Highly Luminescent Liquid Crystals in Aggregation Based on Platinum(II) Complexes

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ABSTRACT: Luminescent liquid crystals (LLCs) attract considerable attention because of their broad applications in displays, chemosensors, and anti-counterfeiting. However, it remains challenging to achieve a high luminescence efficiency in LCs because of the common aggregation-caused quenching effect. Herein, we demonstrate a facile approach to designing LLCs with a high quantum yield up to 88% by deliberately tuning the aggregation behavior of platinum(II) complexes with alkoxy chains (C_nH_{2n+1}O−). LLCs in hexagonal columnar and rectangular columnar phases are achieved when n = 12 and 16, respectively, as revealed by one-dimensional wide-angle X-ray diffraction and small-angle X-ray scattering. These LLCs are able to not only exhibit strong emission at elevated temperatures but also show attractive reversible vapochromism upon alternative CH2Cl2 and EtOH fuming, which imparts added functions and promises technological utility.

KEYWORDS: liquid crystals, platinum(II) complexes, luminescence, aggregation, vapochromism, chemosensors, anti-counterfeiting, metal···metal interactions

INTRODUCTION

Luminescent liquid crystals (LLCs), which exhibit attractive photoluminescence and mesophase behaviors, have drawn considerable attention because of their great potential for applications in displays, organic light-emitting diodes, and field-effect transistors. Very recently, LLCs have also been patterned for anti-counterfeiting through holographic photopolymerization-induced phase separation. Nevertheless, it still remains a formidable challenge to design LLCs with a high photoluminescence efficiency because of the inherent aggregation-caused quenching (ACQ) effect of the common LC luminophores.

As a solution, it would be reasonable to design LLCs based on AIEgens (i.e., aggregation-induced emission luminogens), because AIEgens are able to exhibit much brighter emission with the increase of the aggregation and, thus, could allow one to tackle the challenges related to the ACQ. To this end, AIEgens such as tetraphenylethene, cyanostilbene, tolane, silole, and thiophene have been employed to design LLCs. Nonetheless, the absolute quantum yield (QY) of these LLCs based on organic AIEgens is still lower than 60% and LLCs with much higher QY are limited.

To address this hurdle, platinum(II) complexes, that are described as Pt(II) complexes, come to our attention because of their much higher QY after molecular aggregation. The square-planar geometry of Pt(II) complexes is in favor of their stacking in the aggregated states through intermolecular Pt···Pt and π–π interactions, which provides LC properties by means of tuning the aggregation behaviors. Furthermore, the Pt···Pt distance can be greatly reduced when meeting with volatile organic compounds (VOCs), giving rise to a redshifted emission by metal–metal–ligand charge transfer (MMLCT). More excitingly, the emission color can go back to the original one after getting rid of the VOCs. Therefore, Pt(II) complexes show a great application potential in reusable chemosensors and advanced anti-counterfeiting. It is also reported that Pt(II) complexes are able to exhibit outstanding electrochemiluminescence properties, promising the development of new emitters for advanced biosensing and immuno-assaying.

Nonetheless, only a few LLCs based on Pt(II) complexes have been reported. For instance, Bruce and co-workers have reported columnar mesophases based on the tridentate N,C,N-coordinated Pt(II) complexes with a QY of 12%. Lodeiro and co-workers have developed multistimuli-responsive LLCs sensitive to temperature, pressure, and VOCs based on...
unsymmetrically four-coordinated Pt(II) complexes, with the associated QY of 20%.32 Che,3 Ziessel,33 and co-workers have reported lyotropic LLCs and thermotropic LLCs based on cationic Pt(II) complexes, though their QY is unknown. Hereto, the QY of LLCs based on Pt(II) complexes is still low except for that (86%) of the cationic cyclometalated Pt(II) complexes reported by Swager and co-workers.34 The high QY in this case is ascribed to the special molecular arrangement mediated by the intermolecular hydrogen bonding interactions.

Herein, we demonstrate a different and robust approach to designing LLCs with high QY up to 88%, by tuning the aggregation behaviors of Pt(II) complexes with alkoxy chains. Highly ordered columnar structures are expected in the assembled Pt(II) complexes because of the greatly boosted intermolecular Pt···Pt and π−π interactions by the square-planar core geometry. On the other hand, distinct mesophases, that is, hexagonal columnar (Colh) and rectangular columnar (Colr) phases are achieved by predesigned modifications of the complex core with different flexible peripheral alkoxy chains (e.g., dodecyloxy and hexadecyloxy chains).

■ EXPERIMENTAL SECTION

Materials and Characterization. Methyl gallate (purity: 98%), trifluoroacetic anhydride (purity: 99%), and diethylene glycol dimethyl ether (diglyme, purity: 99%) are purchased from Adamas Reagent Co., Ltd., China. 2,6-Pyridinedicarbonitrile (purity: 97%) was received from Ark Pharm, United States. 1-Bromohexane (purity: 98%), 1-bromododecane (purity: 98%), 1-bromohexadecane (purity: 97%), and 4-aminopyridine (purity: 98%) are obtained from Aladdin, China. Potassium tetrachloroplatinate(II) (purity: 99%), N,N-diisopropylethylamine (DIPEA, purity: 99%), and potassium tert-butanoate (purity: 98%) are obtained from Beijing Innochem Science & Technology Co., Ltd., China. Potassium carbonate (K2CO3, AR), 2-methoxyethanol, and H2O (3/1 by volume) were acquired from Sinopharm Chemical Reagent Co., Ltd., China. Calcium hydride (CaH2, purity: 98%) was purchased from Energy Chemical Co., Ltd., China. THF was purified via distillation under vacuum after stirring for 2 h in the presence of CaH2. Deionized water was obtained through purification on one ultrapure water machine (CS-S, Wuhan Jibari Technology Co., Ltd., China).

Column chromatography was performed on a 200–300 mesh silica gel to purify the synthesized products. Nuclear magnetic resonance (e.g., 1H NMR, 13C NMR, and 19F NMR) spectra were recorded on a 400 or 600 MHz spectrometer (Ascend, Bruker, Germany) with tetramethylsilane as the internal standard. Elemental analysis was performed on an element analyzer (Vario Microcube, Elementar, Germany). High-resolution mass spectrometry studies were implemented with FT-MS (SolarX 7.0T, Bruker Daltonics, United States). The thermal stability was evaluated on a thermogravimetric analyzer (TGA 4000, PerkinElmer, United States) at a ramp rate of 10 °C/min from 30 to 800 °C. Phase transition temperatures were measured by differential scanning calorimetry (DSC, Q2000, TA Instruments, United States) at a ramp rate of 5 °C/min. Polarized optical microscopy (POM) images were captured using a microscope (Axio Scope. A1, Carl Zeiss, Germany) that was equipped with a hot stage (THMS 600, Linkam, United Kingdom). Optical images were taken when cooling the isotropic liquid samples to room temperature at a ramp rate of 5 °C/min. Small-angle X-ray scattering (SAXS) characterizations were carried out using the BL16B1 beamline at the Shanghai Synchrotron Radiation Facility (SSRF), China. UV−vis absorption spectra were recorded using a spectrometer (Evolution 220, Thermo Fisher, United States). The emission spectra, absolute QY, and lifetime were measured on a spectrofluorometer (FLS1000, Edinburgh Instruments, United Kingdom). Powder X-ray diffractions were characterized with a diffractometer (Smart Lab-SE, Rigaku, Japan).

Chemical Synthesis. To show a proof of concept on the design of LLCs based on Pt(II) complexes, Pt-3OCnH2n+1 (n = 6, 12 and 16) with a square-planar skeleton and three alkoxy tails was designed and synthesized (Scheme 1). 2-Methoxyethanol and H2O (3/1 by volume) were mixed and used as the solvent, PtCl6(DMSO)2.

Scheme 1. Illustration on the Synthesis of Pt(II) Complexes
(DMSO = dimethylsulfoxide) was used as the Pt(II) precursor, and DIPEA was employed as the base. The skeleton consisted of a tridentate ligand (e.g., 2,6-bis(3-(trifluoromethyl)-1H-1,2,4-triazol-5-yl)pyridine) and an ancillary pyridine ligand with a substitution at the position 4. The tridentate ligand and PtCl₂(DMSO)₂ were synthesized according to the procedures reported by De Cola and co-workers (see details in the Supporting Information), (1) and the ancillary ligands with different chain lengths were synthesized through a sequential etherification and amidation procedures. (2)

Synthesis of Methyl 3,4,5-Tris(hexadecyloxy)benzoate (1a). 1-Bromohexane (24.87 g, 81.46 mmol) was added into the stirred solution of methyl gallate (3.00 g, 16.29 mmol) and potassium carbonate (22.52 g, 162.91 mmol) in 2-butanone (100 mL) under the protection of nitrogen gas. After stirring under reflux for 2 h, solids were filtered off and the filtrate was concentrated under vacuum that was subsequently purified by silica gel column chromatography. DCM and petroleum ether (1/1 by volume) were employed as the mobile eluent. The final product was a yellow solid substance (yield: 91%). ¹H NMR (400 MHz, CDCl₃): δ 7.18 (s, 2H), 3.94 (td, 6H), 3.81 (s, 3H), 1.79–1.63 (m, 6H), 1.47–1.35 (m, 6H), 1.31–1.20 (m, 12H), 0.87–0.78 (m, 9H).

Synthesis of Methyl 3,4,5-Tris(dodecylxyloxy)benzoate (1b). The synthesis was similar to the preparation of 1a, and 1-bromododecane was employed as one reactant. The product was a white solid substrate (yield: 86%). ¹H NMR (400 MHz, CDCl₃): δ 7.19 (s, 2H), 3.94 (td, 6H), 3.82 (s, 3H), 1.79–1.62 (m, 6H), 1.45–1.33 (m, 6H), 1.32–1.13 (m, 48H), 0.81 (t, 9H). 19F NMR (400 MHz, CDCl₃): δ −7.54 (d, 2H), 6.97 (s, 2H), 3.93 (dt, 6H), 1.71 (m, 6H), 1.44–1.36 (m, 6H), 1.26 (dd, 12H), 0.83 (t, 9H). ESI-HR-MS (positive scan, m/z): [M + H⁺], calcd 499.3530; found, 499.3529.

Synthesis of the Ancillary Ligand 2b. The preparation was similar to that of 2a, starting from 1b and yielding a white solid substance (yield: 57%). ¹H NMR (400 MHz, CDCl₃): δ 8.48 (d, 2H), 7.77 (s, 1H), 7.52 (d, 2H), 6.96 (s, 2H), 3.96 (q, 6H), 1.77–1.66 (m, 6H), 1.53 (s, 6H), 1.40 (dd, 6H), 1.19 (s, 42H), 0.81 (t, 9H). ESI-HR-MS (positive scan, m/z): [M + H⁺], calcd 751.6347; found, 751.6344.

Synthesis of the Ancillary Ligand 2c. The preparation was similar to that of 2a and 2b, starting from 1c and yielding a white solid substrate (yield: 58%). ¹H NMR (400 MHz, CDCl₃): δ 8.55 (d, 2H), 7.84 (s, 1H), 7.59 (d, 2H), 7.03 (s, 2H), 4.03 (td, 6H), 1.85–1.72 (m, 6H), 1.63 (s, 6H), 1.52–1.43 (m, 6H), 1.26 (s, 6H), 0.88 (t, 9H). ESI-HR-MS (positive scan, m/z): [M + H⁺], calcd 919.8225; found, 919.8223.

Synthesis of Pt-3OC₆H₁₃, Pt-3OC₁₂H₂₅, and Pt-3OC₁₆H₃₂. The tridentate ligand (1.0 equiv), PtCl₂(DMSO)₂ (1.0 equiv), ancillary ligands (e.g., 2a, 2b, or 2c, 1.0 equiv), and 100 μL of DIPEA were added in 20 mL solvent of 2-methoxyethanol and H₂O (3/1 by volume). The reaction mixture was stirred overnight at 83 °C under the nitrogen gas atmosphere. After reaction, the target compound was obtained through column chromatography with silica gel as the stationary phase and DCM/EtOH (25/1 by volume) as the eluent. The final product was a yellow solid substrate (yield: 70%).

Characterization of Pt-3OC₆H₁₃. ¹H NMR (400 MHz, CDCl₃): δ 8.84 (s, 2H), 8.54 (s, 1H), 7.81 (t, 1H), 7.39 (s, 4H), 7.00 (s, 2H), 3.97 (t, 2H), 3.89 (t, 4H), 1.78–1.71 (m, 6H), 1.51–1.41 (m, 6H), 1.34 (dd, 12H), 0.95–0.90 (m, 9H). ¹⁹F NMR (400 MHz, CDCl₃): δ −64.17. ¹³C NMR (400 MHz, CDCl₃): δ 165.88, 160.98, 152.32, 150.99, 150.39, 145.89, 145.45, 145.39, 141.11, 126.41, 119.53, 118.84, 115.87, 104.95, 72.48, 68.16, 30.74, 30.58, 29.34, 28.21, 24.72, 24.64, 21.68, 21.54, 13.07, 12.99. ESI-HR-MS (negative scan, m/z): [M – H⁻], calcd 1038.3366; found, 1038.3347.

Characterization of Pt-3OC₁₂H₂₅. ¹H NMR (400 MHz, CDCl₃): δ 9.00 (s, 2H), 8.38 (s, 1H), 7.89 (s, 1H), 7.61–7.48 (m, 4H), 6.93 (s, 2H), 3.95 (t, 2H), 3.86 (t, 4H), 1.79–1.68 (m, 6H), 1.45 (dd, 6H), 1.28 (d, 48H), 0.89 (t, 9H). ¹⁹F NMR (400 MHz, CDCl₃): δ −64.08. ¹³C NMR (400 MHz, CDCl₃): δ 165.99, 160.89, 152.36, 151.05, 150.41, 145.86, 145.40, 141.44, 141.00, 126.32, 119.51, 116.83, 116.17, 104.92, 72.48, 68.15, 30.96, 28.83–28.61, 28.43–28.33, 28.21–28.19.
Although green and gold colors are also observed at 25 °C for Pt-3OC_{16}H_{33}, cyan blue- and brown-polarized interference colors appear at a high temperature (125 °C, Figure 2b), which are different from those of Pt-3OC_{12}H_{25}. These colors can be correlated with different alignments of LC director relative to crossed polarizers of POM and are characteristics of such optically anisotropic mesophases with spatially varying director fields.

DSC results show that both Pt-3OC_{12}H_{25} and Pt-3OC_{16}H_{33} can show LC phases at room temperature. As shown in Figure 3a, there is one exothermic peak at 139 °C for Pt-3OC_{16}H_{33} during the first run of cooling, which is ascribed to the liquid-mesophase transition in combination with the POM results. Upon heating, the mesophase-liquid transition peak shifts to 153 °C. Differently, one finds two exothermic peaks when cooling Pt-3OC_{16}H_{33} from 180 to −30 °C, in which the peak at 129 °C is ascribed to the liquid-mesophase transition, while another peak at 15 °C may correspond to the crystallization of the hexadecyl chains (Figure 3b). This assumption is supported by the large enthalpy (24.1 J/g) during phase transition and the closer alkyl chain packing from 0.46 to 0.44 nm upon cooling by liquid nitrogen (Figure S28a). The crystallization of hexadecyl chain can show an enthalpy as large as 163 J/g (Figure S29). However, there is no change in the POM textures when cooling Pt-3OC_{16}H_{33} by liquid nitrogen (Figure S28b). Upon heating, the low-temperature transition peak shifts to 22 °C and the mesophase-liquid transition peak shifts to 142 °C, respectively. Both the mesophase-liquid transition temperature and enthalpy are much smaller than those of the crystalline Pt-3OC_{16}H_{33} during the melting because of the less ordered structures of LCs (Figure S27).

To probe the symmetry of the LC phases, 1D wide-angle X-ray diffraction (WAXD) and SAXS characterizations were performed. Figure 4 illustrates the 1D-WAXD results. As shown in the wide-angle region, the diffraction peak corresponds to a close intermolecular stacking of Pt-3OC_{16}H_{33} with a d-spacing of 0.33 nm, which agrees well with the intermolecular distance of Pt(II) complexes reported by Yam and co-workers.\footnote{37} In addition, a broad halo is clear, which is indicative of the amorphous packing of alkyl chains. Although a diffraction peak corresponding to the intermolecular stacking is also observed in the 1D-WAXD pattern of Pt-3OC_{16}H_{33}, the packing of hexadecyl chains exhibits a diffraction peak rather than a typical halo at room temperature due to that the crystallization of hexadecyl chains can occur near the room temperature according to the DSC measurements. It is worth noting that there is another diffraction peak with a d-spacing of 1.05 and 1.06 nm in the WAXD patterns for Pt-3OC_{12}H_{25} and Pt-3OC_{16}H_{33}, respectively, which implies the formation of ordered structures. However, the lattice parameters need to be further identified using SAXS analysis. As shown in Figure 5a, four diffraction peaks are clear in the small-angle region of SAXS patterns for Pt-3OC_{12}H_{25}, corresponding to the d-spacings (d_{hk0}) of 3.64, 2.10, 1.82, and 1.37 nm and being indexed to the (100), (110), (200), and (210) crystal planes based on eq 1, respectively. The hexagonal columnar (Col_{h}) LC phase is confirmed based on the reciprocal d-spacing ratio, that is, 1: 1/\sqrt{3}: 1/2: 1/\sqrt{7}, \footnote{38} and the lattice parameter a equals 4.20 nm.

\[ 1/d_{hk0}^2 = 4(h^2 + k^2 + 2hk)/3a^2 \]  

where \( h, k, \) and \( l \) represent the Miller indices.
By comparison, clearly distinct peaks are observed for Pt-3OC16H33 during the SAXS analysis (Figure 5b). Four diffraction peaks in the small-angle region are observed, corresponding to the $d$-spacings of 3.73, 3.23, 2.37, and 1.82 nm and being indexed to (100), (010), (110), and (200) crystal planes according to eq 2, respectively. Thus, a rectangular columnar (Colr) LC phase is confirmed, similar to how it was identified in previous reports on the basis of the reciprocal $d$-spacings ratio, that is, 1:1/1.2:1/1.6:1/2. In addition, the lattice parameters, that is, $a$ and $b$ are calculated to be 3.73 and 3.23 nm, respectively, from the spacings of $d_{100}$ and $d_{010}$.

$$\frac{1}{d_{hkl}^2} = h^2/a^2 + k^2/b^2$$

Both Pt-3OC12H25 and Pt-3OC16H33 exhibit columnar LC phases due to that the square-planar geometry of Pt(II) complexes favors the molecular stacking in the aggregated states through intermolecular Pt···Pt and $\pi$−$\pi$ interactions. However, distinct LC phases (i.e., Colh and Colr phases) are produced by modifying the complex core with different flexible peripheral alkoxy chains. The hexagonal packing array of Pt-3OC12H25 can be observed in most Pt(II) complexes which can form LC phases, metalgels, and supramolecular structures. Compared with Pt-3OC12H25, Pt-3OC16H33 with much longer flexible peripheral chains generates a different columnar LC phase with the rectangular packing lattice. The Pt-3OC16H33 molecules are unlikely to be coplanar because of the large steric perturbation by longer chains. To reach close packing and thus minimize the free energy, the long alky chains with increased internal freedom of rotation may extend in one direction when confined by the metal core, resulting in the formation of slanted columns, in favor of packing in the rectangular columnar phase. Similar LC phase transition behaviors have been reported by Kishikawa, Zhang, and co-workers.

Photophysical Properties. Photophysical properties of the Pt(II) complex-based LLCs are studied. As observed in other Pt(II) complexes reported by De Cola and co-workers and in the crystalline Pt-3OC6H13 (Figure S30), intense absorption of these LLCs peaked at 305 nm is clear in the UV wavelength region when dissolved in CH2Cl2.
Figure 6. Absorption and emission spectra of (a) Pt-3OC_{12}H_{25} and (c) Pt-3OC_{16}H_{33} in CH_{2}Cl_{2} (concentration: 10^{-5} M) at room temperature; emission spectra of (b) Pt-3OC_{12}H_{25} and (d) Pt-3OC_{16}H_{33} in powder. Excitation wavelength: 365 nm.

Figure 7. Emission intensity against temperature of (a) Pt-3OC_{12}H_{25} and (b) Pt-3OC_{16}H_{33} when excited by 365 nm UV light. Insets: LLCs in vials at room temperature and 170 °C under UV light, respectively.

Figure 8. Emission spectra of (a) Pt-3OC_{12}H_{25} and (b) Pt-3OC_{16}H_{33} in different forms when fuming with CH_{2}Cl_{2} and EtOH, respectively. Excitation wavelength: 365 nm. Inset: Color change under ambient light during the fuming process. (c,d) Reversible vapochromic patterns written on the filter paper and viewed under ambient light: (c) Pt-3OC_{12}H_{25}, (d) Pt-3OC_{16}H_{33}. Scale bars: 1 cm.
after treating the Y-form powder with CH2Cl2 vapor (Figure O-form powder is smaller, and the di-gap.52,54 The emission peak of can be ascribed to the MMLCT that is boosted by the Pt to yellow color to their powder. These yellow color emissions aggregation peaks at 588 and 592 nm, respectively, gives rise to yellow color to their powder. These yellow color emissions can be ascribed to the MMLCT that is boosted by the Pt interaction.26,45 Interestingly, a significant redshift of emission is observed for these LLCs when aggregated (Figure eb,d). The emission of Pt-3OC12H25 and Pt-3OC16H33 in aggregation peaks at 588 and 592 nm, respectively, gives rise to yellow color to their powder. These yellow color emissions can be ascribed to the MMLCT that is boosted by the Pt interaction.26,45 Interestingly, a significantly redshifted emission is observed for these LLCs when aggregated (Figure 6b,d). The emission of Pt-3OC12H25 and Pt-3OC16H33 in aggregation peaks at 588 and 592 nm, respectively, gives rise to yellow color to their powder. These yellow color emissions can be ascribed to the MMLCT that is boosted by the Pt interaction.26,45 Interestingly, a significantly redshifted emission is observed for these LLCs when aggregated (Figure S31), in consistency with the reports from Che, Yam, DeCola, Wang and co-workers.47−50 Excitingly, these LLCs in aggregation exhibit a high QY, that is, 88% for Pt-3OC12H25 and 83% for Pt-3OC16H33, respectively. Besides, they show a relatively long photoluminescence lifetime, that is, 443 and 467 ns, respectively (Figure S32). It is worth noting that the photoluminescence QY and lifetime of the Pt(II) complexes are highly dependent on aggregation states and their environment.27 Although the emission intensity is decreased upon heating, these LLCs can maintain their emission properties in the mesophase at high temperature (Figure 7).

Reversible Vapochromism. These Pt(II) complexes show reversible vapochromism, as previously reported for other Pt(II) complexes.51−53 When dried, they are yellow solid substances (referred to as Y-form) and exhibit yellow color emissions upon 365 nm light irradiation at room temperature. However, the emission color turns to orange within several minutes when the powder is exposed to the CH2Cl2 vapor (Figure 8a,b). The orange solid state is referred to as O-form. The redshift of the emission color is because of the reduced Pt···Pt distance in the presence of low molecular weight halohydrocarbons such as CH2Cl2 50,52 It is reported that the CH2Cl2 molecules can enter into the crystal lattice of the complexes via C−H(CH2Cl2)···π interactions, resulting in a decrease of the Pt···Pt distance and HOMO−LUMO energy gap.52,54 The emission peak of Pt-3OC12H25 and Pt-3OC16H33 is significantly redshifted from 588 and 592 to 612 and 601 nm (Figure 8a,b) upon CH2Cl2 fuming, respectively, although the QY decreases from 88 and 83 to 52 and 73%. Compared with these LLCs, the crystalline Pt-3OC12H11 shows a larger redshift for 29 nm in emission (Figure S33). It seems that complexes with shorter chains are more sensitive to CH2Cl2 vapor, probably due to that the shorter side chains show less influence on the intermolecular stacking. Excitingly, the emission of all complexes can return to the original state upon EtOH fuming. This process is fully reversible for at least seven cycles (Figure S34). Powder WAXD analyses show that the d-spacing of the O-form powder is smaller, and the diffraction peaks are greater after treating the Y-form powder with CH2Cl2 vapor (Figure S35), indicating that the molecular packing of the complexes tends to be closer and more ordered.52−54 After fuming by EtOH, the O-form is regenerated.

The reversible vapochromism of these LLCs shows a great application potential in vapor sensing and anti-counterfeiting. For instance, reversible vapochromic patterns (e.g., “Pt(II)” and “LLCs”) can be achieved by writing the LLCs/CH2Cl2 solution using a brush on the filter paper (Figure 8c,d). Color change from yellow to orange can be observed by fuming the patterns with CH2Cl2 for 10 s, which reverses upon drying in air. Such vapochromism behavior has also been reported for many organometallic and coordination complexes.51 However, this is one report of the LLCs with both the high QY and the vapochromism properties.

CONCLUSIONS

Highly efficient luminescent platinum(II) complexes were designed and synthesized, which exhibit an absolute QY up to 88%. Pt-3OC12H25 showed the Colh LC phase, while Pt-3OC16H33 exhibited the Colr LC phase via delicately modifying the complex core with different flexible peripheral alkoxy chains. These complexes exhibited reversible vapochromic physical behaviors and maintained their emission properties in the mesophase at high temperature, showing a great potential to be applied in advanced anti-counterfeiting and vapor sensing.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c13935.

Synthesis, characterization, and other experimental details (PDF)

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