



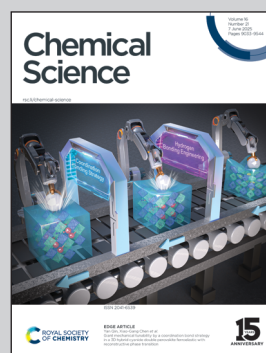
Showcasing research from Professor Jintong Song's laboratory, College of Chemistry and Materials Science, Sichuan Normal University, and Professor Haifeng Xiang's laboratory, College of Chemistry, Sichuan University, Chengdu, China.

Building metal-induced inherent chirality: chiral stability/phosphorescence enhancement *via* a ring expansion strategy of Pt(II) complexes

In the present work, inherently chiral (cR)/(cS)Pt(II) complexes with 3D boat form were designed and prepared by using achiral ligands for highly chiral stability and phosphorescence quantum yield (up to 81.0%).

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# Building metal-induced inherent chirality: chiral stability/phosphorescence enhancement *via* a ring expansion strategy of Pt(II) complexes†

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Chirality is indeed a fundamental aspect of nature, particularly in chemistry and biology. Herein, we have demonstrated a straightforward strategy to create a novel type of metal-induced inherent chirality by expanding coordination rings. Typically, tetracoordinated d<sup>8</sup> Pt(II) complexes with two five-membered coordination rings are 2D square-planar, resulting in the absence of chirality. However, if one of the coordination rings is expanded to six or seven members, the molecular structures of Pt(II) complexes would transition from a 2D plane to a 3D boat-like configuration. This not only facilitates the construction of inherently chiral scaffolds but also addresses the problem of emission aggregation-caused quenching. Furthermore, the strategy of ring expansion can enhance the chiral stability and phosphorescence quantum yield (up to 81.0%). Thus, the present work introduces a new structural motif with promising potential for application as chiroptical and luminescent materials.

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## Introduction

Chirality, referring to molecules that cannot fully overlap with their mirror images, is a fundamental property present in nature,<sup>1</sup> and thus the development of novel chiral molecules plays a pivotal role in biochemistry, asymmetric synthesis,<sup>2</sup> supramolecular chemistry,<sup>3</sup> chiral optics,<sup>4</sup> and so on. In general, chirality of organic molecules can be classified into four categories: point, axial, helical, and planar.<sup>5</sup> The term “inherently chiral” was first suggested by Böhmer for chiral calixarenes, which do not strictly fall into definitions of other types of chirality.<sup>6</sup> Later, a more general definition was formulated in 2004 by the group of Mandolini and Schiaffino.<sup>7</sup> It states that inherent chirality derives from the “introduction of a curvature in an ideal planar structure that is devoid of symmetry axes in its bidimensional representation”.<sup>8</sup> Since then, the concept of inherent chirality has been increasingly used to denote chirality arising from the rigid structures in both medium-sized rings (no less than a seven-membered ring)<sup>9</sup> and large-sized rings (such as rotaxanes, catenanes, fullerenes, cavitands, and capsular assemblies).<sup>10</sup> However, these pure organic molecules usually exhibit fluorescence.<sup>9a,11</sup>

Cyclometalated Pt(II) complexes have been extensively investigated in the past two decades owing to their rich phosphorescence properties and wide applications in phosphorescent organic light emitting diodes,<sup>12</sup> chemosensors,<sup>13</sup> bio-imaging,<sup>14</sup> circularly polarized luminescence (CPL),<sup>5a,d,15</sup> and so on. Typically, tetracoordinated d<sup>8</sup> Pt(II) complexes with two five-membered coordination rings are 2D square-planar,<sup>16</sup> resulting in the lack of chirality. Moreover, these square-planar molecules are far more likely to encounter the problem of emission “aggregation-caused quenching” (ACQ), because they readily form dimers through not only intermolecular  $\pi$ - $\pi$  stacking interactions but also Pt<sup>II</sup>-Pt<sup>II</sup> interactions.<sup>14</sup> Therefore, the chirality of Pt(II) complexes is primarily introduced by chiral ligands.<sup>5d,15,17</sup> Although there are limited examples of chiral Pt(II) complexes with achiral ligands,<sup>18</sup> their chiroptical properties, especially CPL, have seldom been reported before, mainly due to not only the weak chirality but also low phosphorescence quantum yields ( $\Phi$ ). Herein, we have demonstrated a straightforward strategy to build a novel type of metal-induced inherent chirality by expanding coordination rings (Fig. 1). When using N1^O, N2^O, N^P, N^PS, and N^PO bidentate ligands, one of the coordination rings expands into six or seven members. The molecular structures of Pt(II) complexes would change from 2D plane into 3D boat-like configuration, which not only facilitates the construction of inherently chiral scaffolds but also resolves the ACQ problem. Moreover, the strategy of ring expansion can improve the chiral stability and phosphorescence quantum yield (up to 81.0%). Furthermore, the resultant enantiomers of complexes can be separated by chiral high-performance liquid chromatography (HPLC), and their

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Fig. 1 The designed scheme and chemical structures of inherently chiral Pt(II) complexes ( $\angle$  dihedral angles: angle between the phenyl plane and the PtC<sup>N</sup> coordination plane;  $\Delta G_{(rac)}^\ddagger$ : racemization energy barriers of inherently chiral Pt(II) complexes).

absolute configuration is confirmed by X-ray diffraction, circular dichroism, CPL, and density functional theory calculation.

## Results and discussion

### Synthesis and characterization

The synthetic methods for the ligands and Pt(II) complexes are detailed in the ESI.† Initially, we utilized **N1^O**, **N2^O**, and **N^P** ligands to synthesize the Pt(II) complexes with six-membered coordination rings. **N^PS** and **N^PO** ligands were used to prepare the Pt(II) complexes with seven-membered coordination rings. Single crystals of **rac-N1^O-Pt-A** (CCDC: 2378928), **rac-N2^O-Pt-B** (CCDC: 2378929), **rac-N^P-Pt-A** (CCDC: 2378930), **rac-N^PS-Pt-A** (CCDC: 2378935), **rac-N^PO-Pt-A** (CCDC: 2378936), **rac-N^PS-Pt-B** (CCDC: 2378939), and **rac-N^PO-Pt-B** (CCDC: 2386027) were obtained through slow diffusion and evaporation of a hexane/CH<sub>2</sub>Cl<sub>2</sub> solution.

First, chiral HPLC was used to analyze and separate enantiomers of the Pt(II) complexes. For **rac-N1^O-Pt-A** and **rac-N2^O-Pt-B** (Fig. S1†), there exists only one chromatographic peak in the HPLC trace. The possible reason is that the steric hindrance of **N1^O** and **N2^O** is too small to stabilize chirality in solution. With strong steric hindrance from two phenyl

groups in triphenyl phosphine, **rac-N^P-Pt-A**, **rac-N^PS-Pt-A**, **rac-N^PO-Pt-A**, **rac-N^PS-Pt-B**, and **rac-N^PO-Pt-B** have two separated chromatographic peaks featuring a 1 : 1 ratio of the area (Fig. 2). The first peak (black line) refers to the optically pure **cR-N^P-Pt-A**, **cR-N^PS-Pt-A**, **cR-N^PO-Pt-A**, **cR-N^PS-Pt-B**, and **cR-N^PO-Pt-B**, while the second one (red line) corresponds to the **cS-N^P-Pt-A**, **cS-N^PS-Pt-A**, **cS-N^PO-Pt-A**, **cS-N^PS-Pt-B**, and **cS-N^PO-Pt-B** (see the later discussion). Enantiopure *cR* and *cS*-Pt(II) complexes (>98% ee) were collected by chiral HPLC, albeit the recovered yield being inferior to 30%.

### Photophysical properties and calculations

Table 1 presents the UV/visible absorption and emission data of Pt(II) complexes at room temperature. As illustrated in Fig. 3, **rac-N1^O-Pt-A**, **rac-N^P-Pt-A**, **rac-N^PO-Pt-A**, and **rac-N^PS-Pt-A** with a common **HC^N** ligand of 2-(4',6'-difluorophenyl)pyridine (**A**) exhibit low-energy absorption bands at  $\lambda_{abs} = 402, 380, 375$ , and 358 nm, respectively, demonstrating a gradual blue shift. This trend contrasts with the trend of corresponding dihedral angles, which are 35.07°, 56.87°, 76.38°, and 84.01° for **rac-N1^O-Pt-A**, **rac-N^P-Pt-A**, **rac-N^PO-Pt-A**, and **rac-N^PS-Pt-A**, respectively. A bigger dihedral angle would lead to a smaller degree of conjugation and a blue-shifted absorption band consequently (see the later discussion). **rac-N^PO-Pt-A** and **rac-**





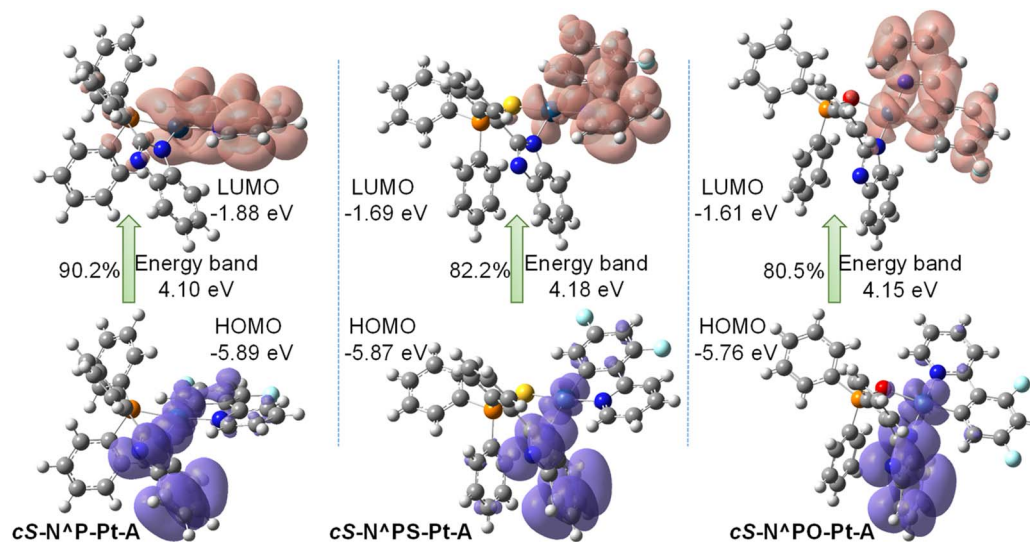


Fig. 4 Energy level diagram and frontier molecular orbitals of cS-N<sup>A</sup>P-Pt-A, cS-N<sup>A</sup>PS-Pt-A, and cS-N<sup>A</sup>PO-Pt-A (in CH<sub>2</sub>Cl<sub>2</sub>).

All the Pt(II) complexes are weakly emissive or non-emissive in a dilute degassed CH<sub>2</sub>Cl<sub>2</sub> solution. In comparison with solution samples, their powders show significant aggregation-induced emission (AIE)<sup>19</sup> with promising quantum yields (3.76%, 4.40%, 0.45%, 6.61%, 29.4%, 3.39%, and 81.0% for **rac-N1<sup>A</sup>O-Pt-A**, **rac-N2<sup>A</sup>O-Pt-B**, **rac-N<sup>A</sup>P-Pt-A**, **rac-N<sup>A</sup>PS-Pt-A**, **rac-N<sup>A</sup>PO-Pt-A**, **rac-N<sup>A</sup>PS-Pt-B**, and **rac-N<sup>A</sup>PO-Pt-B**, respectively) (Fig. 5, S5, Tables 1 and S1†). Based on their relatively long emission decay lifetimes in the microsecond range (μs, Fig. S6, S7,† and Table 1) and significant Stokes shifts (ranging from 140 nm to 170 nm) between the absorption and emission bands, the emission from Pt(II) complexes can be classified as phosphorescence, originating from triplet excited states. As illustrated in Fig S8,† the frontier molecular orbitals in the triplet excited states of Pt(II) complexes (in CH<sub>2</sub>Cl<sub>2</sub> solution) are analogous to those in singlet excited states, suggesting that their phosphorescence predominantly arises from <sup>3</sup>MLCT and <sup>3</sup>LLCT.

### X-ray single-crystal structures

The molecular structure and packing in X-ray single crystals of **rac-N<sup>A</sup>PS-Pt-A** and **rac-N<sup>A</sup>PO-Pt-A** are illustrated in Fig. 6. Unlike the traditional inherently chiral molecules, according to the definition of calixarenes, curvature is denoted as 'c', with clockwise as 'cR' and counterclockwise as 'cS'.<sup>12,13</sup> The core skeletons of these Pt(II) complexes are chiral (Fig. 1), and such metal-induced chirality can also be defined as inherent chirality for simplicity. An ideal observer standing on the cabin (the concave side of the surface) will see a seven-membered ring (Pt, O, P, C, C, C, and N atoms) at the side of the boat. The clockwise or counterclockwise array of the three highest priority atoms is designated as (cR) or (cS), respectively, as shown in Fig. 6. As anticipated, there are a pair of (cR)/(cS) enantiomers in their single crystals [**cR-N<sup>A</sup>PO-Pt-A** and **cS-N<sup>A</sup>PO-Pt-A**; **cR-N<sup>A</sup>PS-Pt-A** and **cS-N<sup>A</sup>PS-Pt-A**], corroborating the viability of our design strategy. Additionally, the enantiomers of **rac-N1<sup>A</sup>O-Pt-A**, **rac-N2<sup>A</sup>O-Pt-B**, **rac-N<sup>A</sup>P-Pt-B**, and **rac-N<sup>A</sup>PO-Pt-B** (Fig. S9–S11†) are also discernible within the single-crystal structures.



Fig. 5 PL spectra of **rac-N<sup>A</sup>P-Pt-A**, **rac-N<sup>A</sup>PS-Pt-A**, **rac-N<sup>A</sup>PO-Pt-A**, **rac-N<sup>A</sup>PS-Pt-B**, and **rac-N<sup>A</sup>PO-Pt-B** in the powder and doped film. Photographs of **rac-N<sup>A</sup>PO-Pt-A**, and **rac-N<sup>A</sup>PO-Pt-B** in the powder under a 365 nm UV lamp.





Fig. 6 X-ray single-crystal structures of **rac-N<sup>A</sup>PO-Pt-A**: (a) one crystal cell and (b) **cR-N<sup>A</sup>PO-Pt-A** and **cS-N<sup>A</sup>PO-Pt-A** molecular structures and the definition of (*cR*)/(*cS*) chirality (some atoms are omitted); X-ray single-crystal structures of **rac-N<sup>A</sup>PS-Pt-A**: (c) one crystal cell and (d) **cR-N<sup>A</sup>PS-Pt-A** and **cS-N<sup>A</sup>PS-Pt-A** molecular structures and the definition of (*cR*)/(*cS*) chirality (some atoms are omitted).

The photoluminescence properties of Pt(II) complexes are significantly influenced by their molecular structures and arrangements. There are no freely rotating groups for **rac-N1<sup>O</sup>-Pt-A**, and **rac-N2<sup>O</sup>-Pt-B**; however, their solutions are weakly emissive. This suggests the molecular backbone vibration to promote the non-radiative decay process.<sup>11,20</sup> The other Pt(II) complexes contain not only molecular backbone vibration but also C–P bond-linked phenyl groups, which are capable of free motion and consequently offer a possible pathway for the non-radiative annihilation of their excited states in solution. On the other hand, there are many strong intermolecular interactions, such as F–H (2.627–2.933 Å), C–H (2.665–2.886 Å), N–H (2.551–2.862 Å), O–H (2.410–2.713 Å), and H–H (2.350–2.769 Å) interactions (Fig. S9–S12†) in the single crystals of **rac-N<sup>A</sup>P-Pt-A**, **rac-N<sup>A</sup>PS-Pt-A**, **rac-N<sup>A</sup>PO-Pt-A**, **rac-N<sup>A</sup>PS-Pt-B**, and **rac-N<sup>A</sup>PO-Pt-B**. These strong intermolecular interactions can inhibit the rotation of C–P single bonds. The metal–metal interactions can significantly alter the photophysical properties of the complexes, such as red-shifted spectra and changes in the nature of the charge transfer transitions.<sup>21</sup> Moreover, these resultant Pt(II) complexes adopt a 3D boat-like structure, which hinders intermolecular face-to-face  $\pi$ – $\pi$  stacking interaction and intermolecular Pt<sup>II</sup>–Pt<sup>II</sup> interactions (5.871–8.033 Å, Fig. S10–12†) between adjacent complexes. Under the above synergistic effects, these Pt(II) complexes exhibit a substantial AIE phenomenon<sup>19</sup> (0.45%, 6.61%, 29.4%, 3.39%, and 81.0% for **rac-N<sup>A</sup>P-Pt-A**, **rac-N<sup>A</sup>PS-Pt-A**, **rac-N<sup>A</sup>PO-Pt-A**, **rac-N<sup>A</sup>PS-Pt-B**, and **rac-N<sup>A</sup>PO-Pt-B**, respectively).

In theory, the emission quantum yield of a square-planar Pt(II) complex is strongly dependent on the planeness of coordination. The lesser the torsion is, the higher the quantum yield. For all the AIE-active Pt(II) complexes, the Pt atoms and HC<sup>N</sup> ligands are nearly coplanar. However, their emission quantum yields are quite different. The torsion angle of C1–C2–Pt–P, C1–C2–Pt–S, C1–N1–Pt–O, C1–C2–Pt–S, and C1–N1–Pt–O is 16.99°, 1.68°, 1.01°, 3.87°, and 3.01° for **cS-N<sup>A</sup>P-Pt-A**, **cS-N<sup>A</sup>PS-Pt-A**, **cS-N<sup>A</sup>PO-Pt-A**, (**cS**)**N<sup>A</sup>PS-Pt-B**, and **cS-N<sup>A</sup>PO-Pt-B**, respectively. Additionally, the torsion angle of C3–N1–Pt–N2, C3–N1–Pt–N2, C2–C3–Pt–N2, C3–N1–Pt–N2, and C2–C3–Pt–N2 is 15.54°, 9.66°, 7.53°, 9.60°, and 4.42° for (**cS**)**N<sup>A</sup>P-Pt-A**, **cS-N<sup>A</sup>PS-Pt-A**, **cS-N<sup>A</sup>PO-Pt-A**, **cS-N<sup>A</sup>PS-Pt-B**, and **cS-N<sup>A</sup>PO-Pt-B**, respectively. **cS-N<sup>A</sup>PO-Pt-A**, and **cS-N<sup>A</sup>PO-Pt-B** have a less distorted square-planar geometry, resulting in their high emission quantum yields (Fig. 7).

### Racemization experiment

The chirality of these Pt(II) complexes originated from their 3D boat-type structures. If the cocked phenyl group in **N1<sup>O</sup>**, **N2<sup>O</sup>**, **N<sup>A</sup>P**, **N<sup>A</sup>PS**, and **N<sup>A</sup>PO** ligands flips down into the coplane with the coordination system, racemization would occur. Therefore, the chiral stability is determined by the dihedral angle between the phenyl group and the coordination system. The dihedral angles of these Pt(II) complexes exhibit a positive correlation with both the size of the ring and the peripheral substituent groups. It is reported that enantiomers with racemization energy barriers more than 22.2 kcal mol<sup>−1</sup> could be separable at





Fig. 7 The relationship between emission quantum yields and torsion angles of coordinated atoms among the representative products: cS-N<sup>1</sup>P-Pt-A, cS-N<sup>1</sup>PS-Pt-A, cS-N<sup>1</sup>PO-Pt-A, cS-N<sup>1</sup>PS-Pt-B, and cS-N<sup>1</sup>PO-Pt-B.

room temperature.<sup>22</sup> The chirality of **rac-N<sup>1</sup>O-Pt-A** and **rac-N<sup>2</sup>O-Pt-B** is not stable in solution, because they don't have a large steric group of triphenyl phosphine. The chirality of other Pt(II) complexes with a triphenyl phosphine group is stable and separable. The dihedral angle of **cS-N<sup>1</sup>O-Pt-A**, **cS-N<sup>2</sup>O-Pt-B**, **cS-N<sup>1</sup>P-Pt-A**, **cS-N<sup>1</sup>PO-Pt-A**, and **cS-N<sup>1</sup>PS-Pt-A** is measured to be 35.07°, 47.46°, 56.87°, 76.38°, and 84.01°, respectively (Fig. 8a). Following Curran's methodology,<sup>23</sup> the fitting of **cS-N<sup>1</sup>P-Pt-A**, **cS-N<sup>1</sup>PO-Pt-A**, and **cS-N<sup>1</sup>PS-Pt-A** is to

calculate the flipping energy barrier. The energy barriers calculated by fitting are shown in Fig. 8b, which are 25.0 kcal mol<sup>-1</sup> (half life,  $t_{1/2}$  = 1.50 days at 25 °C), 27.6 kcal mol<sup>-1</sup> ( $t_{1/2}$  = 0.31 years at 25 °C), and 31.0 kcal mol<sup>-1</sup> ( $t_{1/2}$  = 94 years at 25 °C), respectively (Tables S1–S3†). The sulfur atom in the **N<sup>1</sup>PS** ligands is undoubtedly larger than the oxygen atom in the **N<sup>1</sup>PO** ligands. Therefore, the increased repulsive force from the sulfur atom results in a more distorted seven-membered ring in **cS-N<sup>1</sup>PS-Pt-A** compared to **cS-N<sup>1</sup>PO-Pt-A**, which is evidenced by the



Fig. 8 (a) X-ray single-crystal structures, dihedral angles, and experimental interconversion energy barriers of **cS-N<sup>1</sup>O-Pt-A**, **cS-N<sup>2</sup>O-Pt-B**, **cS-N<sup>1</sup>P-Pt-A**, **cS-N<sup>1</sup>PO-Pt-A**, and **cS-N<sup>1</sup>PS-Pt-A**; (b) investigation of rotation barriers of **cS-N<sup>1</sup>P-Pt-A**, **cS-N<sup>1</sup>PO-Pt-A**, and **(cS)N<sup>1</sup>PS-Pt-A**.





