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Formation of Hetero-binuclear Pt(II)-M(II) Complexes Based on (2-(1H-Tetrazol-5-yl)phenyl)diphenylphosphine Oxide for Superior **Phosphorescence of Monomers**

Juan Huang,[†] Zhuo Liu,[†] Hui Chen,[‡] Hailing Zhang,[†] Han Zhang,[†] Chunmei Liu,[†] Qin Gao,[†] Chenxia Du,^{*,†} and Bin Zhang^{*,†}

[†]College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, China [‡]Institute of Chemistry, Henan Academy of Sciences, Zhengzhou 450002, China

Supporting Information

ABSTRACT: Novel hetero-binuclear platinum complexes (HBC-Pt(II)-M(II), M = Ca(II), Mg(II), Zn(II), and Cd(II))have been synthesized by the reaction of the corresponding precursors $[Pt(ppy)(\mu-Cl)]_2$ with (2-(1H-tetrazol-5-yl)phenyl)diphenylphosphine oxide (TTPPO). The X-ray structures of the complexes show that two ancillary ligands TTPPO in the square-planar Pt(II) moiety act as a quadridentate chelating agent for the other metal center, eventually forming a distorted octahedral configuration. There



are no significant $\pi - \pi$ interactions and Pt-M metallophilic interactions in the crystal lattice, due to the steric hindrances associated with the rigid octahedral structure together with the bulky TTPPO. Consequently, HBC-Pt-M complexes show monomer emission characteristics with quantum yields up to 59% in powder, suggesting their great potential for practical applications. DFT and TD-DFT calculations on HBC-Pt-Zn reveal that the phosphorescence can be ascribed to intraligand charge transfer (³ILCT) combined with some metal-to-ligand charge transfer (³MLCT) in the Pt(ppy) moiety, which is consistent with the observations from the photophysical investigations.

■ INTRODUCTION

The platinum can induce strong spin-orbit coupling (SOC) and promote an effective intersystem crossing (ISC), which results in a near unity internal electronic-optical conversion efficiency in electro-photonic devices.^{1,2} Luminescent cyclometalated platinum(II) complexes are thus a hot research topic in organic light-emitting diodes (OLEDs) and light-emitting electrochemical cells (LEECs).^{3–7} Meanwhile, phosphorescent Pt(II) complexes also find widespread applications in bioimaging applications and luminescent chemosensing.⁸⁻¹¹ However, the square-planar coordination geometry of d⁸ Pt(II) favors structural distortion and intermolecular interactions, resulting in reduction of color purity, luminescent efficiency decrease, and poor stability of the emitters in the device.^{12–17} Recently, studies have uncovered that it is an efficient way to promote the phosphorescence property of platinum(II) complexes by introducing steric hindrance into the structure.¹⁸⁻²⁵ In 2015, Cheng et al. demonstrated a novel type of Pt(II) dendrimers with bidentate ligands, and realized distinct optoelectronic properties.²⁶ In 2016, Spokoyny et al. showed a Pt(II) complex based on 1,10-bis(o-carborane) effectively shuts down undesired intermolecular interactions in the solid state.²⁷ In our previous work,²⁸ the Pt(II) complex based on 2-(diphenylphosphino) benzoic acid also exhibited phosphorescence of monomers with a higher quantum yield. In fact, developing new ligands with steric hindrance for highly

efficient Pt(II) phosphor is becoming one of the most challenging issues.

Notably, it is well-known that the octahedral geometry could also hinder the intermolecular interactions well, such as sixcoordinate Ir(III) complexes.²⁹ Zhu et al. demonstrated that the heterobimetallic platinum-iridium complex could effectively prevent the aggregation formation in neat film.³⁰ Thus, the introduction of octahedral metal ions in the Pt(II) complexes would pave a more simple way for efficient phosphorescence of monomers. However, to the best of our knowledge, the reported phosphorescent Pt(II)-M heterometallic complexes until now have been mainly focus on the d^8-d^{10} metallophilic interaction in the complexes.³¹⁻³⁵ Moreover, the additional Pt-M intermetallic usually changes the structured emission spectrum into a broad one, which is detrimental to the color purity.^{36–38}

Aiming at exploring new types of phosphorescent platinum complexes with monomers character, in this context, a series of heterometallic binuclear Pt(II) complexes (HBC-Pt-M, M = Mg(II), Ca(II), Zn(II), and Cd(II)) are designed based on 2phenylpyridine (ppy) with (2-(1H-tetrazol-5-yl)phenyl)diphenylphosphine oxide (TTPPO) as a bridging ligand. Doerrer has demonstrated that the metal-metal interactions

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Scheme 1. Synthetic Pathway for the Synthesis of the Ligand TTPPO



Scheme 2. Synthetic Pathway for the Synthesis of the HBC-Pt-M Complexes



Figure 1. Molecular structure (a) and crystal packing (b) of the HBC-Pt-Zn. The ground-state structure of HBC-Pt-Zn (c). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

between Pt(II) and Zn(II), Mg(II), or Ca(II) are very weak, especially for Ca(II) and Mg(II).³⁹ Thus, the design strategy in this paper takes advantage of rigid octahedral structures without significant metal-metal bond affects. Meanwhile, additional steric hindrance by the bulky TTPPO is also favorable for hindering the intermolecular interactions. Finally, the use of environmentally friendly and low-cost Zn(II), Mg(II), or Ca(II) is advantageous for potential applications. The solid-state structures of HBC-Pt-M complexes have been elucidated by X-ray diffraction analysis. The photophysical properties of the complexes have been systematically investigated and corroborated by theoretical calculations.

RESULTS AND DISCUSSION

Synthesis of the Complexes. The synthetic procedures for (2-(1H-tetrazol-5-yl)phenyl)diphenylphosphine oxide (TTPPO) is shown in Scheme 1. The triarylphosphine oxide (TAPO) is directly synthesized from 2-bromobenzonitrile and Ph₂HP(O) by a reported method.⁴⁰ The TTPPO is then accomplished by the reaction of TAPO with sodium azide in the presence of ammonium chloride in DMF. The chemical structure of TTPPO is confirmed by ¹H and ³¹P NMR spectroscopy. The HBC-Pt-M complexes are prepared by a debridging reaction of the chloride-bridged dimer precursor $[Pt(ppy)Cl]_2$ with TTPPO in the presence of corresponded metal salt together with sodium carbonate as base (Scheme 2). The molecular structures of all the HBC-Pt-M complexes are determined by NMR spectroscopy and single crystal X-ray structure analysis.

Crystal Structure. The crystals of HBC-Pt-M complexes suitable for X-ray diffraction analysis are obtained by evaporation of the solvent at room temperature. The crystallographic details are summarized in Tables S1 and S2. The selected bond lengths and angles of the complexes are given in Table S3 in the Supporting Information (SI). As shown in Figure 1a and Figures S1a, S2a, and S3a in the SI, the heterometallic binuclear Pt(II)-M(II) complexes show similar molecular structures containing a slightly deformed squareplanar geometry around the Pt(II) and a distorted octahedral environment for the other metal center. Notably, the Pt(II)-M(II) distances are all longer than the sum of atom radii, ruling out the presence of Pt(II)-M(II) interactions (Table 1). As the different metal ions (M^{2+}) having no significant impact on the molecular structure, the structure of the HBC-Pt-Zn complex is briefly described as a representative.

The structure depicted in Figure 1a reveals that the platinum(II) center adopts a minimally distorted square-planar coordination geometry with the $C1-Pt1-N7_{trans}$ angle of

Table 1. Intramolecular Pt····M Distances

compound	experimental distance (Å)	sum of covalent radii (Å) ^{39,41}	sum of atomic radii (Å) ^{42<i>a</i>}
HBC-Pt-Mg	$3.796 (Pt^{2+}-Mg^{2+})$	2.77	3.22
HBC-Pt-Ca	$3.779 (Pt^{2+}-Ca^{2+})$	3.12	3.71
HBC-Pt-Zn	$3.763 (Pt^{2+}-Zn^{2+})$	2.58	3.19
HBC-Pt-Cd	$3.770 (Pt^{2+}-Cd^{2+})$	2.80	3.38
^a http://period	lictable.com/Properti	es/A/VanDerWaa	lsRadius.v.html.

178.50(18)° and N1-Pt1-N3_{trans} angle of 175.21(16)°. The bond lengths of the Pt1-C1 (ppy) (2.008(5) Å), Pt1-N1 (ppy) (2.021(4) Å), Pt-N3 (tetrazol) (2.014(4) Å), and Pt-N7 (tetrazol) (2.104(4) Å) are similar to those of previously studied mononuclear cyclometalated Pt(II) complexes.43,44 Additionally, there are large dihedral angles $(53.053^{\circ}, 65.326^{\circ})$ between the tetrazol groups of the ancillary ligands (TTPPO) and Pt(ppy), taking advantage to prevent the $\pi - \pi$ interactions between adjacent molecules. More importantly, the Zn^{2+} ion adopts a typical octahedral coordination environment, which is furnished by the $Pt(ppy)(TTPPO)_2$ and another TTPPO. In other words, the Pt(ppy)(TTPPO)₂ moiety acts as a quadridentate chelating agent for Zn(II); the overall structure of the complex HBC-Pt-Zn can be described as a octahedral configuration, which is favorable for reducing intermolecular stacking interactions.

Indeed, the crystal packing of HBC-Pt-Zn (Figure 1b) shows that the shortest distance between the centers of the aryl rings is 3.95 Å. Additionally, the dihedral angles of the corresponding aromatic rings are about 26°. Sander and Hunter have suggested that the van der Waals interactions are strongest between the overlapped aromatic rings when the interplanar separations is more than 3.4 Å.^{45,46} As a result, the complex rules out any significant $\pi - \pi$ interactions. The shortest Pt…Pt separation distance amounts to 9.90 Å, precluding any noticeable Pt…Pt interactions in the crystal lattice of HBC-Pt-Zn. Projection of the crystal structure of HBC-Pt-Zn along the (ac) plane shows no apparent layering, and the intermolecular interactions along the b-axis are also negligible (Figure S4). As shown in Figure S3, the view along the *b*-axis of the HBC-Pt-Cd is identical to that of HBC-Pt-Zn. Additionally, when viewed along the *b*-axis, the projections of the crystal structures of HBC-Pt-Mg and HBC-Pt-Ca are the same (Figures S1 and S2), which are also similar to that of the HBC-Pt-Zn. These nearly identical crystal packing modes

indicate that the different ions do not significantly influence the molecular accumulation. More importantly, the rigid octahedral structures together with the bulky TTPPO effectively hinder the intermolecular interactions, which is one of the most essential features for realizing efficient phosphorescence of monomers.

DFT calculations in a solution of CH_2Cl_2 for the HBC-Pt-M have been carried out to predict the energy minimized structure. As shown in Figure 1c, Figure S5, Table S4, and Table S5, calculated bond distances and angles for the optimized geometry in the ground state are well-correlated with the crystallographic values, ensuring the accuracy of DFT optimization studies at the B3LYP level.

Absorption Properties. UV–vis absorption spectra for these HBC-Pt(II)-M(II) complexes are investigated in CH_2Cl_2 solution with a concentration of 1.0×10^{-5} mol L⁻¹ at room temperature. The pertinent data are summarized in Table S6. It is notable that the spectral patterns of these complexes are almost identical (Figure 2a), which can be due to the lack of significant changes in structure among the complexes. Clearly, this phenomenon also confirms that there is no obvious metal–metal interactions between the additional M(II) ions and Pt(II) ion. In particular, strong UV–vis absorption peaks of the complexes in the solid state are observed at ca. 400 nm (Figure S6 in the SI), which is in line with the low-lying absorption band of the complexes in CH_2Cl_2 , demonstrating the intermolecular interactions of HBC-Pt-M are very weak.

Obviously, strong absorption at $\lambda < 320 \text{ nm}$ ($\varepsilon > 1 \times 10^4 \text{ L} \text{mol}^{-1} \text{ cm}^{-1}$) in CH₂Cl₂ is observed, normally attributed to intraligand charge transfer (ILCT) transitions. To gain further insights into the origins of the electronic transitions for the low-lying absorption band in CH₂Cl₂, locating in the range of 340–420 nm, time-dependent density functional theory (TD-DFT) calculation has been carried out at the B3LYP level on the optimized geometries of HBC-Pt-M.⁴⁷ Only HBC-Pt-Zn is considered here, because the influence of the additional M(II) ions on the low-lying absorption band is identical (Figures 2a and 3, Tables S7 and S8). The positions of the first 15 singlet—singlet transitions are obtained and used to generate the simulated absorption curves (Figure 2b). Clearly, the fit between calculated and observed lowest energy bands is acceptable.

The simulated UV-vis absorption results have shown that the moderately intense absorption band at the 328 nm region is mainly attributed to the H-2 \rightarrow L transition. According to



Figure 2. UV/vis absorption spectra of the HBC-Pt-M complexes in CH_2Cl_2 solution (a). Comparisons between the simulated and experimental absorption spectra of HBC-Pt-Zn in the low-energy region (b).



Figure 3. Calculated low-energy transitions for HBC-Pt-Zn (f (oscillator strengths)) together with the energy levels of the LUMO (L), HOMO (H), H-1, and H-2 and contribution of Pt and ppy moieties (the contributions of zinc ion for these frontier molecular orbits are nearly zero).

the molecular orbital (MO) calculations (Figure 3), the H-2 for the HBC-Pt-Zn is mainly constructed from the platinum center (34%) and cyclometalated ppy ligand (37%), while the LUMO for the complex is mainly situated on the ppy (88%). Thus, this absorption band is tentatively attributed to combinations of intraligand $\pi - \pi^*$ transitions (ILCT) and metal-to-ligand (MLCT) charge transfer. The absorption bands located at ~343 nm are probably due to H-1 \rightarrow L transition. The platinum(II) gives a substantial contribution to the H-1 (89%). Therefore, MLCT transition should be responsible for this absorption. The lowest energy transition at 371–391 nm mainly corresponds to the H \rightarrow L excitation. The HOMO refers to the π orbital localized on the ppy unit mixed with the $d\pi(Pt)$ orbital. Consequently, this low-lying absorption band can be described by an admixture of ILCT and MLCT transitions.

Photoluminescence Properties. The photoluminescent (PL) properties of the complexes in dichloromethane solution at 298 K are obtained with excitation at 391 nm (Figure 4, Table 2). Notably, the akin spectroscopic profiles, peaking at 482 and ca. 516 nm with a shoulder at ca. 546 nm, are similar



Figure 4. Normalized emission spectra of HBC-Pt-M complexes in CH_2Cl_2 solution ($\lambda_{ex} = 391$ nm).

to those of the Pt(ppy) analogues.⁴⁸⁻⁵⁰ Thus, the luminescence from HBC-Pt-M complexes tentatively originates from Pt(ppy) centered triplet radiative transitions (³(ILCT/ MLCT)). Notably, the HBC-Pt-M complexes show high emission quantum yields (Φ) of up to 31% (HBC-Pt-Ca). The phosphorescence lifetimes of complexes in CH₂Cl₂ at 298 K require a double exponential fit (Figure S7), dominated by the short lifetime component τ_1 (around 3 μ s). This phenomenon can be due to the presence of weakly coordinating solvent CH₂Cl₂, which results in an increasing freedom for the structural change in the excited state for the most molecules. Meanwhile, along with the slight decrease in molecular rigidity, the nonradiative decay rates (k_{nr}) of the complexes in CH₂Cl₂ are more than 24×10^4 s⁻¹, and the emission peak wavelengths of the complexes in CH₂Cl₂ are even a little longer than that of the HBC-Pt-M (except for HBC-Pt-Cd) in powder. The timeresolved emission spectra of the complexes in CH₂Cl₂ at 298 K are measured and presented in Figure S8. The shapes of the spectra remain unvaried except in their amplitudes, which corresponded to delay times before or after the two decay components (τ_1 and τ_2).

Considering that the similarities of results may be ascribed to monometallic Pt(II) species left after dissociation of M^{2+} ions, HBC-Pt-Mg and HBC-Pt-Cd in CH₃OH are further characterized by mass spectrometry (MS). For both complexes, the MS responses of HBC-Pt-M are the most abundant peaks (Figures S9 and S10), indicating that the reference complexes are relatively stable in CH₃OH. It is well-known that the coordination ability of CH₃OH is higher than that of CH₂Cl₂ for the Pt(II) and the relevant M(II) ions;⁵¹ the HBC-Pt-M complexes are obviously more stable in CH₂Cl₂ and the properties being thus due to heterometallic binuclear Pt(II) complexes.

On the other hand, if the emission properties of monometallic Pt species left after decoordination of M2+ ion are different from those of the HBC-Pt-M complexes, it will further confirm that the photoluminescent properties of the HBC-Pt-M in CH₂Cl₂ ascribe to heterometallic binuclear Pt(II) complexes. HBC-Pt-Mg is chosen as a representative. In order to remove Mg²⁺ cation from HBC-Pt-Mg, a mixture of HBC-Pt-Mg and EDTA-2Na (1:1, mol/mol) in DMSO-d₆/ D_2O (5:1, V/V) is treated by an ultrasonic reflux reactor at 50 °C for 15 min. A ¹H NMR spectrum of the mixture is carried out at room temperature. As can be seen in Figure S11, the aromatic region is a set of multiplets within the range 8.10-6.80 ppm (ca. 59H), as well as resonances for the protons of EDTA-2Na at 3.12 ppm (8H) and 2.60 ppm (4H). Obviously, the ¹H NMR features of the mixture are clearly different from those of HBC-Pt-Mg and EDTA-2Na, confirming Mg²⁺ cation could be removed from the HBC-Pt-Mg molecular framework by using the chelating ligand EDTA. The photoluminescent property of HBC-Pt-Mg in DMSO/H₂O (5:1, V/V) in the presence of different amounts of EDTA-2Na is investigated. When excited at 345 nm, the shapes of emission spectra of the solutions hardly changed by addition of EDTA-2Na (Figure S12), proving that the luminescence probably originates from the Pt(ppy) moiety. However, in the presence of 1 equiv of EDTA-2Na, the luminescent intensity is reduced to 77% of that of the solution without EDTA-2Na. These observations not only indicate that the adjacent $M(\mathrm{II})$ cation has considerable influence on the luminescent properties of HBC-Pt-M in solution but also infer that HBC-Pt-M is stable in common solvent except for the presence of a chelate ligand

Table 2. Photophysical Data for the HBC-Pt-M Complexes in CH ₂ Cl ₂ at 298	K
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complexes	λ_{\max} (nm)	$ au_{ m obs} \ (\mu s)^a$	Φ (%) ^b	$k_{\rm r} \ (10^4 \ { m s}^{-1})^c$	$k_{\rm nr} \ (10^4 \ { m s}^{-1})^d$
HBC-Pt-Mg	482, 516, 545 sh	2.29	22	9.6	34.1
HBC-Pt-Ca	482, 515, 547 sh	2.77	31	11.2	24.9
HBC-Pt-Zn	482, 516, 546 sh	2.65	27	10.2	27.5
HBC-Pt-Cd	482, 516, 547 sh	3.04	25	8.2	24.7

^{*a*}Average emission lifetimes $\tau_{obs} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$. ^{*b*}The Φ was measured in CH₂Cl₂ solutions relative to fac-[Ir(ppy)₃] ($\Phi = 40\%$).⁵² ^{*c*}Radiative decay rate $k_r = \Phi/\tau$. ^{*d*}Nonradiative decay rate $k_{nr} = (1 - \Phi)/\tau$.

(EDTA-2Na). Thus, the intense emissions of HBC-Pt-M in CH_2Cl_2 could be due to heterometallic binuclear Pt(II) complexes.

As expected, the emission profiles of the complexes in neat powder show no obviously red shift, indicating that the emissions of HBC-Pt-M mainly originate from the monomer (Figure 5 and Table 3). More importantly, under the condition



Figure 5. Normalized emission spectra of HBC-Pt-M complexes in powder at 298 K (λ_{ex} = 400 nm).

of without solvent, the radiative and nonradiative decay rates became slower (less than $4 \times 10^4 \text{ s}^{-1}$), especially for k_{nr} . Consequently, the photoluminescent quantum yields (Φ) of these complexes are up to 59% in powder, which are even higher than that of $Ir(ppy)_3$.^{29,53} These unique properties confirm that the intermolecular interactions of the HBC-Pt-M complexes in the concentrated phases are effectively hindered, which is coincident well with the crystal-packing characteristics of the complex discussed above. Additionally, the short decay lifetimes of the complexes (Table 3 and Figure S13) in powder (<19 μ s) suggest the heterometallic platinum complexes promote an effective intersystem crossing (ISC). Notably, although the emission properties of HBC-Pt-M mainly originate from the monomer in the solid state, the emission shapes are slightly affected by aggregation. As the projection of the crystal structures of HBC-Pt-Mg and HBC-Pt-Ca along the (ac) plane are identical, the spectroscopic profiles are very similar. Meanwhile, the spectral shapes of the HBC-Pt-Zn and

HBC-Pt-Cd are close to each due to their identical crystal packing modes.

Low temperature emission spectra for the HBC-Pt-M complexes in powder at 77 K are investigated. As shown in Figure 6 and Table 4, the Pt(II)-M(II) complexes show



Figure 6. Normalized emission spectra of HBC-Pt-M complexes in powder at 77 K (λ_{ex} = 400 nm).

Table 4. Photophysical Data for the HBC-Pt-M Complexes at 77 K (λ_{ex} = 400 nm)

compounds	λ_{\max} (nm)
HBC-Pt-Mg	491, 520 sh, 528, 561
HBC-Pt-Ca	472, 481, 490, 496, 508, 525, 536
HBC-Pt-Zn	471, 490, 518 sh, 528, 560 sh
HBC-Pt-Cd	472, 483, 495, 518, 535 sh, 551

remarkably well-resolved vibrational satellite peaks without distinctly rigidochromic shift than that at 298 K. These unique PL properties further confirmed that the emissions mainly arise from the ligand-centered triplet state.^{54–56} Interesting, the emission spectra of HBC-Pt-Mg and HBC-Pt-Zn are very similar. Che et al. have found that the solid-state emission of some Pt(II) complexes in low temperature could be provisionally taken as monomeric emission,⁵⁷ implying that the intermolecular interactions are reduced at 77 K. Meanwhile, the bond lengths of the Pt1–C1 (ppy) and Pt1–N1 (ppy) as well as the C1–Pt1–N1 angle for HBC-Pt-Mg are more similar to those for HBC-Pt-Zn (Table S3). Thus, the

Table 3. Photophysical Data for the HBC-Pt-M Complexes in Powder at 298 K (λ_{ex} = 400 nm)

complexes	λ_{\max} (nm)	$ au_{ m obs}~(\mu m s)$	Φ (%) ^a	$k_{\rm r} \ (10^4 \ {\rm s}^{-1})^b$	$k_{\rm nr} \; (10^4 \; {\rm s}^{-1})^c$
HBC-Pt-Mg	477, 501, 512, 531 sh	18.73	59	3.2	2.2
HBC-Pt-Ca	477, 501, 512, 531 sh	18.14	43	2.4	3.1
HBC-Pt-Zn	479 sh, 494, 513	16.45	55	3.3	2.7
HBC-Pt-Cd	489, 516, 550 sh	18.13	42	2.3	3.2

^aThe Φ of the powder was measured using an integrating sphere. ^bRadiative decay rate $k_r = \Phi/\tau$. ^cNonradiative decay rate $k_{nr} = (1 - \Phi)/\tau$.

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luminescences from HBC-Pt-Zn and HBC-Pt-Mg complexes, tentatively originating from Pt(ppy), are nearly identical with each other.

Since the HBC-Pt-M complexes show similar PL properties, the influence of the additional M(II) ions on the photophysical properties is semblable. In order to elucidate the PL behaviors of the studied complexes, the triplet state structure of HBC-Pt-Zn in CH₂Cl₂ solution is selected to be optimized. Although the singlet ground state and the lowest triplet states are geometrically similar to each other (Figure 1c, Figure S14, Tables S5 and S10), a little reduction of the Pt-ppy bond length can be observed, indicating the MLCT transition process induces the phosphorescence emission. The $S_0 \rightarrow T_1$ wavelength (589 nm) for HBC-Pt-Zn, determined by using the time-dependent density functional theory (TD-DFT), is a little longer than the corresponding experimental emission wavelength, which have been widely observed for the simulation of phosphorescence.^{58,59} Additionally, the lowest triplet states T_1 of HBC-Pt-Zn mainly arise from the HOMO \rightarrow LUMO transition (89%). As shown in Figure 7, the analysis of the



Figure 7. Calculated $S_0 \rightarrow T_1$ transition for HBC-Pt-Zn in the triplet state and contribution of Pt, Zn, and ppy moieties.

frontier molecular orbitals reveals that the Zn(II) ion makes negligible contribution to the HOMO and LUMO (~0%). The HOMO orbital is mainly located on the Pt(II) center and ppy skeleton (32% and 65%, respectively), while the ppy moiety makes the predominate contribution to the LUMO (88%). Consequently, the ³ILCT-dominated transition together with some ³MLCT features should account for the emission, which agrees well with its PL properties.

CONCLUSION

A series of hetero-binuclear platinum complexes (HBC-Pt-M) are successfully prepared. The rigid octahedral structures together with the bulky TTPPO ligand effectively rule out any significant $\pi - \pi$ interactions and metallophilic interactions in the crystal lattice. Indeed, comparing with the emission spectra of the complexes in CH₂Cl₂ solutions, the emission spectra in powder showed no obvious red shift. The distinct vibronic fine structure of the luminescence suggests that the photoemission of these complexes is dominated by cyclometalating ligand (ppy) centered ³ILCT transition. This delineation is coincident with the negligibly rigidochromic shift of the low temperature emission spectra. Furthermore, the quantum

chemical calculations indicate the phosphorescence is predominantly a ³ILCT (ppy) transition, with mixing of a ³MLCT $[d\pi(Pt) \rightarrow \pi^*(ppy)]$ character. Remarkably, this design strategy allows the platinum complexes to show monomer emission characteristics with quantum yields up to 59% in powder. The present work affords a feasible approach to settle some defects of the luminescent cyclometalated platinum(II) complexes, including the low emission quantum yield and poor color purity in high concentration.

EXPERIMENTAL SECTION

Materials and Methods. All commercial chemicals of analytical grade were used without further purification, unless otherwise stated. All air and moisture sensitive reactions were carried out under an argon atmosphere. 2-Diphenylphosphoryl-benzonitrile (TAPO) was prepared according to the reported procedures.⁴⁰ The platinum(II) chlorobridged dimer [Pt(ppy)Cl]2 was also synthesized following literature methods.⁶⁰ The HBC-Pt-M complexes were grinded into powder and dried at 329 K under vacuum for measurements (except for single crystal X-ray diffraction analysis). ¹H and ³¹P NMR spectra of the compounds were recorded on a Bruker DPX-400 MHz spectrometer at room temperature. C, H, and N analyses were carried out by employing a Carlo-Erba1106 Elemental Analyzer. Mass spectra of HBC-Pt-Mg and HBC-Pt-Cd in CH₃OH were recorded with a Q-TOF Micro MS spectrometer. UV-vis absorption spectra of the complexes were carried out on a Cary 5000 UV-vis-NIR spectrophotometer. Steady-state Phosphorescence spectra, luminescence lifetime, time-resolved emission spectra, and photoluminescence quantum yields were obtained by an Edinburgh Instruments Ltd. (FLS980). Additionally, the Φ of the complexes in solution was calculated by a comparison of the emission intensities (integrated areas) of a standard sample $(Ir(ppy)_3, \Phi = 40\%)$.⁵² The Φ of the complexes in powder was obtained through an absolute method by employing an integrating sphere.

Synthesis of 5-[2-(Diphenylphosphoryl)phenyl]-1H-tetrazole (TTPPO). A mixture of the TAPO (1.82g, 6 mmol), sodium azide (0.78 g, 12 mmol), and ammonium chloride (0.64 g, 12 mmol) were added in a flame-dried, argon flushed three-neck flask. Anhydrous DMF (20 mL) was injected through a syringe, and the reaction contents were stirred at 130 °C until TLC (thin-layer chromatography) showed complete consumption of TAPO (ca. 5 h). After cooling to room temperature, the solvent was poured into water. A solution of HCl (2 mol L^{-1}) was added to adjust the pH = 3, and then the whole was extracted with CH2Cl2. The combined organic extract was dried with anhydrous sodium sulfate and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: EtOAc/CH₂Cl₂) to give 1.25 g of TTPPO as a white powder in 60% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.63–8.59 (m, 1H), 7.78 (tt, J = 7.8, 1.5 Hz, 1H), 7.62–7.52 (m, 6H), 7.52–7.44 (m, 5H), 7.21–7.15 (m, 1H). ³¹P NMR (162 MHz, CDCl₃) δ 38.79. Elemental analysis calcd (%) for $C_{19}H_{15}N_4OP\!\!:$ C 65.89, H 4.37, N 16.18. Found: C 65.81, H 4.39, N 16.16.

General Syntheses of Complexes (HBC-Pt-M). The complexes were synthesized according to similar procedures. A slurry of the crude chloro-bridged Pt(II) dimer (0.39 g, 0.5 mmol), TTPPO (0.70 g, 2 mmol), and 10 equiv of Na₂CO₃ (1.10 g, 10 mmol) in the presence of corresponding metal salt (MgCl₂ (0.11 g, 1.1 mmol), CaCl₂ (0.12 g, 1.1 mmol), ZnCl₂ (0.15 g, 1.1 mmol), and CdCl₂ (0.20 g, 1.1 mmol)) was stirred in 2-ethoxyethanol (15 mL) under an argon atmosphere at 110 °C for 20 h. After the mixture was cooled to RT, the reaction mixture was concentrated under reduced pressure. An excess of water was added gradually to give a precipitate of crude product. The precipitate was filtered and purified by silica gel column chromatography using a mixture of CH₃OH/CH₂Cl₂ as eluent to give the HBC-Pt-M complexes. Yellow-green crystals were grown from the slow evaporation of a saturated 2-ethoxyethanol solution.

HBC-Pt-Mg. Yield 35%. ¹H NMR (400 MHz, DMSO- d_6) δ 8.36–8.15 (m, 2H), 8.11–7.93 (m, 4H), 7.93–7.50 (m, 16H), 7.49–7.24 (m, 12H), 7.24–7.00 (m, 7H), 6.99–6.85 (m, 2H), 6.83–6.67 (m,

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4H), 6.58–6.43 (m, 1H), 6.12–5.94 (m, 2H). ^{31}P NMR (162 MHz, DMSO- $d_6)$ δ 33.88, 33.67, 31.83. Anal. Calcd (%) for $C_{68}\text{H}_{50}\text{N}_{13}\text{O}_3\text{-}\text{P}_3\text{PtMg:}$ C 57.94, H 3.58, N 12.92. Found: C 57.85, H 3.55, N 12.90.

HBC-Pt-Ca. Yield 30%. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.34– 8.17 (m, 2H), 8.10–7.94 (m, 4H), 7.93–7.47 (m, 17H), 7.47–7.24 (m, 11H), 7.24–7.06 (m, 6H), 7.04–6.84 (m, 3H), 6.83–6.67 (m, 4H), 6.58–6.43 (m, 1H), 6.12–5.93 (m, 2H). ³¹P NMR (162 MHz, DMSO-*d*₆) δ 33.87, 33.67, 31.83. Anal. Calcd (%) for C₆₈H₅₀N₁₃O₃-P₃PtCa: C 57.30, H 3.54, N 12.78. Found: C 57.35, H 3.52, N 12.71.

HBC-Pt-Zn. Yield 45%. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.34– 8.16 (m, 2H), 8.12–7.93 (m, 4H), 7.93–7.50 (m, 15H), 7.50–7.24 (m, 13H), 7.23–7.07 (m, 6H), 7.06–6.85 (m, 3H), 6.85–6.65 (m, 4H), 6.57–6.42 (m, 1H), 6.14–5.93 (m, 2H). ³¹P NMR (162 MHz, DMSO-*d*₆) δ 38.62, 38.42, 36.57. Anal. Calcd (%) for C₆₈H₅₀N₁₃O₃-P₃PtZn: C 56.30, H 3.47, N 12.55. Found: C 56.40, H 3.45, N 12.61.

HBC-Pt-Cd. Yield 49%. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.36– 8.21 (m, 1H), 8.20–7.99 (m, 4H), 7.99–7.48 (m, 19H), 7.48–7.20 (m, 12H), 7.19–7.07 (m, 4H), 7.07–6.99 (m, 3H), 6.98–6.80 (m, 5H), 6.38–6.27 (m, 1H), 6.15–6.03 (m, 1H). ³¹P NMR (162 MHz, DMSO-*d*₆) δ 34.74, 33.68, 30.59. Anal. Calcd (%) for C₆₈H₅₀N₁₃O₃-P₃PtCd: C 54.54, H 3.37, N 12.16. Found: C 54.45, H 3.35, N 12.14.

X-ray Crystallography. X-ray data for complexes HBC-Pt-M were collected by an Oxford Diffraction Xcalibur CCD diffractometer (Mo-Kα radiation ($\lambda = 0.71073$ Å) for HBC-Pt-Ca, HBC-Pt-Zn and HBC-Pt-Cd, Cu-Kα radiation ($\lambda = 1.54184$ Å) for HBC-Pt-Mg). The diffraction frames were integrated and corrected from absorption by the program suite CrysAlisPro.⁶¹ Using Olex2,⁶² the crystal structures of the HBC-Pt-M complexes were solved by direct methods using SHELXS⁶³ and refined anisotropically by full-matrix least-squares method on F^2 with SHELXL.⁶⁴ All hydrogen atoms were included in calculated positions and refined in a riding model along with attached atoms. CCDC 1879296 for HBC-Pt-Mg, 1879294 for HBC-Pt-Ca, 1879297 for HBC-Pt-Zn, and 1879295 for HBC-Pt-Cd contain the supplementary crystallographic data for this paper, which can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Computational Methodology. All the calculations are implemented by the Gaussian 09 program package.⁶⁵ The initial coordinates of models were derived from the crystal structure of HBC-Pt-Zn. The geometries in ground state and triplet state were optimized via using restricted and unrestricted density functional theory DFT (RDFT and UDFT) with the B3LYP hybrid exchangecorrelation functional, respectively.^{66,67} The absorption and phosphorescence properties of the investigated complex were explored by using the time-dependent density functional theory (TD-DFT). Since the spectroscopic properties of HBC-Pt-Zn were obtained in CH₂Cl₂ solution, all the calculations were performed in CH₂Cl₂ solvent with the polarized continuum model (PCM).^{71,72} Throughout the calculation, the "double- ζ " quality basis set (LANL2DZ) was employed for heavy metal atoms (Pt, Zn, and Cd) and the 6-31G(d,p) basis set was applied to the light atoms (C, H, N, O, P, Mg, ⁷⁵ Visualization of the optimized structures and frontier and Ca)." molecular orbitals was performed by GaussView. The Multiwfn 3.3.7 was used for analyzing the simulated absorption spectrum.⁷⁰

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b03326.

Additional experimental data, including tables and figures (PDF)

Accession Codes

CCDC 1879294–1879297 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: dcx@zzu.edu.cn (C.D.). *E-mail: bz@zzu.edu.cn (B.Z.).

ORCID

Bin Zhang: 0000-0001-8600-0850

Notes

The authors declare no competing financial interest.

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