Electrochemical properties**

As was just discussed above, the two peripheral alkoxy chains could hardly influence the energy gap of the frontier molecular orbitals. Therefore, here we just take **Pt-L<sup>16</sup>** as a representative to analyse the electrochemical properties of this kind of



Fig. 5 Time-dependent density functional theory (TD-DFT) calculation of the orbital density for HOMO (left) and LUMO (right) of  $Pt-L^{16}$ .



Fig. 6 Cyclic voltammograms of  $Pt-L^{16}$  in DCM solution containing 0.1 mol dm<sup>-3</sup> Bu<sub>4</sub>NPF<sub>6</sub> at a scan rate of 50 mV s<sup>-1</sup>.

complex. The cyclic voltammogram of Pt-L<sup>16</sup> in degassed DCM is shown in Fig. 6. Pt-L<sup>16</sup> shows an irreversible, oxidation peak with the observed peak potential at 0.52 V and this can be attributed to the oxidation of Pt(II) to Pt(III). The oxidation of tetradentate Pt(II) complexes is typically irreversible because of the rapid solvolysis of the resultant platinum(III) species.<sup>14,18</sup> The reduction process of Pt-L<sup>16</sup> also exhibited an irreversible behaviour with the peak potential at -1.52 V, which is presumably assigned to molecular reduction localized on the cyclometalated tetradentate ligand.<sup>2</sup> As the HOMO and LUMO energy levels ( $E_{\rm HOMO}$  and  $E_{\rm LUMO}$ ) can be estimated from the  $E_p^{\text{ox}}/E_p^{\text{red}}$  values based on the empirical equations  $E_{\text{HOMO}} = [-(E_p^{\text{ox}} - 0.14) - 4.8]$  and  $E_{\text{LUMO}} = [-(E_p^{\text{red}} - 0.14) - 4.8]$  eV, in which  $E_p^{\text{ox}}/E_p^{\text{red}}$  is the peak potential of chemically irreversible oxidation/reduction,<sup>19</sup> 0.14 V is the potential of ferrocene vs.  $\mathrm{Ag}/\mathrm{Ag}^{\scriptscriptstyle +}$  and 4.8 eV is the energy level of ferrocene versus the vacuum energy level. Thus the  $E_{HOMO}/E_{LUMO}$  values of -5.17/-3.13 eV for Pt-L<sup>16</sup> were obtained. As a result, Pt-L<sup>16</sup> displays an electrochemical band gap of 2.04 eV, which is in agreement with the optical band gap (2.17 eV) estimated from the absorption spectra.

#### Mesomorphic properties

The mesomorphic properties of the complexes  $Pt-L^{16}$ ,  $Pt-L^{12}$ and  $Pt-L^6$  were determined *via* thermogravimetric analysis (TGA), polarized optical microscopy (POM), differential scanning calorimetry (DSC) as well as variable-temperature X-ray diffraction (XRD). The TGA profiles reveal that these complexes are thermally stable close to 350 °C (Fig. 7, top left). Complex  $Pt-L^6$  with the shortest alkoxy chain length melts directly into the isotropic fluid at 190 °C on heating and no liquid crystalline textures are found in the succeeding cooling process. In contrast, for  $Pt-L^{16}$  and  $Pt-L^{12}$ , the typical thermotropic smectic phase with the focal-conic fan textures is observed by POM on slow cooling from the isotropic liquid (Fig. 7, top right). We note that for  $Pt-L^{16}$  and  $Pt-L^{12}$  no liquid crystal textures emerge on the repeating heating processes, indicating



Fig. 7 TGA thermograms of platinum complexes (top left) and polarized light microphotographs of the smectic mesophases observed on cooling from the isotropic phase at 95 °C (top right) for Pt-L<sup>16</sup>. Bottom left: Heating and cooling DSC curves of Pt-L<sup>16</sup>. Bottom right: Variabletemperature XRD patterns of Pt-L<sup>16</sup> obtained from the cooling process at 140 °C, 95 °C and 25 °C, respectively. Inset shows the magnified XRD patterns at high-angle regions.

that  $\mathbf{Pt}$ - $\mathbf{L}^{16}$  and  $\mathbf{Pt}$ - $\mathbf{L}^{12}$  possess monotropic liquid crystal properties. DSC data of complexes  $\mathbf{Pt}$ - $\mathbf{L}^{16}$ ,  $\mathbf{Pt}$ - $\mathbf{L}^{12}$  and  $\mathbf{Pt}$ - $\mathbf{L}^{6}$  are summarized in Table S5 (ESI†). Like most thermotropic metallomesogens,<sup>12,15,20</sup> the melting and clearing points decrease and the temperature range of the mesophase widens on increasing the length of the aliphatic chain. The range of the mesophase temperature of  $\mathbf{Pt}$ - $\mathbf{L}^{16}$  and  $\mathbf{Pt}$ - $\mathbf{L}^{12}$  is 57–116 °C (Fig. 7, bottom left) and 127–140 °C (Fig. S6, ESI†), respectively.

In order to further confirm the nature of the mesophase of these platinum(II) complexes, powder X-ray diffraction analysis (XRD) at variable temperatures was explored both in heating and in cooling processes. In the heating process, Pt-L<sup>16</sup> only displays crystalline patterns in regions of the phase transition indicated by the DSC thermogram (Fig. S7, ESI†). When cooling down from the isotropic state to 95 °C, the XRD patterns of Pt-L<sup>16</sup> exhibit sharp inner reflections and diffuse outer halos (Fig. 7, bottom right). In the low-angle region, the XRD diffractograms reveal four well-defined peaks (33.45, 16.70, 11.12, 8.34 Å) in a 1:1/2:1/3:1/4 d-spacing ratio that can be indexed to the  $(d_{10})$ ,  $(d_{20})$ ,  $(d_{30})$ , and  $(d_{40})$  reflections of a lamellar structure. In the high-angle region, the XRD pattern reveals a diffuse scattering halo centered at 3.80 Å, which could be attributed to the liquid-like order of the alkoxy chains. As is discussed above, it is further proved that Pt-L<sup>16</sup> forms a monotropic smectic liquid crystal. Pt-L<sup>12</sup> reveals similar mesophase properties (Fig. S8 ESI<sup>†</sup>). The XRD pattern of Pt-L<sup>12</sup> at 25 °C (before heating) indicated that the crystalline phase is a lamellar structure as well, and the *d*-spacing value of the reflection is consistent with that of the single crystal. Furthermore, for Pt-L<sup>12</sup>, the layer spacing calculated from the XRD patterns in the mesomorphic phase is 31.8 Å, which is larger than the



Fig. 8 Polarized PL spectra from Pt-L<sup>16</sup> on an aligned nylon-6 film at room temperature (||: parallel emission light; 1: perpendicular emission light;  $\lambda_{ex} = 412$  nm).

molecule length estimated from the single crystal molecule structure ( $L \approx 24$  Å), indicating that the layer spacing in the smectic phase is formed through the interdigitation arrangement of molten alkoxy chains between molecules by the dipole-dipole interactions.<sup>12,15</sup> Remarkably, layer spacing in the mesomorphic phase is larger than that in the crystalline phase, which is ascribed to the stretched structure of the molten alkoxy chains induced by thermal motion in the mesomorphic phase at higher temperatures.

#### Polarized emission

The polarized emission based on luminescent metallomesogens has attracted a great deal of attention from both academic and industrial research communities.<sup>21</sup> Therefore, various methodologies<sup>12,22</sup> have been developed to prepare the aligned films which are, generally speaking, crucial to achieve polarized emission with a high dichroic ratio. Herein, referring to the reported approach,<sup>22</sup> we prepared the pre-aligned films by spin-coating nylon-6 onto clean glass substrates, then drying at 110 °C, and finally rubbing glass substrates uniaxially with a dust-free cloth. The powder of Pt-L<sup>16</sup> was deposited on the surface of the aligned nylon-6 film, and the film was heated in an isotropic liquid, then subsequently cooled in the liquid-crystal temperature region, and finally quenched to room temperature. As a result, when the polarizer is parallel (||) to the rubbing direction, the emission intensity is much higher than that when the polarizer is perpendicular ( $\perp$ ). The aligned film of **Pt-L**<sup>16</sup> on a rubbed nylon-6 film exhibits polarized emission at 581 nm under polarized photo-irradiation with a dichroic ratio  $(I_{\parallel}/I_{\perp})$  of 5.1 (Fig. 8). PL spectra of the aligned sample at different degrees of polarization are given in Fig. S9 (ESI<sup>+</sup>).

### Conclusions

In summary, a new series of room temperature phosphorescent tetradentate platinum(II) complexes with two attached peripheral alkoxy chains on the phenoxide fragments of the tetradentate ligand were obtained. All complexes are emissive in degassed DCM solutions and the solid state at room temperature. Furthermore, the new complexes Pt-L<sup>16</sup> and Pt-L<sup>12</sup> show monotropic smectic liquid crystal characteristics. Moreover, these liquid crystal complexes can be aligned on a rubbed nylon-6 glass substrate and produce polarized emission with a dichroic ratio of 5.1. This kind of complex may be a promising lead structure for the future development of luminescent liquid crystal materials based on tetradentate cyclometalated complexes, and optimization studies to further improve the photoluminescence quantum yield are in progress.

## **Experimental section**

#### Measurements and materials

All commercially available starting materials were used directly without further purification. The solvents were carefully dried prior to use. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Varian INOVA-400 MHz and 100 MHz spectrometers. Mass spectra were recorded on a Finnigan-LCQDECA Mass spectrometer. Elemental analyses were performed with a Finnigan-LCQDECA microanalyzer. UV-Vis absorption spectra were recorded at room temperature on a Perkin Elmer Lambda 950 spectrophotometer. Time-dependent density functional theory (TD-DFT) calculations based on BHANDHLYP and B3LYP were performed on all three platinum(II) complexes. The photoluminescence (PL) spectra at 298 K and 77 K were recorded on a Horiba Fluorolog-4 spectrophotometer. The samples were degassed by more than three freeze-pump-thaw cycles prior to measurement. Quantum efficiency measurements were carried out at room temperature in a solution of dichloromethane; [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> in degassed aqueous solution (excitation wavelength = 436 nm,  $\phi_{\text{lum}} = 0.042$ )<sup>23</sup> was used as a reference. The equation  $\Phi_{\rm s} = \phi_{\rm r} (A_{\rm r}/A_{\rm s})(n_{\rm s}/n_{\rm r})^2 (I_{\rm s}/I_{\rm r})$  was used to calculate the quantum yields, where s is the quantum yield of the sample, r is the quantum yield of the reference, n is the refractive index of the solvent,  $A_s$  and  $A_r$  are the absorbance of the sample and the reference at the wavelength of excitation and  $I_s$  and  $I_r$  are the integrated areas of emission bands.<sup>24</sup> Phosphorescence lifetime measurements were performed on a Horiba Fluorolog-4 spectrophotometer. The excitation source is NANOLED 370  $(\lambda = 370 \text{ nm})$  and the photo collection adopts the TCSPC (timecorrelated single photo counts) method.

Electrochemical measurements were carried out on a voltammetry analyzer (Model LK2003 from Tianjin Lanlike Instrument Co.) in a 0.1 mol dm<sup>-3</sup> tetrabutylammonium hexafluorophosphate ( $Bu_4NPF_6$ ) DCM solution at a 50 mV s<sup>-1</sup> scan rate under nitrogen protection. Cyclic voltammograms were measured using a three-compartment three electrode cell. A Pt wire was used as the counter-electrode and an Ag/AgNO<sub>3</sub> (0.1 M in acetonitrile) electrode functioned as the reference electrode. The working electrode was glassy carbon. All of the electrochemical data reported here were measured relative to

an external ferrocenium/ferrocene reference (Fc<sup>+</sup>/Fc). TGA was carried out on a TA Discovery TGA. Polarized optical microscopy (POM) was performed on an OPLYMUS BX41. Differential scanning calorimetry (DSC) experiments were performed on a TA Discovery DSC. X-ray diffractions (XRD) were measured on a Rigaku SmartLab (Cu K $\alpha$ ).

#### Synthesis and analytical data

Ligands (L), ligand precursors (P) and cyclometalated platinum complexes (Pt-L<sup>n</sup>) are mentioned in this paper.

**4-(Hexyloxy)phenol (P<sup>6</sup>).** 1-Bromohexane (2.00 g, 0.012 mol) was added to a solution of hydroquinone (1.6 g, 0.015 mol) and potassium carbonate (5.02 g, 0.036 mol) in EtOH (80 ml). The solution was stirred for 24 h at 90 °C. After cooling to room temperature, the mixture was filtered and washed with DCM (2 × 20 ml). The filtrate was rotary evaporated to dryness and the residue was purified by column chromatography on silica using petroleum ether/ethyl acetate (5 : 1) as an eluent to obtain P<sup>6</sup> as a white solid (1.94 g, 82.6%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H} = 0.94$  (3H, t, J = 8.9 Hz, CH<sub>3</sub>), 1.35 (4H, m, CH<sub>2</sub>), 1.46 (2H, m, γ-CH<sub>2</sub>), 1.78 (2H, m, β-CH<sub>2</sub>), 3.93 (2H, t, J = 6.7 Hz, α-CH<sub>2</sub>), 6.80 (4H, m, phenyl).

**4-(Dodecyloxy)phenol (P**<sup>12</sup>). It was synthesized following the preparation procedure of **P**<sup>6</sup>. A white solid of **P**<sup>12</sup> was obtained in 80.6% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  = 0.88 (3H, t, *J* = 6.8 Hz, CH<sub>3</sub>), 1.29 (18H, m, CH<sub>2</sub>), 1.43 (2H, m, γ-CH<sub>2</sub>), 1.75 (2H, m, β-CH<sub>2</sub>), 3.89 (2H, t, *J* = 6.6 Hz, α-CH<sub>2</sub>), 6.77 (4H, m, phenyl).

4-(Hexadecyloxy)phenol (P<sup>16</sup>). It was synthesized following the preparation procedure of P<sup>6</sup>. A white solid of P<sup>16</sup> was obtained in 82.3% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  = 0.88 (3H, t, *J* = 6.8 Hz, CH<sub>3</sub>), 1.29 (24H, m, CH<sub>2</sub>), 1.43 (2H, m, γ-CH<sub>2</sub>), 1.75 (2H, m, β-CH<sub>2</sub>), 3.89 (2H, t, *J* = 6.6 Hz, α-CH<sub>2</sub>), 6.77 (4H, m, phenyl).

6,6'-Bis(4-(hexyloxy)phenoxy)-2,2'-bipyridine (L<sup>6</sup>). This compound was synthesized according to the preparation procedure described by J. Li.<sup>5</sup> Under a nitrogen atmosphere, a dry Schlenk tube was charged with 6,6'-dibromo-2,2'-bipyridine  $(0.20 \text{ g}, 0.64 \text{ mmol}), 4-(\text{hexyl-oxy})\text{phenol} (\mathbf{P}^6) (0.50 \text{ g},$ 2.54 mmol), 1-methylimidazole (0.052 g, 0.64 mmol), potassium carbonate (0.35 g, 2.54 mmol), and anhydrous toluene (10 mL). The solution was degassed by the method of freezepump-thaw cycles for three cycles. Copper(1) iodide (0.025 g, 0.13 mmol) was then added, and the solution was degassed by the method mentioned above for another 3 times, and the vessel was sealed. The mixture was stirred and heated at 120 °C under a nitrogen atmosphere for 2 days. On cooling to room temperature, the mixture was filtered and washed with DCM ( $2 \times 15$  ml). The filtrate was then poured into 100 ml of water and was extracted with DCM (3  $\times$  10 ml). The mixed organic layer was washed with water and brine, dried with magnesium sulfate and filtered. The filtrate was rotary evaporated to dryness. The residue was then purified by column chromatography on silica using DCM/PE (4:5) as an eluent to gain L<sup>6</sup> as a light-grey solid (0.277 g, 80.6%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  = 0.92 (6H, t, J = 7.0 Hz, CH<sub>3</sub>), 1.36 (8H,

m, CH<sub>2</sub>), 1.48 (4H, m, γ-CH<sub>2</sub>), 1.80 (4H, m, β-CH<sub>2</sub>), 3.97 (4H, t, J = 6.6 Hz, α-CH<sub>2</sub>), 6.77 (2H, d, J = 8.1 Hz, pyridyl), 6.93 (4H, d, J = 9.2 Hz, phenyl), 7.11 (4H, d, J = 9.2 Hz, phenyl), 7.67 (2H, t, J = 7.8 Hz, pyridyl), 7.86 (2H, d, J = 7.5 Hz, pyridyl).

**6,6'-Bis**(4-(**dodecyloxy**)**phenoxy**)-2,2'-**bipyridine** (L<sup>12</sup>). It was synthesized following the preparation procedure of L<sup>6</sup>. A lightgrey solid of L<sup>12</sup> was obtained in 78.8% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  = 0.88 (6H, t, *J* = 6.8 Hz, CH<sub>3</sub>), 1.32 (32H, m, CH<sub>2</sub>), 1.47 (4H, m, γ-CH<sub>2</sub>), 1.80 (4H, m, β-CH<sub>2</sub>), 3.97 (4H, t, *J* = 6.6 Hz, α-CH<sub>2</sub>), 6.77 (2H, d, *J* = 8.1 Hz, pyridyl), 6.93 (4H, d, *J* = 9.2 Hz, phenyl), 7.11 (4H, d, *J* = 8.8 Hz, phenyl), 7.67 (2H, t, *J* = 7.8 Hz, pyridyl), 7.86 (2H, d, *J* = 7.5 Hz, pyridyl).

**6,6'-Bis(4-(hexadecyloxy)phenoxy)-2,2'-bipyridine (L<sup>16</sup>).** It was synthesized following the preparation procedure of L<sup>6</sup>. A lightgrey solid of L<sup>16</sup> was obtained in 81.3% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  = 0.88 (6H, t, *J* = 6.4 Hz, CH<sub>3</sub>), 1.26 (48H, m, CH<sub>2</sub>), 1.47 (4H, m, γ-CH<sub>2</sub>), 1.80 (4H, m, β-CH<sub>2</sub>), 3.97 (4H, t, *J* = 6.4 Hz, α-CH<sub>2</sub>), 6.77 (2H, d, *J* = 8.1 Hz, pyridyl), 6.93 (4H, d, *J* = 7.2 Hz, phenyl), 7.11 (4H, d, *J* = 7.1 Hz, phenyl), 7.67 (2H, t, *J* = 7.8 Hz, pyridyl), 7.867 (2H, d, *J* = 7.5 Hz, pyridyl).

Preparation of (C<sub>6</sub>OphObpy)Pt (Pt-L<sup>6</sup>). A mixture of 6,6'-bis (4-(hexyloxy)phenoxy)-2,2'-bipyridine (L<sup>6</sup>) (0.15 g, 0.277 mmol), K<sub>2</sub>PtCl<sub>4</sub> (0.12 g, 0.289 mmol), and glacial acetic acid (10 mL) was degassed and then refluxed under nitrogen for 2 days. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using DCM/PE (1:1.2) as an eluent to gain Pt-L<sup>6</sup> as a yellow solid (0.167 g, 82.3%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H}$  = 0.89 (6H, t, J = 6.4 Hz, CH<sub>3</sub>), 1.32 (8H, m, CH<sub>2</sub>), 1.42 (4H, m, γ-CH<sub>2</sub>), 1.74 (4H, m, β-CH<sub>2</sub>), 3.96 (4H, t, J = 6.5 Hz,  $\alpha$ -CH<sub>2</sub>), 6.70 (2H, dd, J = 8.7, 2.9 Hz, phenyl), 7.17 (2H, d, J = 8.7 Hz, phenyl), 7.29 (2H, d, J = 8.4 Hz, phenyl), 7.45 (2H, d, J = 2.9 Hz, pyridyl), 7.57 (2H, d, J = 7.6 Hz, pyridyl), 7.90 (2H, t, J = 7.9 Hz, pyridyl). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 156.0, 155.0, 153.4, 147.4, 138.2, 126.5, 125.8, 116.5, 115.8, 115.7, 111.5, 77.3, 77.0, 76.7, 68.4, 31.7, 29.6, 25.9, 22.6, 14.1. MS(ESI+) m/z: 756.2371 for  $[M + Na]^+$ . Calcd for  $C_{34}H_{38}N_2O_4Pt$  (733.2479): C 55.65, H 5.22, N 3.82; found C 55.56, H 5.16, N 3.73.

**Preparation of (C**<sub>12</sub>**OphObpy)Pt (Pt-L**<sup>12</sup>). It was synthesized following the preparation procedure of **Pt-L**<sup>6</sup>. A yellow solid of **Pt-L**<sup>12</sup> was obtained in 79.5% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_{\rm H} = 0.88$  (6H, t, J = 6.8 Hz, CH<sub>3</sub>), 1.26 (32H, m, CH<sub>2</sub>), 1.41 (4H, m, γ-CH<sub>2</sub>), 1.74 (4H, m, β-CH<sub>2</sub>), 3.95 (4H, t, J = 6.5 Hz, α-CH<sub>2</sub>), 6.70 (2H, dd, J = 8.7, 3.0 Hz, phenyl), 7.17 (2H, d, J = 8.7 Hz, phenyl), 7.30 (2H, d, J = 8.3 Hz, phenyl), 7.45 (2H, d, J = 3.0 Hz, pyridyl), 7.58 (2H, d, J = 7.5 Hz, pyridyl), 7.91 (2H, t, J = 8.0 Hz, pyridyl). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm): 156.0, 155.0, 153.4, 147.4, 138.2, 126.5, 125.8, 116.4, 115.8, 115.7, 111.5, 77.3, 77.0, 76.7, 68.4, 31.9, 29.7, 29.7, 29.6, 29.5, 29.4, 26.2, 22.7, 14.1. MS(ESI+) *m*/*z*: 924.4250 for [M + Na]<sup>+</sup>. Calcd for C<sub>46</sub>H<sub>62</sub>N<sub>2</sub>O<sub>4</sub>Pt (901.4357): C 61.25, H 6.93, N 3.11; found C 61.16, H 6.85, N 3.04.

**Preparation of (C<sub>16</sub>OphObpy)Pt (Pt-L<sup>16</sup>).** It was synthesized following the preparation procedure of **Pt-L<sup>6</sup>**. A yellow solid of **Pt-L<sup>16</sup>** was obtained in 81.7% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

 $\delta_{\rm H}$  = 0.88 (6H, t, *J* = 6.8 Hz, CH<sub>3</sub>), 1.25 (56H, m, CH<sub>2</sub>), 1.41 (4H, m, γ-CH<sub>2</sub>), 1.74 (4H, m, β-CH<sub>2</sub>), 3.95 (4H, t, *J* = 6.5 Hz, α-CH<sub>2</sub>), 6.70 (2H, dd, *J* = 8.7, 3.0 Hz, phenyl), 7.17 (2H, d, *J* = 8.7 Hz, phenyl), 7.31 (2H, d, *J* = 8.3 Hz, phenyl), 7.45 (2H, d, *J* = 3.0 Hz, pyridyl), 7.60 (2H, d, *J* = 7.6 Hz, pyridyl), 7.93 (2H, t, *J* = 8.0 Hz, pyridyl). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm): 156.0, 155.0, 153.4, 147.4, 138.2, 126.5, 125.8, 116.4, 115.8, 115.7, 111.5, 77.3, 77.0, 76.7, 68.4, 31.9, 29.7, 29.69, 29.7, 29.5, 29.4, 26.2, 22.7, 14.1. MS(ESI+) *m/z*: 1036.5503 for [M + Na]<sup>+</sup>. Calcd for C<sub>54</sub>H<sub>78</sub>N<sub>2</sub>O<sub>4</sub>Pt (1013.5609): C 63.94, H 7.75, N 2.76; found C 63.82, H 7.64, N 2.70.

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