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ARTICLE TYPE

Platinum(II) complex bearing deprotonated 2-(diphenylphosphino)benzoic acid for superior phosphorescence of monomers

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The (ppy)-based Pt(II) complex (Pt-1) with deprotonated 2-(Diphenylphosphino)benzoic acid as anionic ligand displays phosphorescence of monomers with remarkably higher quantum yield than that of the corresponding iridium complex (Ir-1). A prototype OLED using Pt-1 exhibits high-performance with an external quantum efficiency of 4.93%.

Interest in cyclometalated complexes based on iridium and platinum has soared over the past decade, following the demonstration of their potential in the manufacture of highly efficient organic light-emitting devices (OLEDs).¹ The spin-orbit coupling exerted by the heavy metal effect allows the harvest of both singlet and triplet electro-generated excitons in devices, leading to a theoretically achievable 100% internal quantum efficiency.² However, the luminance efficiencies of devices containing such compounds are still low due to the concentration quenching.³ In this respect, compared with Ir(III) complexes, the square-planar Pt(II) complexes particularly have a great tendency towards aggregation through platinum-platinum and π - π interactions, resulting in detrimental effects on photoluminescence quantum yields and color purity.⁴ It is well understood that the introduction of steric hindrance into the structure can hinder the intermolecular interactions. Phosphorescent quantum efficiencies of the complexes have been significantly improved by the incorporation of bulky substituent.⁵ For example, the functionalization of 2-phenylpyridine chelate with a dimesitylboryl moiety has been proven to greatly enhance the phosphorescent efficiency of Pt(II) compound.⁶

Very recently, the emission quantum yield up to 100% has been achieved by Ir(III) phosphor complexes with the steric C[^]P ligand, where C[^]P = benzyldiphenylphosphine.⁷ The preliminary results demonstrate that the steric structural feature and electronic

factors of PPh₂ group can efficiently enhance phosphorescent properties of cyclometalated complexes. However, developing new phosphorescent complexes containing PPh₂ group ligands is not always feasible because of the difficult to synthesize. Another effective strategy is the use of anionic ligand containing diphenylphosphine structure to gain the new complexes high phosphorescent efficiency. Until now, the utilizations of anionic ligands modified with diphenylphosphine moiety for phosphorescent material are still rare.⁸ Moreover, to the best of our knowledge, no effort has been devoted to investigate the influence of this kind ligands on the photophysical properties of both Pt(II) and Ir(III) complexes. Herein, deprotonated 2-(Diphenylphosphino)benzoic acid (HL1) is chosen as a new anionic ligand system in this paper to conjecture whether promising luminescent Pt(II) and Ir(III) complexes can be obtained based on this ligand. Two heteroleptic platinum and iridium complexes with the formula (C[^]N)Pt(P[^]O) and (C[^]N)₂Ir(P[^]O) are synthesized respectively, where P[^]O is L1⁻ and C[^]N is 2-phenylpyridine (ppy). Comprehensive investigation including structural characterizations, photophysical properties and quantum chemical calculations of these complexes are presented. Interestingly, unlike the rather low photoluminescent quantum yield (Φ) of Ir-1 (Φ = 0.91% in CH₂Cl₂), Pt-1 exhibits efficient green phosphorescence of monomers character both in solution (Φ = 18.32%) and in powder (Φ = 23.30%). The impressive external quantum efficiency of 4.93% for a prototype phosphorescent OLED ranks Pt-1 as one of the most efficient Pt(ppy)-based electroluminescent materials.

The Pt-1 and Ir-1 complexes are prepared by the reaction of the corresponding chloride-bridged dimers [(C[^]N)Pt(μ -Cl)]₂ and [(C[^]N)₂Ir(μ -Cl)]₂ with the HL1 in the presence of base. Detailed reaction conditions along with the NMR spectra, elemental analysis and crystallographic data of the complexes are available in the ESI.

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† Electronic supplementary information (ESI) available: Synthesis and characterization details. CCDC 969995 for Pt-1, 969996 for Ir-1. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x

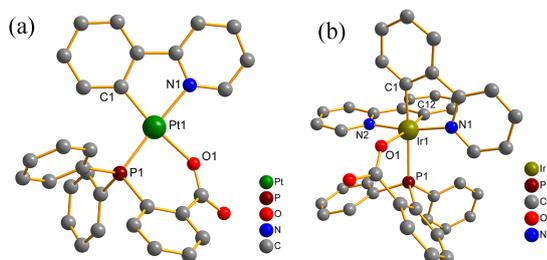


Fig. 1 Molecular structure of the Pt-1 (a) and Ir-1 (b) complexes. Hydrogen atoms omitted for clarity.

As shown in Fig. 1a, the platinum of Pt-1 maintains good square-planar coordination geometry with P atom opposite to the nitrogen atom of ppy ligand. Additionally, the Pt-1 units are stacked in a head-to-tail fashion with a separation of about 3.51 Å between the only partially overlapping 2-phenylpyridine rings of the complex (Fig. S1a), indicating only weak π - π interactions between the Pt-1 units.⁹ Furthermore, the long Pt-Pt distance (9.37 Å) rules out the presence of Pt-Pt bimetallic interactions. The Iridium of Ir-1 is coordinated by two N atoms and two C atoms of 2-phenylpyridines (ppy) together with P and O atoms from HL1, forming a slightly deformed octahedral coordination geometry (Fig. 1b). The PPh₂ fragment exerts notable *trans*-effect and results in relatively longer Ir-C(1) bond distance of 2.053(6) Å versus that of Ir-C(12) (2.002(7) Å).^{8c, 10} The crystal packing of Ir-1 (Fig. S1b) also shows that no apparent stacking interactions can be detected due to the steric repulsion of the HL1 ligand.

Calculated bond distances and angles in gas as well as in CH₂Cl₂ solution are in very good agreement with that of crystal structure data (Table S2), which ensure the accuracy of DFT studies at the B3LYP level for Pt-1 and Ir-1 complexes.¹¹ The frontier orbital analysis indicates that the HOMO levels of the both Pt-1 and Ir-1 have significant contributions from the d orbital of the Pt(II) and Ir(III) centers, whereas the LUMO levels are dominated by the ligands (Fig. S2, Table S4).

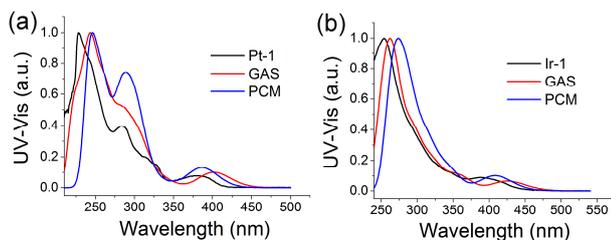


Fig. 2 Comparisons between the calculated (in gas (GAS) and in CH₂Cl₂ with PCM mode (PCM), respectively) and experimental absorption spectra for Pt-1 (a) and Ir-1 (b) in CH₂Cl₂ solution (1.0×10⁻⁵ mol/L).

The UV-Vis absorption spectra of both complexes recorded in CH₂Cl₂ at room temperature are displayed in Fig. 2 with pertinent data summarized in Table S3. Simulated absorption curves based on the calculated results at the TD-DFT level agree well with the corresponding experimental data, especially by PCM model for the CH₂Cl₂. In general, both complexes exhibit intense absorptions in the region below 350 nm with maxima ϵ values being above $1.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. Two absorption bands are observed for compound Pt-1 in this region, which can be ascribed to mixed characters of predominant π - π^* transition of the ligands

and minor metal to ligand charge transfer in the singlet manifold. Meanwhile, the main absorption at $\sim 260 \text{ nm}$ for Ir-1 in this region can be mainly assigned to spin-allowed π - π^* transition of the ligands. The less intense absorption bands ($\epsilon < 1.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) for Pt-1 and Ir-1 in the region of 360-450 nm can be assigned to an admixture of metal-perturbed MLCT and LLCT transitions.

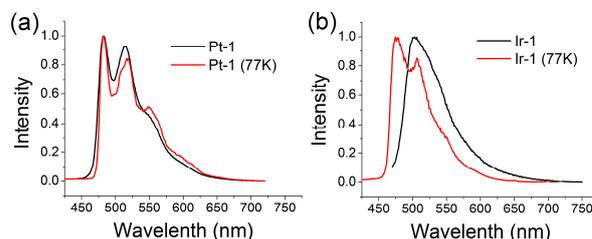


Fig. 3 The emission spectra of Pt-1 (a) and Ir-1 (b) in solution (1×10⁻⁵ mol/L) at room temperature and 77 K.

Characteristic phosphorescences in degassed dichloromethane solution are observed for both Pt-1 and Ir-1 at room temperature and 77K (Fig. 3). Pt-1 shows well-resolved vibronic-structured emissions at 482 and 516 nm due to the C=C and C=N stretching frequencies of the ligand both at room temperature and 77K. The highly structured emission spectrum, independent of temperature, indicates the strong spin-orbit coupling effect imposed by Pt atom promotes the phosphorescence with substantial ligand-centered (LC) character. Ir-1 displays a broad emission band ($\sim 505 \text{ nm}$) at room temperature and shows vibronic-structured emissions at 77K, owing to the increased rigidity of the solvent decreasing the electronic mixing of states.

It is noteworthy that the photoluminescence quantum yield of complex Pt-1 in dichloromethane solution at room temperature is 18.32%, which is comparable to that of Pt(ppy)(acac) (about 15%)¹², while the quantum yields of Ir-1 is only 0.91% (Table S5, ESI). Further studies for Pt-1 find that the emission profile of Pt-1 is independent of the applied concentration in the range from 10⁻⁵ mol/L to 10⁻² mol/L (Fig. S3, ESI). Remarkably, Pt-1 maintains the phosphorescence of monomers in powder with attractive luminescence quantum yields of 23.30%.

The TD-DFT calculations on the optimized structures in the triplet (T_1) excited states for Pt-1 and Ir-1 in CH₂Cl₂ demonstrate that the lowest energy triplet states are dominated by HOMO-LUMO transitions (Table S5). As shown in Table S6, the orbital distributions of Pt-1 suggest the HOMO is composed of platinum- d_{π} (16.20%) and ppy- π orbitals (77.90%), while the LUMO is dominated by the ppy ligand (92.10%). Therefore, the emission of Pt-1 is mainly derived from the [Pt(ppy)] moiety based on LC and some contribution of the MLCT transition. For Ir-1, the HOMO and LUMO levels are mainly localized on the ligands (90.92% and 99.02%, respectively). The drastic decreased contribution from Ir(d_{π}) to the HOMO (9.08%) might be rationalized by the significant changes of geometry in T_1 state (Table S7 vs. Table S2, ESI) and the *trans*-effect imposed by the bulky L1⁻ ligand. Knowing that the overlap between π -orbital of ligand and d orbital of metal atom is a key factor to give out a much allowed transition,¹³ the relatively small contributions of MLCT transition hence can be attributed to the poor solution quantum yield of Ir-1.¹⁴ Deduced from the calculated results of

Ir-1, another remark worthy to mention is that the HOMO is predominantly composed of the L1⁻ (60.43%) with a smaller contribution of ppy (30.49%), while the populations are different from the LUMO with 34.44% L1⁻ and 64.58% ppy. As a result, the emissive excited states of Ir-1 contain considerable LLCT (ligand-to-ligand charge transfer), a partially forbidden transition, which could further reduce the emission quantum yield of Ir-1.¹⁵

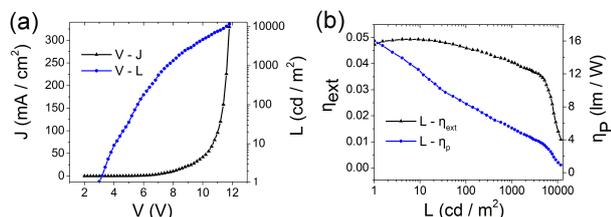


Fig. 4 The current density (J)-voltage (V)-luminance (L) characteristics of the device (a). The external quantum efficiency (η_{ext}) and power efficiency (η_p) of the EL device versus luminance (b).

The appealing luminescent properties of Pt-1 prompt us to investigate its application in OLEDs. A optimized triple-layered device using Pt-1 as emitting material has been fabricated through thermal deposition under vacuum: ITO (indium tin oxide) / NPB (N,N'-di[(1-naphthyl)-N,N'-diphenyl]-1,1'-biphenyl)-4,4'-diamine, 40 nm)/10% Pt-1 : mCP (N,N'-dicarbazolyl-3,5-benzene, 30 nm)/TPBI (1,3,5-tris(N-phenylbenzimidazole-2-yl)-benzene, 40 nm)/LiF (1.0 nm)/Al (100 nm). The EL spectrum of the device matches very well with the photoluminescence spectrum of the Pt-1 in powder (Fig. S4, ESI), which is independent of the driving voltage from 3 to 12 V (not shown). Notably, as shown in Fig. 4 and Table S8, the employment of Pt-1 allows the achievement of high performances with maximum brightness of 11651 cd/m² at 12 V and a low turn-on voltage of 3 V. At a luminance of 6 cd/m², the device is able to achieve a maximal power efficiency (η_p) of 14.64 lm/W and an external quantum efficiency (η_{ext}) of 4.93%, respectively. Of particular significance, the device shows a low efficiency roll-off (Fig. 4b), the peak η_{ext} of 4.93% only decreases to 4.60% and 4.06% at 100 and 1000 cd/m², respectively.

In summary, two phosphorescence complexes (Pt-1 and Ir-1) bearing HL1 as a new P⁺O ligand are reported. Unlike the rather weak phosphorescence of Ir-1 ($\Phi = 0.91\%$ in CH₂Cl₂), Pt-1 exhibits efficient green phosphorescence of monomers both in solution ($\Phi = 18.32\%$) and in powder ($\Phi = 23.30\%$), which is a rarely reported phenomenon. Theoretical calculations suggest that the emission of Pt-1 is mainly assigned to ILCT with some MLCT character while the observed emission of Ir-1 is dominated by ILCT and LLCT transitions, which may rationalize the surprising difference in the photophysics of Pt-1 and Ir-1. The devices based on Pt-1 exhibit outstanding performance with maximal external quantum efficiency (η_{ext}) of 4.93% and power efficiency (η_p) of 14.64 lm W⁻¹, which would be the highest reported to date for a Pt(II)-ppy based complexes. The results highlight the pivotal role of HL1 in the structure and luminescence behavior of Pt(II) complex. Screening better phosphorescence-emitting compounds based on this anionic ligand system are in progress.

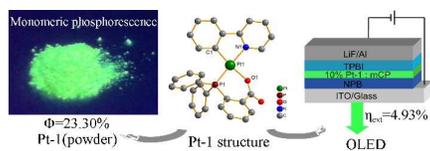
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