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Highly Emissive Dinuclear Platinum(III) Complexes

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ABSTRACT: Dinuclear Pt(III) complexes were commonly reported to have short-lived lowest-lying triplet states, resulting in extremely weak or no photoluminescence. To overcome this obstacle, a new series of dinuclear Pt(III) complexes, named as **Pt2a-Pt2c**, were strategically designed and synthesized using donor (D)-acceptor (A)-type oxadiazole-thiol chelates as bridging ligands. These dinuclear Pt(III) complexes possess a d⁷-d⁷ electronic configuration and exhibit intense phosphorescence under ambient conditions. Among them, **Pt2a** exhibits orange phosphorescence maximized at 618 nm in degassed dichloromethane solution ($\Phi_p \sim 8.2\%$, $\tau_p \sim 0.10 \,\mu$ s), near-infrared (NIR) emission at 749 nm ($\Phi_p \sim 10.1\% \,\tau_p \sim 0.66 \,\mu$ s) in the crystalline and at 704 nm ($\Phi_p \sim 33.1\%$, $\tau_p \sim 0.34 \,\mu$ s) in the spin-coated neat film. A blue shifted emission by more than 3343 cm⁻¹ is observed under mechanically grinding crystalline **Pt2a**, affirming intermolecular interactions in the solid states. Time-dependent density functional theory (TD-DFT) discloses the lowest lying electronic transition of **Pt2a-Pt2c** complexes to be a bridging ligand-to-metal-metal charge transfer (LMMCT) transition. The long-lived triplet states of these dinuclear platinum(III) complexes may find potential use in lighting. Employing **Pt2a** as an emitter, high performance organic light-emitting diodes (OLEDs) were fabricated with NIR emission at 716 nm ($\eta = 5.1\%$), red emission at 614 nm ($\eta = 8.7\%$) and white-light emission ($\eta = 11.6\%$) in non-doped, doped (in mCP) and hybrid (in CzACSF) devices, respectively.

INTRODUCTION

Phosphorescent transition metal complexes with the closed-shell d⁶, d⁸ and d¹⁰ electronic configurations have attracted enormous attention during the past three decades due to their peculiar photophysical and rich redox properties.¹ Thanks to the potentially 100% electron to photon conversion efficiencies, these transition metal based complexes have been widely applied in organic light-emitting diodes (OLEDs). Among them, platinum complexes, including square planar mononuclear Pt(II),²⁻¹⁰ dinuclear Pt(II) complexes¹¹ ²⁷ and octahedral Pt(IV) complexes,²⁸⁻²⁹ are considered to be the most common transition metal complexes in phosphorescent OLEDs on account of their high stability and intense luminescence. Despite that extensive research of Pt(III) complexes have been reported to reveal their potentials in catalytic reactions,³⁰⁻³² the studies on luminescent Pt(III) complexes are lagging far behind. Ultimately their short-lived triplet states restrict the energy and electron transfer processes in practical applications.³³⁻³⁵

Dinuclear Pt(III) complexes with d⁷-d⁷ electronic configuration and octahedral coordination structure are endowed with many attractive properties. Firstly, the Pt(III) complexes are similar to the iridium(III) emitters with octahedral coordinating architecture. The corresponding stereo-structure is beneficial to decrease quenching by intermolecular interactions such as π -stacking.³⁶ Secondly, dinuclear Pt(III) complexes are believed to be more stable and could accommodate more intimate Pt^{...}Pt interactions than those of the dinuclear Pt(II) complexes because of the invulnerability toward nucleophilic reagents (e.g., halide (X[.])) for the Pt(III) complexes.^{33, 37-38} Thirdly, the octahedral coordination geometry allows the attachment of multidentate chelate ligands with various functionalities, so that the synergy among axial coordination ligand, bridging ligand and cyclometalated ligand can finely harness the Pt...Pt distance, endowing the corresponding complexes with unique properties.^{23, 39-41}

Despite the fact that many ligands have been employed (e.g. pyridine deriatives,^{11, 24, 33} 2-mercaptobenzothiazole and 2-mercaptobenzoxazole^{25, 42-43}), the endeavors aimed to synthesize emissive dinuclear Pt(III) complexes were not successful. The main reason lies in the short-lived lowest-lying charge-transfer electronic states of the dinuclear Pt(III) complexes, resulting in inefficient electron-transfer kinetics and lack of photoluminescence (*vide infra*).^{14, 23, 25, 33, 37-40, 44-48 It is worth noting that only two types of dinuclear Pt(III) complexes have been reported with luminescent properties, i.e., [Pt₂(μ pop)₄X₂]⁴ (pop = *P*,*P*-pyrophosphite, P₂O₃H₂²⁻, X = Cl, Br, SCN), [Pt₂(μ -pop)₄X₂]²⁻ (X = py) and [Pt₂(μ -C₆H₃-S-R-2-AsPh₂)₄X₂] (R= methyl or isopropyl; X = Cl, Br or I).³⁴⁻³⁵ Among them, the former}



Figure 1. (a) Synthetic routes of Pt2a-c complexes. Among them, the crystal structure of Pt2a (CCDC No. 1885885) is presented, which is depicted with thermal ellipsoids shown at a 50% probability level. (b) The depiction of short interactions existing in the molecular packing of Pt2a.

 $[Pt_2(\mu \text{-pop})_4X_2]^{n}$ (n = 2, 4) analogs exhibited red luminescence only in the 77 K ethanol glass, while the latter displayed weak emission in the NIR region at room temperature with no emission yield provided and without applications. To the best of our knowledge, there have been no application of platinum(III) complexes to OLEDs so far.

The crucial electronic transitions of non-emissive phosphorescent Pt(III) complexes normally possess metal centered (MC) $d\sigma_{M^{-}}$ $d\sigma_{M}^{*}$ character as the lowest lying electronic excited state.^{24, 28-31, 35-39} We thus proposed that judiciously designed rigid bridging ligands may reoder the frontier molecular orbitals, such that the electron clouds of the highest occupied molecular orbital (HOMO) of the dinuclear platinum(III) complexes locate on the coordinated ligands rather than the two platinum atoms. The approach to achieve this goal is the usage of donor (D)-acceptor (A) type bridging ligands to alter the nature of the electronic excited state, which has been employed in designing emissive Au or Ag complexes in previous reports.⁴⁹⁻⁵¹ Accordingly, the electronic transition of dinuclear Pt(III) complexes may no longer be dominated by the $d\sigma_M\text{-}d\sigma_M^*$ metal centered (MC) $d^7\text{-}d^7$ electronic transition but the bridging ligand-to-metal-metal charge transfer (LMMCT), resulting in emissive dinuclear Pt(III) complexes.

With the aim to prove the above concept, in this study, a new bridging ancillary ligand 5-phenyl-1,3,4-oxadiazole-2-thiol (**oxdt**, see **Figure 1**) possessing D-A property was designed and exploited to form a series of highly emissive dinuclear Pt(III) complexes named **Pt2a**, **Pt2b** and **Pt2c** (see **Figure 1** and **Scheme S1** in the **Supporting Information** (**SI**)). In this approach, **oxdt** served as the ancillary ligand; 2,4-difluorphenyl pyridine (**dfppy**) was used as the cyclometalated ligand, and chloride (**Cl**) acted as an axial ligand. Time-dependent density functional theory (TD-DFT) calculations were then conducted to unveil the lowest lying electronic transition of these dinuclear Pt(III) complexes to be the bridging ligand-to-metal-metal charge transfer (MLCT), which is distinct from typical MC, metal-to-ligand charge transfer (MLCT) and metal-metal-to-ligand charge transfer (MMLCT) electronic transitions reported

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for the Pt(III) and Pt(II) complexes. Also, prominent mechanochromism was explored in these dinuclear Pt(III) complexes via the observation of morphology-dependent phosphorescence.⁵² The highly emissive **Pt2a** was then employed to fabricate OLEDs via solution processes; the results demonstrate, for the first time, high performance OLEDs using dinuclear Pt(III) complexes.

RESULTS AND DISCUSSION

Synthesis and crystal analysis. Pt2a was synthesized from the reaction between Pt precursor 4 and ligand oxdt 3 (see Figure 1) in which the acidic hydrogen of the -SH functional group in oxdt was deprotonated, forming the corresponding thiolate in the chloroform solution during the reaction.53 Note that the coordinated chloride (Cl) resulted from an oxidative addition of chloroform or from the Cl-bridged precursor complex.33, 38, 41 Similar procedures were carried out for **Pt2b** and **Pt2c** except that the Pt precursors **5** and **6** were used as the starting materials (Scheme S1 in SI). Pt2a, Pt2b and Pt2c were all well characterized by ¹H NMR, ¹³C NMR, MALDI-TOF-MS and elemental analysis (see SI). The deconvolutions of X-ray photoelectron spectra (XPS), shown in Figure S3, indicate that the title molecules (Pt2a, Pt2b and Pt2c) possess similar binding energies ranging from 72.71-72.93 eV to 75.95-76.25 eV for $4f_{7/2}$ and $4f_{5/2}$, respectively. The result supports the same oxidation state for the dinuclear Pt centers, i.e., platinum(III).54-55

Single crystals **Pt2a** then grew in dichloromethane (DCM)/methanol solution at room temperature. Supported by single crystal X-ray diffraction (XRD) analysis, the Pt-Cl distance is determined as 2.384 Å in **Pt2a**, which is shorter than that in $[Pt_2(ppy)_2(pyt)_2]Cl_2(2.482 Å),^{23}$ implying the stronger π -donor coordinating ability of **Cl** in **Pt2a**. The stronger π -donor ability of **Cl** leads to elongation of the opposite Pt-Pt distance (2.750 Å), which is longer than that (2.615 Å) of $[Pt_2(ppy)_2(pyt)_2]Cl_2.^{23}$ The result also indicates the existence of a single bond between the two Pt atoms. Furthermore, the robust Pt-C bond formed by σ -donor ligand weakens the opposite-bonded N-coordination of the **oxdt**-ligand, resulting in a longer Pt(1)-N(2) distance (2.104 Å) compared with Pt(1)-N(1) (2.053Å) that is oppositely bonded to the sulfur atom (see **Figure 1b**, and data listed in **Table S1**).

The arrangement of molecules of **Pt2a** in the crystalline structure, shown in **Figure 1b**, exhibits a head-to-tail packing of the cyclometalated ligands, corresponding to the mean plane of both the bidentate 2,4-difluorobenzyl and pyridyl ligand. The two 2,4-difluorobenzyl and pyridyl bidentate ligands are arranged nearly in parallel to each other with a dihedral angle of 8.46° and a small interplane distance ranging from 3.074 to 3.255 Å between the centroids of pyridyl and 2,4-difluorobenzyl planes, indicating the potential of π - π interactions. Furthermore, multiple intermolecular interactions occur throughout the molecular stacking, including noncovalent intermolecular C-H… π (ranging from 2.735 to 2.899 Å), π … π (3.320, 3.388, and 3.320 Å) and C-H…Cl (2.792, 2.799, and 2.882 Å) in **Figure 1** (**b**). These provide ample intermolecular interactions which are relevant for their photophysical properties^{16, 56} as elaborated in the following section.

Photophysical Properties. The absorption profile of **Pt2a** in dichloromethane (DCM) solution is shown in **Figure 2 (a)**. The absorption bands at < 300 nm can be ascribed to the spin-allowed intraligand π - π^* transitions. Another intense absorption band around 350 nm is attributed to the intraligand charge transfer from the electrondonating carbazole to the electron-withdrawing **oxdt** moiety.⁵⁷ Moreover, the weakest absorption band at ~448 nm in **Pt2a** is attributed to the LMMCT transition, which is evidenced by the absence in the absorption profile of the coordinated ligand as shown in **Figure S4**. The assignment of LMMCT will be further validated by computational approaches (*vide infra*).²⁵



Figure 2. UV-Vis (dash lines) and PL (solid lines) spectra of (a) **Pt2a** (b) **Pt2b** and (c) **Pt2c** in degassed DCM solution (conc. = 1.0×10^{-5} M, magenta line), spin-coated film (55 nm thickness, red line), and solid crystalline powder (black line). λ_{ex} = 430 nm. Inserts: photograph of Pt complexes in degassed DCM solution under ambient light and UV light.

 Table 1. Photophysical data for Pt2a, Pt2b and Pt2c in different phases.

Name	State	$\lambda_{abs}\left(nm\right)$	$\lambda_{em}\left(nm\right)$	$\Phi_{em}(\%)$	$ au_1$ (pre-exp. factor)/ $ au_2$ (pre-exp. factor)	$k_{r}^{c}\left(s^{\cdot1} ight)$	$k_{\mathrm{nr}^{\mathrm{c}}}(\mathrm{s}^{-1})$
	DCM ^a	294, 350, 448	618	8.2	103 ns (1.00)	7.96×10^{5}	8.91×10^{6}
Pt2a	Neat film ^b	294, 366, 531	704	33.1	93 ns (0.50) / 340 ns (0.50)	9.76×10^{5}	1.97×10^{6}
	Crystal	-	749	10.1	663 ns (1.00)	1.52×10^5	1.36×10^{6}
Pt2b	DCM ^a	294, 355, 514	706	5.0	131 ns (1.00)	3.82×10^{5}	7.25×10^{6}
	Neat film ^b	296, 363, 520	740	21.4	88 ns (0.57) / 325 ns (0.43)	6.58×10^{5}	2.42×10^{6}
	Crystal	-	760	8.5	1306 ns (1.00)	6.51×10^{4}	7.01×10^{5}
Pt2c	DCM ^a	295, 354, 447	625	6.8	101 ns (1.00)	6.73×10^{5}	9.23×10^{6}
	Neat film ^b	298, 361, 549	711	23.0	80 ns (0.64) / 326 ns (0.36)	$7.06 imes 10^{5}$	2.36×10^{6}
	Crystal	-	735	9.5	581 ns (1.00)	$1.64 imes 10^5$	1.56×10^{6}

^{a)} In DCM solution (10⁻⁵ M) ^{b)} The neat film with a thickness about 55 nm by spin-coating^{c)} Radiative decay rate constants (k_r) and non-radiative decay rate constants (k_{rr}) were calculated according to the equations $k_r = \Phi/\tau_2$ and $k_{rr} = (1/\tau_2) - k_r$, respectively.

In the neat film, it is worth noting that a new absorption peak appears around 531 nm for **Pt2a** (**Figure 2 (a)**). Furthermore, the emission peak of **Pt2a** is bathochromically shifted from 618 nm in DCM solution to 704 nm in the neat film. The results draw a conclusion of aggregation associated changes of the physical and photophysical properties for **Pt2a** in the solid film (see **Figure 2**). The driving force for aggregation, and hence ordered packing, can be attributed to multiple intermolecular interactions such as the short C-H… π , C-H…Cl and π … π distances shown in the X-ray analysis of **Pt2a** in single crystal (see **Figure 1(b)** and **Figure S1**), though fewer intermolecular interactions are expected in the neat film. Further firm support of this viewpoint is given by the 749 nm emission in the single crystal of **Pt2a**, which is further red shifted with respect to that of the neat film (see **Figure 2**).

Because of the different degrees of intermolecular interactions, it is possible to fine-tune the emissive property under various weight percentages (wt%) of the dinuclear Pt(III) complexes in doped solid films. As a result, concentration dependent photoluminescence measurements of Pt2a blend films dispersed in PMMA were conducted. Figure S5 displays the intensities of the ratiometric emission for the 618 nm (monomer) versus the 704 nm (aggregated) emission bands. The result supports the synergistic participation of intramolecular π - π stacking interactions and multiple intermolecular short contacts (C-H... π , π - π stacking, H-bonds).^{17,58} Similar aggregation modulated phosphorescence of Pt2a was observed in tetrahydrofuran (THF)/H₂O mixtures with various water volume ratios (Figure S6). The appearances of micro-aggregation and the aligned arrays were identified by confocal laser scanning fluorescence microscopy when the water fraction exceeds 60% (Figure S8), giving another support for the influence of intermolecular interactions on the photophysical properties. Although the intermolecular interactions can be evidenced in films and crystals, the normalization of absorption, emission spectra and the corresponding emission lifetimes are independent of varied concentrations in DCM solutions ranging from 2.0×10⁻⁴ to 5.0×10⁻⁶ M, as shown in Figure S9. The result indicates that the intermolecular interactions between Pt2a have negligible influences in solution under the concentration of interest.

A similar trend of photoluminescence properties was observed for **Pt2b** and **Pt2c** in solution, neat film and crystalline powder, as shown in **Figure 2 (b)** and **(c)**, respectively. The steady state photophysical

data for all **Pt2** complexes, such as emission peak and photoluminescence quantum yields (PLQY) in solution, neat film and crystal solid are listed in **Table 1**. PLQY of **Pt2a** was measured to be as high as 33.1% at 704 nm in the neat film, which is approximately 4 times higher than that (8.2%) in degassed DCM solution. Strong emissions of **Pt2b** and **Pt2c** in the neat film were also observed with PLQY of 21.4% (740 nm) and 23.0% (711 nm), respectively (see **Figure 2** and **Table 1**).

Time-correlated single photon counting (TCSPC) measurements were conducted to investigate the relaxation kinetics of Pt2a-Pt2c emission in different phases. The results are shown in Figures S10-S12 with pertinent parameters tabulated in Table 1. As shown in Figures S10-S12 and Table 1, the emission decays of Pt2a-Pt2c in degassed DCM solutions exhibit single exponential decay kinetics, for which the time constant is fitted to be 103 ns (Pt2a), 131 ns (Pt2b) and 101 ns (Pt2c). In the neat film, the plot of the logarithm of intensity versus time seems to be deviated slightly from linearity for all Pt2 complexes (see Figures S10-S12, (b)). The resulted nonsingle exponential decay dynamics for Pt2a-Pt2c in neat films, in a qualitative manner, may be rationalized by the involvement of different aggregation sites. This viewpoint can be supported by the decay kinetics shown in the crystalline solid where the decay can be mainly fitted by a single exponential decay (see Figures S10-S12, c and Table 1). Nevertheless, the decays in the neat film can be well fitted by a minor, fast component (τ_1) and a major, slow component (τ_2) , which are recorded to be 93 ns (τ_1) and 340 ns (τ_2) for **Pt2a**. The fitted parameters for the decay of Pt2b and Pt2c emissions are also listed in Table 1. Fundamentally, it is noteworthy that the steadystate emission intensity is proportional to the integrated area of the decay of interest. Therefore, despite that the pre-exponential factor of τ_1 is slightly larger than that of τ_2 in thin films, the integrated area from the τ_1 component has a much smaller contribution than that of the τ_2 component. Accordingly, the slow decay component should make a major contribution to the steady-state emission intensity in the neat film; we thus use the τ_2 component for further investigations. Thereby, both radiative rate constant (k_r) and non-radiative decay rate constant (k_{nr}) can be deduced from the relationship of PLQY = $k_{\rm r} / (k_{\rm r} + k_{\rm nr}) = k_{\rm r} \times \tau_2$. As a result, a radiative decay rate constant $k_{\rm r}$ of 9.76×10^6 s⁻¹ is obtained for **Pt2a** in neat film, which is similar to that $(7.96 \times 10^6 \text{ s}^{-1})$ in DCM solution. However, the non-radiative

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decay rate constant (k_m) was largely suppressed in the neat film by a factor of 5 (see **Table 1**), manifesting in rigidity enhanced emission yields.

Mechanochromic Properties. Aside from the above features, Pt2a exhibits remarkable emissive characteristics and color changes under mechanical grinding and vapor exposure. The poly-crystalline powder obtained from precipitation in supersaturated DCM solution exhibits NIR emission at 749 nm, while the ground powder of Pt2a displays a much blue-shifted emission recorded at 623 nm, which can even be ultimately blue-shifted to 599 nm by exposure to DCM vapor (see Figure 3). The phenomena reaffirm that the NIR emission of the crystal Pt2a is due to the intermolecular interactions, whereas the orange emission of the fumed powder (599 nm) more likely reveals its single molecular behavior.⁵⁹⁻⁶¹ This uniqueness of the exceedingly large blue-shift by 3343 cm⁻¹ (from 749 to 599 nm) makes Pt2a advantageous toward further potential applications such as information security storage.⁶²⁻⁶⁶



Figure 3. The mechanochromic properties of **Pt2a.** (a) Emission spectra of poly-crystalline powder (black line), ground sample (red line), and the ground samples fumed to DCM vapor (blue line). (b) Photographic images of samples under ambient light and UV light (365 nm) irradiation.

Computational Approaches. Computational approaches were further conducted to unveil the electronic transition behaviors of **Pt2** series complexes. **Figure 4** shows the structural and electronic properties of **Pt2a** in its optimized ground state (S_0) and excited state (T_1) as calculated by the PBE1PBE functional associated with LANL2DZ/6-31g (d, p) basic sets, respectively (see **Theoretical calculation** section in **SI** for details).



Figure 4. (a) Optimized geometries of **Pt2a** in its ground state (S_0) and triplet excited state (T_1) with the Pt…Pt distances. (b) and (c) HOMO and LUMO distribution of **Pt2a** in its ground state (S_0) and triplet excited state (T_1) with the percentage of the electron density from the Pt atoms.

The HOMO electron density mainly resides on the carbazole donors of the oxdt-bridging ligands, whereas the LUMOs are localized at the two platinum atoms with ~53% computed contribution. Further, the character of the lowest lying electronic transitions in absorption $(S_0 \rightarrow S_1)$ and emission $(T_1 \rightarrow S_0)$ are dominated by the electronic transition between HOMO and LUMO rather than the very high lying $d\sigma_M \rightarrow d\sigma_M^*$ metal centered (MC) transition ascribed to either HOMO-5 or HOMO-4 to LUMO electronic transition (T4 or T₅) in all title diplatinum complexes (see **Figure S13-S15**). Thus, the computational results confirm the remarkable ligand-to-metal-metal charge transfer (LMMCT), in part (>50% in every case), which is distinct from the typically reported MC and MLCT for Pt complexes. Moreover, to make the assignment more precise, the optimized Pt...Pt bond lengths for the ground state (S₀) of Pt2a, Pt2b and Pt2c are around 2.777 Å. Combining with the observation in single crystal XRD, the result affirms the formations of metal centered (MC) $d\sigma_M$ and $d\sigma_M^*$ orbitals, as shown in Figure 5. Further, the computed distances are elongated in their triplet states (T_1) (~3.402 Å, c.f. 2.777 Å in S_0). The result can be rationalized by the singly occupied metal centered (MC) $d\sigma_M^*$ orbitals, in part between the Pt(III) ions, upon electronic transition. This decreases the bond order of the Pt(III) M-M bond, resulting in the elongation of the Pt…Pt bond lengths as depicted in Figure 5.⁶⁷⁻⁶⁹In brief, the charge transfer process from the **oxdt**-bridged ligand (π_L) to $d\sigma_M^*$ orbital vindicates the occurrence of bridging ligand-to-metal-metal charge transfer (LMMCT).⁷⁰

Based on the assignment of LMMCT, the different emission wavelengths among the title Pt(III) complexes are mainly attributed to the different energy levels of the metal centered (MC) dimeric $d\sigma_M^*$ arising from different ligand field strengths of the cylometalating ligand. A stronger metal-to-ligand bonding is expected to increase the ligand field strength and to destabilize the higher lying $d\sigma_M^*$ orbital.⁷¹⁻⁷² Owing to the elongated π -conjugation in the isoquinoline cyclometalated ligand of **Pt2b**, the electron clouds of the nitrogen atom in isoquinoline tend to locate at the aromatic ring compared with that in **Pt2a** and **Pt2c**, leading to a less destabilized $d\sigma_M^*$ orbital and hence a smaller LMMCT energy gap, which is also evidenced by the observed absorption onsets in DCM solutions, i.e., 514 nm for **Pt2b**, compared with 448 and 447 nm for **Pt2a** and **Pt2c**, respectively.



Figure 5. Molecular orbital (MO) diagrams of d^7-d^7 Pt(III) complexes in the ground (S₀, left) and the lowest lying triplet (T₁, right) states. Note that the subscripts M and L present the origins from the metal and the ligand (**oxdt** in this work), respectively. Note that the relatively energy is in arbitrary value.

Vibrational Analysis. The vibrational analyses were conducted by Raman spectroscopy to investigate the intramolecular vibrational motions involving Pt…Pt bond stretching, which are further supported by computational approaches. The ground state (S₀) Raman spectra of **Pt2a**, **Pt2b** and **Pt2c** films are shown in **Figure 6**. To summarize, similar to the previously reported Pt…Pt interactions around 80-120 cm⁻¹,⁷³⁻⁷⁶ the title complexes exhibit one major peak at 95, 89 and 96 cm⁻¹ for **Pt2a**, **Pt2b** and **Pt2c**, respectively. These vibrational modes are associated with the stretching of Pt…Pt bond coupled with other vibrations, as supported by the computational approach (*vide infra*). Note that the broadened peak profiles plausibly result from the overlaps of multiple low frequency vibrational modes which are discernible in the case of **Pt2a**.



Figure 6. Ground state (S₀) Raman spectra of **Pt2a**, **Pt2b** and **Pt2c** films. $\lambda_{ex} = 532$ nm.

To verify the assignment of the singly occupied dimeric metal centered $d\sigma_M^*$ orbital in its T_1 state, the computational approaches were conducted to obtain the Raman active vibrational modes in both its ground (S₀) and triplet (T₁) states. The calculated Raman

frequencies and the vibrational modes involving Pt…Pt bond stretching are put forward for further discussion as shown in **Figure** 7 and **Figure S16** for **Pt2a**, respectively (see **Figures S17** to **S21** for **Pt2b** and **Pt2c**). The Raman transition of **Pt2a** in its S₀ state involving Pt…Pt bond stretching was calculated at 167.40 cm⁻¹, while the transition in the T₁ state was at 146.05 cm⁻¹ with an appreciable lowenergy shift about 20 cm⁻¹. For the ground state, the noticeable discrepancy of Raman frequencies between experimental and computational approaches is due to the anharmonic coupling and/or insufficient functional used for the formidably large dimeric Pt(III) complexes in this study. Nevertheless, the results reveal a trend where a relatively weaker Pt…Pt bond is observed in the T₁ state compared with that in the S₀ state, supporting the electronic transition from the bridged ligand (π_L) to the dimeric metal centered (MC) d σ_M^* orbital for the title Pt(III) complexes.



Figure 7. The computed low frequency Raman spectra of **Pt2a** in its ground (S_0 , black) and triplet (T_1 , red) states. Note that only the Raman transitions involving the stretching of Pt…Pt bond are labeled.

Cyclic Voltammetry Analysis and Electroluminescent (EL) Properties. As comprehensively investigated in the previous sections, Pt2a, Pt2b and Pt2c all possess LMMCT as lowest lying electronic transition with good to high emission yields in solution and solid phases (summarized in Table 1). This makes the use of these dinuclear Pt(III) complexes feasible to fabricate OLEDs. To achieve this goal, the electrochemical properties of the title Pt2 complexes were investigated by cyclic voltammetry using ferrocene as a reference for oxidation and reduction potentials (Figure S22). As tabulated in Table S6, all Pt2 analogues have similar oxidation potential of ~1.25 V, reaffirming that oxdt ligands mainly contribute to the HOMO electron density with the calculated energy level of ~-5.55 eV. Also, from the onsets of reduction potentials as tabulated in Table S6, the LUMO energy levels of Pt2a, Pt2b and Pt2c were calculated to be -3.57, -3.73 and -3.62 eV, respectively. The results reveal similar HOMO energy level but different LUMO energy. The latter indicates different energy levels of the $d\sigma_M^*$ orbitals by varying the ligand field strengths among three title complexes (vide supra). Further, owing to the highest PLQY, good thermal stability with only a 5% weight loss at 354 °C (Figure S2) and good surface morphology in the neat film (Figure S23), Pt2a-based OLEDs were then fabricated by solution process. Figure S24 shows the molecular structures of materials utilized in device fabrications.

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Figure 8. (a) Energy level diagrams of **device I**. (b) The configuration of **device I**. (c) Electroluminescent characteristics of **device I**. Insets: The electroluminescence spectra of **device I** and the photograph of **device I** under operation. (d) Current density-voltage-radiance (*J-V-R*) curve of **device I**. For structures of HIL, HTL and ETL, please see **Figure S24**.

Table 2. The overall performance of EL Performances of devices I-III.

Device	$V_{on}{}^{a}\left(v\right)$	$\lambda_{\text{EL}^{b}}\left(nm\right)$	R _{max} ^c / L _{max}	$EQE_{max}^{c}(\%)$	$CE_{max}^{d}(cd/A)$	$PE_{max}^{e}(lm/W)$	CIE ^f (x,y)
Ι	6.8	716	34630	5.1	-	-	-
II	6.2	614	4112	8.7	14.3	4.1	0.56,043
III	4.2	470/612	5865	11.6	17.4	7.3	0.46,0.38

^{a)} V_{on} is the turn-on voltage measured at 1 cd m⁻². ^{b)} λ_{EL} is the maximum EL peak. ^{c)} R_{max} and L_{max} is the maximum irradiance (mW/Sr/m²) and the maximum luminance (cd/m²), respectively. ^{c)} EQE_{max} is the maximum external quantum efficiency. ^{d)} CE_{max} is the maximum current efficiency. ^{e)} PE_{max} is the maximum power efficiency. ^{f)} CIEs are measured at 1000 cd m⁻².

The non-doped **device I** was fabricated according to a configuration of ITO / PEDOT: PSS (40nm) / PVK (30 nm) / **Pt2a** (55 nm) / TPBI (60 nm) / CsF (0.8 nm) / Al (120 nm) as shown in **Figure 8(b)**. The energy-level diagram and the electroluminescent (EL) characteristics are illustrated in **Figure 8**, respectively. As a result, strong NIR emission at 716 nm is observed with a maximum external quantum efficiency (EQE) value of 5.1% and a notably bright irradiance of 34630 mW/Sr/m^{2,6,77-78} Importantly, the efficiency roll-off of the device is effectively controlled and retains 3.8% of EQE even at high current density of 100 mA cm^{-2,79}

Moreover, taking the advantage of concentration dependent emissive properties of **Pt2a** in doped films, the performances of a red OLED using doped **Pt2a** film (in mCP, see **Figure S24** for the chemical structure) with a configuration of ITO / PEDOT: PSS (40 nm) / mCP: **Pt2a** (90:10, 50 nm) / DPEPO (10 nm) / TmPyPB (50 nm) / Liq (1 nm) / Al (100 nm), named as **device II**, are shown in **Figure S25** with EL peak at 614 nm and EQE_{max} of 8.7%. The results demonstrate the advantage of **Pt2a** for fine-tuning the EL peak via various **Pt2a**/host ratios. To make a fair comparison, some excellent NIR emitters with the solution-processed NIR-OLEDs are put forward for further discussion.⁸⁰⁻⁸² For instance, Adachi et al reported the curcuminoid boron difluoride dyes to achieve solution-processed NIR emitter with EL maximum at 758 nm and EQE_{max} of 5.1%.⁸¹ Zhu et al. reported a solution-processed NIR-OLED based on an iridium complex with EL maximum at 674 nm and EQE_{max} of 7.04%,⁸² which is considered to be one of the best among the reported solution-processed NIR-OLEDs by phosphors materials. Accordingly, the performances of **device I** and **II** are comparable to the academic records. We thus demonstrate, for the first time, that the highly emissive dinuclear Pt(III) complexes can be used for fabricating non-doped NIR-OLEDs with remarkable efficiencies.

A broad, red emission is considered to be a good candidate to obtain hybrid white-light OLEDs. Hence, **Pt2a** doped **device III** was made by the following architecture: ITO/ PEDOT: PSS (40 nm) / CzAcSF: **Pt2a** (90: 10, 25 nm) / DPEPO (10 nm) / TmPyPB (50 nm) / Liq (1 nm) / Al (100 nm). Among them, CzAcSF (10-(4-((4-(9H-carbazol-9-yl)phenyl)sulfonyl)-phenyl)-9,9-dimethyl-9,10-dihydroacridine) is a thermally activated delayed fluorescence (TADF)

material, which can effectively harvest the triplet excitons via reverse intersystem crossing (RISC) process, followed by the partial Förster energy transfer to the dopant.⁸³ It is clear that **device III** exhibits the required EL behavior of blue and red emissions from CzAcSF and **Pt2a** as shown in **Figure S26**, respectively. An efficiency of 7.3 lm W⁻¹ and EQE of 11.6% is observed in **device III**. Therefore, a high-performance solution-processed hybrid white-light OLED can be attained using **Pt2a** as a red emitter together with CzAcSF as blue host and sensitizer.⁸⁴⁸⁶ The overall performances of **I-III** are tabulated in **Table 2**.

CONCLUSIONS

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In summary, with an aim to obtain emissive Pt(III) complexes, Pt2a, Pt2b and Pt2c showing prominent LMMCT transitions are strategically designed and synthesized. The recipe of achieving highly emissive platinum(III) complexes lies in the high energy HOMO of the coordinated ligand, manifesting the electronic transition originating mainly from the ligand and hence the LMMCT character. The computational approaches also validate this viewpoint. For Pt2a, the red emission at 618 nm in DCM solution and the NIR emission at 749 nm in the crystalline solid reveal the influence of the intermolecular interactions. An apparently blue-shifted emission by more than 3343 cm⁻¹ is also observed in crystalline Pt2a under mechanical grinding. Furthermore, Pt2a based OLEDs exhibit high-performance NIR, red and white emissions in its nondoped, doped and hybrid devices, in which the maximum EQEs are recorded as 5.1%, 8.7% and 11.6%, respectively. We thus demonstrate, for the first time, highly emissive dinuclear Pt(III) complexes that can be employed in OLEDs. With ingenious manipulation of ancillary ligand by D-A frameworks, attaining high-performance dinuclear platinum(III) phosphors should be achievable.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge via the Internet at http://pubs.acs.org. General information, syntheses, analytical data, DFT studies, photophysical studies, thermal studies, electrochemical studies, EL data are included.

Crystallographic data. The X-ray crystallographic coordinates for the compounds reported in this article has been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition number CCDC 1885885 (**Pt2a**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac</u>

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The authors declare no competing financial interests.

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TOC graphic

