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# Near-Infrared Emission Induced by Shortened Pt-Pt Contact: Diplatinum(II) Complexes with Pyridyl Pyrimidinato Cyclometalates

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**S** Supporting Information

ABSTRACT: Four diplatinum(II) complexes with the formula  $[Pt(pypm)(\mu - F^n)]_2$  (2, 3a-c) bearing both a pyridine-pyrimidinate chelate and formamidinate bridge, where (pypm)H and F<sup>n</sup>H stand for 5-(pyridin-2-yl)-2-(trifluoromethyl)pyrimidine and functional formamidines with various substituents of <sup>i</sup>Pr (n = 1), Ph (n = 2),  $C_6H_4^{t}Bu$  (n = 3), and  $C_6H_4CF_3$  (n = 4), were synthesized en route from a mononuclear intermediate represented by [Pt(pypm)Cl- $(F^{1}H)$ ] (1). Single-crystal X-ray diffraction studies confirmed the structure of 1 and 3a comprised of an individual "Pt(pypm)" unit and two "Pt(pypm)" units with a Pt…Pt distance of 2.8845(2) Å, respectively. Therefore, in contrast to the structured emission of mononuclear 1 with the first vibronic peak wavelength at 475 nm, all other diplatinum complexes with shortened Pt…Pt separation



exhibited greatly red shifted and structureless metal-metal to ligand charge transfer (MMLCT) emission that extended into the near-infrared region in solid states. Their photophysical characteristics were measured under three distinctive morphological states (i.e., crystals, sublimed powders, and vacuum-deposited thin films) by steady-state UV-vis spectroscopy, while retention of Pt…Pt interactions in deposited thin films of 2 and 3a-c was confirmed using Raman spectroscopy, demonstrating lowered Pt···Pt stretching at 80–200 cm<sup>-1</sup>. Most importantly, complexes 3a-c exhibited a gradual red shift with the trends crystals < sublimed powders < vacuum-deposited thin films, a result of increased intermolecular  $\pi - \pi$  stacking interactions and Pt…Pt interactions, while crystalline samples exhibited the highest luminescence among all three morphological states due to the fewest defects in comparison to other morphologies. Finally, 3b was selected as a nondoped emitter for the fabrication of NIR-emitting OLEDs, giving an electroluminescence peak at 767 nm and a maximum external quantum efficiency of 0.14% with negligible roll-off.

### INTRODUCTION

Organic light-emitting diodes (OLEDs) have been widely used in the fabrication of displays of mobile phones and solid-state lighting luminaries. Many of the corresponding red, green, and blue (RGB) emitters have already passed the harsh industrial assessments for commercial applications. However, the development of near-infrared (NIR)-emitting dyes and OLED devices having emission peak wavelengths beyond 700 nm are still lagging behind as well as being relatively unexplored.<sup>1–3</sup> Lighting in the NIR region is virtually invisible to human eyes and can exert greater penetration into human and cell tissues than visible light. As a result, NIR-emitting OLEDs are favored over traditional OLEDs to provide illumination for artificial intelligence, security recognition, biosensing, and therapeutic applications.

From the prospect of material designs, NIR emitters may be classified as either (i) organic or (ii) metal-based (i.e., mainly transition-metal-based) materials,<sup>4-6</sup> and their luminescence efficiencies are both lower than those observed in their redemitting counterparts, mainly due to the increased nonradiative decay rate as predicted by the energy gap law.<sup>7,8</sup> However, among the transition-metal-based NIR emitters, Pt(II) emitters possess a distinctive square-planar geometry, which enables intermolecular  $\pi - \pi$  stacking interactions and intimate Pt…Pt contacts.<sup>9-11</sup> They next induce a drastic change in electronic properties at the excited states, termed metal-metal to ligand charge transfer (MMLCT) or excimeric

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 $\pi\pi^*$  emission,<sup>12,13</sup> which is in sharp contrast to the octahedral Os(II) and Ir(III) emitters that show mixed metal to ligand charge transfer (MLCT) and ligand-centered  $\pi\pi^*$  transition characters.<sup>14-22</sup> Furthermore, the MMLCT transition involves the transfer of an electron from a filled Pt…Pt orbital of the aggregated species (i.e., as dimer or oligomer) to a vacant  $\pi^*$ orbital of chelate, often with a lowered transition energy in comparison to that of the corresponding monomer emission, together with an enhanced emission efficiency and a shortened radiative lifetime. As a proof of concept, Ma et al. reported a series of Pt(II) dimers  $[Pt(C^N)(\mu-pz)]_2$ , where  $(C^N)H = 2$ -(4,6-difluorophenyl)pyridine and (pz)H = pyrazole, 3-methyl-5-tert-butylpyrazole, and 3,5-bis(tert-butyl)pyrazole.<sup>23,24</sup> As expected, these bridging pyrazolates have the capability to hold the Pt(II) atoms in close proximity, while the bulky substituents on pyrazolates force the Pt…Pt separation to turn shorter in distance, inducing a substantial red shift in emission energy gap.

Other bridging chelates useful for making dimeric diplatinum complexes include acetamide,<sup>25</sup> pyridinethio-late,<sup>26,27</sup> pyridonato,<sup>28</sup> tartarate,<sup>29</sup> and their functional analogues.<sup>30–32</sup> The resulting diplatinum dimers were typically prepared from the coupling of bridging ligands with the readily accessible precursors  $[Pt(C^N)(\mu-Cl)]_2$  (or analogues), while the tuning of emission was best executed by varying both  $\pi$ conjugation and electronic properties of C<sup>N</sup> cyclometalates. Their syntheses and photophysical properties were recently reviewed.<sup>33,34</sup> Furthermore, these diplatinum complexes were also found useful for fabrications of NIR-emitting OLEDs.<sup>35–38</sup> In the present contribution, we intend to use 5-(pyridin-2-yl)-2-(trifluoromethyl)pyrimidine<sup>39,40</sup> and functionalized formamidinates<sup>41</sup> as cyclometalating and bridging chelates, respectively, in synthesizing relevant NIR-emitting complexes. Our goal is to explore the structure-property relationship that affects the photophysical properties, such as the corresponding emission peak wavelengths and quantum yields.

# RESULTS AND DISCUSSION

**Synthesis and Characterization.** 5-(Pyridin-2-yl)-2-(trifluoromethyl)pyrimidine (pypm)H was selected for its close resemblance to the chelate 5-(pyridin-2-yl)-3-(trifluoromethyl)-1*H*-pyrazole (pypz)H



for which its functional derivatives have been extensively employed in the assembly of Pt(II)-based phosphors.<sup>42–44</sup> In the present study, the preparation of mononuclear [Pt(pypm)-Cl(F<sup>1</sup>H)] (1) demanded the in situ generation of both the hypothetical Pt(II) dimer [Pt(pypm)( $\mu$ -Cl)]<sub>2</sub> and *N*,*N*'diisopropylformamidine: i.e., F<sup>1</sup>H. Accordingly, the [Pt-(pypm)( $\mu$ -Cl)]<sub>2</sub> dimer was obtained by heating K<sub>2</sub>PtCl<sub>4</sub> with (pypm)H in a mixture of water and ethoxyethanol,<sup>45–49</sup> while the amidine F<sup>1</sup>H was prepared in situ from the coupling of diisopropylamine and triethyl orthoformate.<sup>50</sup> Without further purification, heating of [Pt(pypm)( $\mu$ -Cl)]<sub>2</sub> and F<sup>1</sup>H in 1,2dichloroethane afforded the expected yellow Pt(II) complex 1 (cf. Scheme 1). It is notable that the formation of 1 proceeded with the amidine-induced cleavage of dinuclear [Pt(pypm)( $\mu$ -Cl)]<sub>2</sub>. Similar donor-induced dissociation of dimers has been well documented in the literature.<sup>51–54</sup> Scheme 1. Transformation from Pt(II) Complex 1 to 2 and Drawings of Pt(II) Derivatives 3a-c, While the Void Site of the  $[Pt(pypm)(F^1)]$  Intermediate Is Indicated as a Square



Moreover, due to the coexistence of a chloride and an amidinic N-H fragment in close vicinity, complex 1 should have a high tendency to afford the unsaturated intermediate "[Pt(pypm)(F<sup>1</sup>)]" upon removal of the "HCl" entity. In fact, this transformation can be achieved by heating of 1 with Ag<sub>2</sub>O in refluxing 1,2-dichloroethane, giving the formation of the dark red Pt(II) dimer  $[Pt(pypm)(\mu-F^1)]_2$  (2) from the in situ generated, unsaturated  $[Pt(pypm)(F^1)]$ . In sharp contrast, treatment of  $[Pt(pypm)(\mu-Cl)]_2$  with  $N_iN'$ -diarylformamidines, such as  $F^{2}H$ ,  $F^{3}H$ , and  $F^{4}H$  with the aryl group being phenyl, C<sub>6</sub>H<sub>4</sub><sup>t</sup>Bu and C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>, respectively, afforded the dark red Pt(II) dimers  $[Pt(pypm)(\mu - F^n)]_2$  (n = 2-4, 3a-c) without the isolation of the corresponding yellow intermediate. We hypothesize that such a discrepancy is caused by the relatively electron deficient aryl substituents on amidines, which increased the acidity of its N-H fragment and promoted a faster and concomitant removal of "HCl" in the presence of the less reactive chloride scavenger K<sub>2</sub>CO<sub>3</sub>. Moreover, formation of the bridging amidinate, rather than the chelating amidinate, is probably caused by the lack of an aryl (or alkyl) substituent at the central carbon atom of the amidinate.<sup>5</sup>

All of these Pt(II) complexes were characterized by mass spectrometry, NMR spectroscopy, and elemental analyses. Particularly, complexes **1** and **3a** were subjected to singlecrystal X-ray analyses to unambiguously confirm their structures. Figure 1 illustrates the molecular geometry and labeling scheme of **1**, together with selected bond lengths and angles. This molecule consists of a pypm cyclometalate, to which the chloride and bent amidine are trans to the pyrimidinato and pyridyl fragments, respectively. Furthermore, the amidine group is oriented in such a way as to direct its N– H fragment to the central Pt(II) atom, with a nonbonding N(4)...N(5) distance of 2.328(3) Å; all of these structural features are akin to those observed in the relevant Pt(II) amidine complexes.<sup>58,59</sup>

Next, the cture of 3a is depicted in Figure 2, consisting of two essentially planar [Pt(pypm)] units, together with two *cis*oriented, bridging amidinates. However, the pypm chelate on each [Pt(pypm)] unit is arranged in an antiparallel fashion to



**Figure 1.** Structure of  $[Pt(pypm)Cl(F^{1}H)]$  (1) with thermal ellipsoids shown at 50% probability. Selected bond distances and interaction (Å): Pt-C(6) = 1.950(3), Pt-N(1) = 2.037(2), Pt-N(4) = 2.018(2), Pt-Cl(1) = 2.3901(7), and N(4)...N(5) = 2.328(3). Selected bond angles (deg): N(1)-Pt-N(4) = 175.33(10) and C(6)-Pt(1)-Cl(1) = 172.42(8).

maximize the  $\pi - \pi$  stacking interactions. The observed intramolecular Pt…Pt distance of 2.8845(2) Å is similar to that observed in many structurally characterized dimeric Pt(II) complexes<sup>60</sup> but is significantly longer than the closest intermolecular Pt…Pt contact of ~6.790 Å. In addition, this intramolecular Pt…Pt separation is also longer than the intraligand N···N nonbonding contact of amidinates (i.e., N(4)-N(5A) = 2.339(2) Å) and, as a result, the intramolecular pypm to pypm chelate separation, which is defined by the spatial distance between the C(6) atom of the pyrimidinato fragment and the N(1A) atom of an adjacent pyridine, is calculated to be 3.570(2) Å. Finally, due to the adoption of this clamshell geometry, the intramolecular center to center distances between the adjacent pyrimidinato and pyridyl rings (i.e., 4.144 Å) are notably longer than the corresponding intermolecular pypm to pypm separation (i.e., 3.758 Å).

**Photophysical Properties.** The UV–visible absorption spectra of all studied Pt(II) complexes were measured in  $CH_2Cl_2$  solution, while emission spectra were recorded using three physically distinctive samples, namely crystals (cr), sublimed powders (su), and vacuum-deposited thin films (th),

due to their different intermolecular packing interactions imposed during sample preparation. It is notable that all studied Pt(II) complexes showed no detectable emission in solution at room temperature, which is attributed to the fast collisional quenching by solvents, for having flexible amidine pendant in 1 and, then, lowered the NIR emission efficiency of Pt(II) dimers 2 and 3a-c, respectively.

UV-visible absorptions in  $CH_2Cl_2$  solution/thin film and solid-state emission spectra of Pt(II) monomer 1 and dimer 2 are shown in Figure 3 and Figure S1. The corresponding



Figure 3. UV-vis absorption recorded in  $CH_2Cl_2$  at room temperature and emission spectra of crystalline samples and sublimed powders of Pt(II) complexes 1 and 2.

numerical data are depicted in Table 1. For both complexes 1 and 2, the absorptions below 400 nm are primarily due to  $\pi\pi^*$  transitions originating from pypm cyclometalate and amidine ligand. In comparison, the broadened absorption bands of 2 with multiple peak wavelengths over the region of 400–650 nm are attributed to mixed <sup>1</sup>MMLCT and <sup>3</sup>MMLCT transitions, enhanced by the strong spin–orbit coupling due to the diplatinum unit. In fact, the lack of this lower energy absorption band in 1 also provided critical evidence to support this assignment.



Figure 2. (a) Structural drawing and (b) packing diagram of  $[Pt(pypm)(\mu-F^2)]_2$  (3a) with thermal ellipsoids shown at 50% probability. Selected bond distances and interactions (Å): Pt(1)-N(1) = 2.023(2), Pt(1)-N(4) = 2.020(2), Pt(1)-N(5) = 2.129(2), Pt(1)-C(6) = 1.960(2), C(6)... N(1A) = 3.570(2), Pt(1)...Pt(1A) = 2.8845(2), and N(4)...N(5A) = 2.339(2). Selected bond angles: N(1)-Pt(1)-N(4) = 176.43(8) and N(5)-Pt(1)-C(6) = 176.80(9).

Table	1.	Photop	hysical	Data	of t	he St	tudied	Pt(I	I)-Based	l Monomer	1 and	d Dimers	<b>2</b> and	1 3a–c
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			em $\lambda_{\rm max}/{\rm nm}^b$			$\Phi/\%^{b}$			$\tau/\mathrm{ns}^{b}$	
	abs $\lambda_{\rm max}/{\rm nm}~(\varepsilon/10^3~{ m M}^{-1}~{ m cm}^{-1})^a$	cr	su	th	cr	su	th	cr	su	th
1	265(21), 359(4)	475, 512, 552	477, 511, 552	476, 511, 537	8.4	7.3	5.5	752	578	387
2	256(42), 436(3.5), 524(3.8)	721	729	732	2.8	1.3	<1.0	41	40	26
3a	262(52), 325(36), 417(4.7), 528(2.8)	688	720	758	24.0	4.8	<1.0	177	125	41
3b	263(58), 321(40), 428(4.7), 530(3.1)	692	711	769	12.4	8.2	<1.0	185	167	31
3c	271(29), 331(27), 519(1.5)	698	706	726	12.4	7.0	<1.0	202	187	84
<sup>a</sup> Data	recorded at $1.0 \times 10^{-5}$ M in CH.Cl. <sup>b</sup>	PI data wara raco	orded as crystallin	e samples (cr) su	blimed fi	ne now	dore (en)	and va	-	nosited

"Data recorded at  $1.0 \times 10^{\circ}$  M in CH<sub>2</sub>Cl<sub>2</sub>." PL data were recorded as crystalline samples (cr), sublimed fine powders (su), and vacuum-deposited thin films (th).

Furthermore, the polycrystalline samples of Pt(II) complex 1 showed a structured emission profile with the first peak maximum at 475 nm and two lower-energy vibronic bands at 512 and 552 nm, which suggested the dominant ligandcentered  $\pi\pi^*$  transition character. The lowered emission quantum yield ( $\sim$ 8%) confirmed the existence of effective quenching pathways, which agreed with the existence of many loosely attached functional appendages on the molecule. Upon a switch from crystals to sublimed powders, the highest energy 0-0 emission reveals a notable decreased in relative intensity due to a change in local environment and hence intermolecular interaction. In sharp contrast, the dimer complex 2 exhibits a much broadened and red shifted MMLCT emission, showing that the intermolecular Pt…Pt contact has significantly affected the emission peak wavelength. In addition, complex 2 exhibited a relatively minor change in photophysical properties in all three morphological states: i.e., as crystals, sublimed powders, and deposited thin films (cf. Figure 3 and Table 1).

Next, UV-visible absorption and emission spectral data of the three aryl-substituted Pt(II) dimers 3a-c are depicted in Figure 4, Figure S2, and Table 1. Their photophysical



Figure 4. UV–vis absorption recorded in  $CH_2Cl_2$  and solid-state emission of crystalline samples of Pt(II) dimers 3a-c.

properties are similar to those of aforementioned Pt(II) complex 2 with a slight variation in emission peak position. Moreover, the emission peak of the crystalline samples 3a-c appears in a narrow range between 688 and 698 nm, among which the phenyl derivative 3a showed the highest emission efficiency of 24% in comparison to the other Pt(II) complexes (2, 2.8%; 3b, 12.4%; 3c, 12.4%). Moreover, 3a exhibits the greatest blue-shifted emission maximum among all these complexes, as shown in Table 1. Hence, the variation of emission quantum yield correlates with their relative peak emission wavelength: i.e., the longer the wavelength, the

poorer the emission efficiency . This red shifting becomes more noticeable for both the sublimed samples ( $\lambda_{max}$ : 3a, 720 nm; 3b, 711 nm; 3c, 706 nm) and vacuum-deposited thin films ( $\lambda_{max}$ : 3a, 758 nm; 3b, 769 nm; 3c, 726 nm), together with a reduction in emission quantum yield especially for vacuum-deposited thin films, revealing the consequence of the energy gap law.<sup>7,8</sup> Since the emission efficiencies of thin films for 2 and 3a-c are too weak to be detected, we assign the PLQY of these samples to be less than 1%, which is the instrumental detection limit on the basis of an integrated sphere for a solid sample. The detected red shift suggests the formation of more compressed Pt…Pt contacts, a greater number of  $\pi - \pi$  stacking interactions, and enhanced MMLCT transition character for the samples prepared, which follows the qualitative order

vacuum-deposited thin film > sublimed powder

#### > crystalline samples

The dependence of the photophysical properties vs the morphological arrangement was also investigated by powder Xray diffraction studies (XRD). As shown in Figure S3, all studied fine crystals of 3a-c revealed intense and sharp diffraction signals that correspond to the ordered packing structure with larger grain sizes. However, the sublimed powders and vacuum-deposited thin films showed progressively reduced diffraction signals, indicating that these Pt(II) complexes have poor crystallinity in both states. Especially in vacuum-deposited thin films, the latter are even worse than that of an amorphous arrangement. This could explain the dramatic changes in the quantum yields for diplatinum complexes 2 and 3a-c in different solid morphologies. We attribute this phenomenon to the nonradiative process induced by the defects under amorphous conditions, since a triplet exciton is prone to be quenched owing to the longer diffusion length in comparison to that of a singlet exciton.<sup>61,62</sup> This could also rationalize the morphological-dependent PLQY of all title complexes, among which the crystalline samples exhibit the highest PLQY because of their perfectly packed structures, while both the sublimed powder and vacuum-deposited thin film show much lower PLQYs due to the lack of an ordered packing arrangement.

In order to further evaluate the relationship between emission peak wavelengths and quantum yields, we repeated the PL measurement in a PMMA matrix with a doping level of 2 wt % at room temperature, with the aim that the rigid PMMA polymer can restrict both the rotational and vibration motion of Pt(II) emitters, giving improved photophysical properties. The corresponding spectra are shown in Figure S4 in the Supporting Information, while the numerical data are presented in Table 2. As can be seen, the majority of spectral features were akin to those obtained in crystalline samples,

Table 2. Emission Data of 2 wt % of the Studied Pt(II) Complexes in PMMA Matrix at Room Temperature

	em $\lambda_{\rm max}/{\rm nm}$	$\Phi/\%$	$\tau_{\rm obs}/{\rm ns}$	$k_{\rm r}/10^5 {\rm \ s}^{-1} {\ a}$	$k_{\rm nr}/10^5 \ {\rm s}^{-1} \ a$			
1	474, 512, 547	22.6	1911	1.18	4.05			
2	715	8.0	41.4	1.93	222			
3a	698	12.1	177.5	6.81	49.5			
3b	699	20.1	165.4	12.2	48.3			
3c	676	13.5	336.4	4.01	25.7			
${}^{a}k_{\rm r} = {\rm QY}/\tau_{\rm obs}$ and $k_{\rm nr} = (1 - {\rm QY})/\tau_{\rm obs}$ .								

except that the emission peak maximum of 3c in a PMMA matrix is blue-shifted to 676 nm in comparison to that observed for the crystalline sample (698 nm), which can be attributed to the media effect. Moreover, the observed nonradiative rate constants of Pt(II) complexes 2 and 3a-c are found to be proportional to the emission wavelengths, which, in a qualitative manner, confirms the prediction of energy gap law.

**Electrochemical Properties.** The electrochemical properties of Pt(II) complexes 1, 2, and 3a-c were studied using cyclic voltammetry, and their CV traces and numeric data are depicted in Figure 5 and Table 3. First, Pt(II) complex 1



Figure 5. Cyclic voltammograms measured in CH<sub>2</sub>Cl<sub>2</sub> for anodic sweep and in THF for cathodic sweep.

Table 3. Electrochemical Data of All Studied Pt(II) Complexes

	$E_{1/2}^{\mathrm{ox}}/\mathrm{V} \left[\Delta E_{\mathrm{p}}/\mathrm{V}\right]^{a}$	$E_{1/2}^{\rm re}/{\rm V} \left[\Delta E_{\rm p}/{\rm V}\right]^a$
1	1.32 [irr]	-2.25 [0.17]
2	0.14 [0.15]	-2.36 [irr]
3a	0.34 [0.10]	-2.06 [0.15]
3b	0.27 [0.09]	-2.08 [0.12]
3c	0.55 [0.08)	-1.92 [0.05]

<sup>*a*</sup>E<sub>1/2</sub> (V) refers to [ $(E_{pa} + E_{pc})/2$ ], where  $E_{pa}$  and  $E_{pc}$  are the anodic and cathodic peak potentials, respectively, referenced to the ferrocene redox couple (Fc/Fc<sup>+</sup>),  $\Delta E_p = E_{pa} - E_{pc}$  is for the reversible process, and "irr" denotes an irreversible process. The oxidation and reduction experiments were conducted in CH<sub>2</sub>Cl<sub>2</sub> and THF, respectively.

showed a positively shifted oxidation peak potential at 1.32 V and reversible reduction peak at -2.25 V, confirming its mononuclear nature. In contrast, Pt(II) complex 2 exhibited quasi-reversible oxidation and irreversible reduction peaks at 0.14 and -2.36 V, for which the negatively shifted oxidation potential is consistent with the formation of a diplatinum unit, while the small variation of reduction potential indicated a

pypm chelate centered reduction process. Moreover, the redox couples of 3a-c were reversible, among which the phenyl derivative 3a showed the redox peaks at 0.34 and -2.06 V; both of the positive shifts in comparison to those of 2 are attributed to a greater electron withdrawing character of the phenyl groups on bridging amidinates in comparison to that of the isopropyl substituents. After introduction of a 4-tert-butyl substituent in 3b, its redox peaks are cathodically shifted to 0.27 and -2.08 V, while the electron-withdrawing CF<sub>3</sub> substituents caused an opposite shift to 0.55 and -1.92 V for 3c. Both observations are consistent with the anticipated electronic character of these functional aryl substituents. Finally, in all these Pt(II) complexes, the changes in oxidation potentials are found to be much greater than the corresponding changes in reduction potentials. These results indicate the greater influence of amidinates on the intramolecular Pt…Pt bonding but less on the pypm chelate, as all reduction processes occur at the pypm cyclometalate, for which the long separation from bridging amidinates has less influence from their functional substituents.

**Raman Spectroscopy.** To investigate the possible intramolecular Pt…Pt interaction of diplatinum complexes, we measured the ground-state Raman spectra and conducted calculation on Pt–Pt stretching vibrations in the region between 80 and 200 cm<sup>-1</sup> (Figure 6 and Figure S5). Since



Figure 6. Ground-state Raman spectra of 1, 2, and 3a-c of vacuumdeposited thin films with a thickness of 1000 Å and excitation wavelength  $\lambda_{ex} = 532$  nm.

crystalline and powder samples exhibit severe luminescence interference to the Raman signals, we choose the vapordeposited thin film, which is almost nonemissive under the conditions of Raman measurements. In general, there are two major peaks, one occurring at around  $100 \text{ cm}^{-1}$  and the other at 150  $\text{cm}^{-1}$  in the Raman spectra. The broadened peak profile results from the superposition of multiple low-frequency Raman transitions correlated to the Pt…Pt stretching vibration (see Figures S6–S9 for the calculated vibrational modes). This assignment is also supported by the absence of low-frequency bands for monomer 1. The calculated Raman spectra indicate that different substituents give rise to a distinctive distribution of transitions, which show a higher energy peak at 150 cm<sup>-1</sup> in 2 and 3a but are not observable for complexes 3b,c (Figure S5, Raman spectra). In brief, this result, together with the singlecrystal X-ray data of 3a, confirms the existence of non-



Figure 7. (a) Current density-voltage-radiance and (b) EQE-current density characteristics of a complex 3b based device (insert: EL spectrum at 50 mA cm<sup>-2</sup>).

negligible Pt…Pt interactions for 2 and 3a-c, similar to the Pt…Pt interactions documented in the literature.<sup>63-65</sup>

Theoretical Analyses of UV-Vis Transition Properties. As evidenced by the low-frequency Raman spectra and the steady-state UV-vis spectra, the transition characteristics of 1, 2 and 3a-c were next validated by time-dependent density functional theory (TDDFT) calculations, shown in Figures S10–S14. The  $S_0-S_1$  transition of 1 showed typical absorption transition characteristics involving both a ligandcentered  $\pi\pi^*$  transition mixed with some MLCT and interligand chloride to pypm chelate (XLCT) charge transfer contribution. The orbitals involved in the  $S_0-S_1$  transition in 2 and **3a-c** showed a large contribution of  $d_{z^2}-d_{z^2}$  orbitals, leading to a small vibronic progression, which is apparently lacking for complex 1. The deviation of absorption energy between calculated and experimental results arises, in part, from state mixing between singlet and triplet states, which is not considered in the calculation and the incomplete basis set being applied.

Electroluminescent Properties. To determine the electroluminescent (EL) properties of the series of Pt(II) dimer complexes, complex 3b was selected as an emitter to fabricate NIR OLEDs due to its shortest observed emission lifetime in a thin film. The device was fabricated with a multilayered architecture of indium tin oxide (ITO)/ dipyrazino[2,3-f:2',3'-h]quinoxaline-2,3,6,7,10,11-hexacarbonitrile (HATCN, 10 nm)/1,1-bis[4-[N,N'-di(p-tolyl)amino]phenyl]cyclohexane (TAPC, 40 nm)/4,4',4"-tris(N-carbazolyl)-triphenylamine (TCTA, 10 nm)/complex 3b (20 nm)/ 4,7-diphenyl-1,10-phenanthroline (BPhen, 10 nm)/1,3,5-tris-(1-phenyl-1H-benzo[d]imidazole-2-yl)benzene (TPBi, 60 nm)/8-hydroxyquinolatolithium (Liq, 2 nm)/Al (100 nm). As shown in Figure 7, the complex 3b based nondoped device gives emission with an emission peak maximum at 767 nm, which is consistent with the PL peak maximum at 769 nm recorded as a vacuum-deposited neat film. Moreover, the maximum external quantum efficiency (EQE) is measured to be only 0.14%, which is consistent with the poor PLQY recorded in the deposited thin films. Despite this, the asfabricated NIR OLED device exhibits a very small efficiency roll-off at high current density (only dropping by 0.01% even at a current density of 300 mA cm<sup>-2</sup>), which could be attributed to the shortened emission lifetime of 3b.

**Conclusion.** In summary, sky blue emitting mononuclear Pt(II) complex 1 and NIR-emitting diplatinum complexes 2 and 3a-c bearing a pypm cyclometalate were synthesized and

characterized using spectroscopic methods and single-crystal X-ray structure determinations. Complexes 1 and 3a were exploited as paradigms for structural analysis; they consist of one and two quasi-planar "Pt(pypm)" units, together with a single formamidine and two bridging formamidinates, respectively. Furthermore, complex 3a reveals a shortened Pt…Pt contact and a structureless MMLCT emission with a peak wavelength at 688 nm as crystalline samples. In contrast to 2 with isopropyl-substituted formamidinates F<sup>1</sup>, all other diplatinum complexes 3a-c bearing aryl-substituted amidinates, i.e.  $F^2 - F^4$ , exhibited red-shifted emission on changing the morphological states from crystalline solids to sublimed powders and vacuum-deposited thin films. This observation is due to the enhanced  $\pi - \pi$  stacking interactions and Pt…Pt contacts, as their packing density is probably arranged in an ascending order: crystalline samples < sublimed powders < vacuum-deposited thin films. The existence of Pt…Pt contacts in the ground state is also confirmed by Raman spectroscopy, showing Pt…Pt stretching from 80 to 200 cm<sup>-1</sup>. An OLED with nondoped 3b realized electroluminescence with a peak wavelength at 767 nm and maximum EQE of 0.14%. Importantly, despite the existence of a dimeric structure with notable Pt…Pt contacts, its performance was significantly lower than that of the Pt(II) complex [Pt(fprpz)2],10 for which a maximum EQE of over 24% was reported for an NIR OLED device with an emission peak maximum at 740 nm. This seemingly contrary result implies that the extensively delocalized Pt…Pt interactions and high crystallinity are the key factors that boost the NIR emission efficiencies.

# EXPERIMENTAL SECTION

**General Information and Materials.** All reactions were performed under a nitrogen atmosphere. Solvents were distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification. 5-(Pyridin-2-yl)-2-(trifluoromethyl)pyrimidine (pypm)H was prepared using Pd-catalyzed C–C coupling of 5-bromo-2-(trifluoromethyl)pyrimidine and 2-(tributylstannyl)pyridine.<sup>39,66</sup> Mass spectra were obtained on a JEOL AccuTOF GCX instrument operating in field desorption (FD) mode. <sup>1</sup>H and <sup>19</sup>F NMR spectra were recorded on a Bruker AVANCE 500 instrument or a Varian 400-MR instrument. Elemental analysis was carried out with a Heraeus CHN-O rapid elemental analyzer. Synthesis of *N*,*N*'-Dialkyl- and *N*,*N*'-Diarylformamidines.<sup>67</sup>

Synthesis of N,N'-Dialkyl- and N,N'-Diarylformamidines.<sup>67</sup> A mixture of diisopropylamine or functionalized aniline (50 mmol) and triethyl orthoformate (25 mmol) was heated to 160 °C for 2 h. After it was cooled to room temperature, the mixture was dried under vacuum and the residue was recrystallized in a mixture of CH<sub>2</sub>Cl<sub>2</sub> and

hexane to give the desired compound. This compound was relatively unstable and was used for subsequent reaction without further purification.

Selected spectroscopic data of *N,N'*-bis(isopropyl)formamidine (F<sup>1</sup>H): yield 64%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 273 K)  $\delta$  7.22 (s, 1H), 3.51–3.41 (m, 2H), 1.26 (d, *J* = 6.6 Hz, 12H).

Selected spectroscopic data of  $N_iN'$ -diphenylformamidine (F<sup>2</sup>H): yield 80%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 273 K)  $\delta$  8.19 (s, 1H), 7.36– 7.28 (m, 4H), 7.14–7.01 (m, 6H).

Selected spectroscopic data of N,N'-bis(4-*tert*-butylphenyl)-formamidine (F<sup>3</sup>H): yield 86%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 273 K)  $\delta$  8.17 (s, 1H), 7.33 (d, J = 8.5 Hz, 4H), 6.98 (d, J = 8.3 Hz, 4H), 1.32 (s, 18H).

Selected spectroscopic data of *N*,*N*'-bis(4-trifluoromethylphenyl)formamidine (F<sup>4</sup>H): yield 93%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 273 K)  $\delta$  8.19 (s, 1H), 7.59 (d, *J* = 8.2 Hz, 4H), 7.16 (d, *J* = 7.7 Hz, 4H).

Synthetic Procedure for [Pt(pypm)Cl(F<sup>1</sup>H)] (1). A mixture of K<sub>2</sub>PtCl<sub>4</sub> (1.0 mmol) and 5-(pyridin-2-yl)-2-(trifluoromethyl)pyrimidine (pypmH, 1.1 mmol) in a mixture of water and ethoxyethanol was heated to reflux for 36 h. After it was cooled to room temperature, the solution was treated with 30 mL of water. The solid was filtered, thoroughly washed with water, and dried under vacuum to give a black solid. To this black solid were added N,N'diisopropylformamidine (F<sup>1</sup>H, 1.3 mmol), K<sub>2</sub>CO<sub>3</sub> (3 mmol), and 20 mL of 1,2-dichloroethane; the mixture was refluxed for 24 h. After that, the solution was evaporated to dryness and the residue was extracted into CH<sub>2</sub>Cl<sub>2</sub> (50 mL). This solution was next washed with water (50 mL), dried over anhydrous Na2SO4, filtered, and concentrated to dryness. The obtained solid was purified by column chromatography with a 1/1 mixture of hexane and ethyl acetate as eluent to give a yellow solid in 55% yield. It was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> and hexane and purified by vacuum sublimation. Crystals suitable for X-ray diffraction were obtained from a mixture of CH<sub>2</sub>Cl<sub>2</sub> and methanol at room temperature.

Selected spectroscopic data of 1: <sup>1</sup>H NMR (400 MHz, DMSO- $d_{6}$ , 273 K)  $\delta$  9.69 (d, J = 5.7 Hz, 1H), 8.95 (s, 1H), 8.31 (d, J = 7.9 Hz, 1H), 8.24 (t, J = 7.6 Hz, 1H), 7.75 (d, J = 12.6 Hz, 1H), 7.66 (t, J = 6.5 Hz, 1H), 6.77 (td, J = 10.4, 3.7 Hz, 1H), 3.83–3.75 (m, 1H), 3.60–3.53 (m, 1H), 1.31 (d, J = 6.6 Hz, 3H), 1.27 (d, J = 6.6 Hz, 3H), 1.09 (d, J = 6.5 Hz, 3H), 1.00 (d, J = 6.5 Hz, 3H), 1.07 (d, J = 6.6 Hz, 3H), 1.09 (d, J = 6.5 Hz, 3H), 1.00 (d, J = 6.5 Hz, 3H), 1.00 (d, J = 6.5 Hz, 3H), 1.00 (d, J = 6.5 Hz, 3H), 1.07 (Li<sub>3</sub>N<sub>5</sub>Pt [M<sup>+</sup>] m/z 582.1, found 583.1. Anal. Calcd for C<sub>17</sub>H<sub>21</sub>ClF<sub>3</sub>N<sub>5</sub>Pt: C, 35.03; H, 3.63; N, 12.01, Found: C, 35.40; H, 3.55; N, 12.08.

Selected X-ray data of 1:  $C_{17}H_{21}ClF_3N_5Pt$ ;  $M_r = 582.93$ ; orthorhombic; space group *Pbca*; a = 9.9600(4) Å, b = 18.9150(8) Å, c = 20.7628(9) Å; V = 3911.6(3) Å<sup>3</sup>; Z = 8;  $\rho_{calcd} = 1.980$  Mg m<sup>-3</sup>; F(000) = 2240; crystal size  $0.291 \times 0.058 \times 0.029$  mm<sup>3</sup>; T = 150 (2) K;  $\mu = 7.350$  mm<sup>-1</sup>; 24704 reflections collected, 5690 independent reflections ( $R_{int} = 0.0346$ ), maximum and minimum transmission 0.7460 and 0.5409; restraints/parameters = 0/252, GOF = 1.099, final  $R1(I > 2\sigma(I)) = 0.0214$  and wR2(all data) = 0.0422; largest diffraction peak and hole 1.660 and -1.234 e Å<sup>-3</sup>.

**Conversion of [Pt(pypm)Cl(F<sup>1</sup>H)] (1) to [Pt(pypm)(\mu-F<sup>1</sup>)]<sub>2</sub> (2).** A mixture of 1 (1.0 mmol) and Ag<sub>2</sub>O (1.1 mmol) in 20 mL of 1,2dichloroethane was heated to reflux for 24 h. After that, the solution was evaporated to dryness and the residue was extracted into CH<sub>2</sub>Cl<sub>2</sub> (50 mL). This solution was next washed with deionized water (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated to dryness under vacuum. The crude product was purified by column chromatography with pure CH<sub>2</sub>Cl<sub>2</sub> as eluent to give a red solid in 70% yield. It was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> and hexane and further purified by vacuum sublimation.

Selected spectroscopic data of 2: <sup>1</sup>H NMR (400 MHz, DMSO- $d_{6}$ , 273 K)  $\delta$  8.83 (d, J = 5.9 Hz, 2H), 8.35 (s, 2H), 8.17 (s, 2H), 7.78 (tdd, J = 7.8, 1.4, 1.3 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.28 (t, J = 6.6 Hz, 2H), 4.12–4.05 (m, 2H), 4.00–3.93 (m, 2H), 1.56 (d, J = 6.8 Hz, 6H), 1.50 (d, J = 6.8 Hz, 6H), 1.39 (d, J = 6.7 Hz, 6H), 1.32 (d, J = 6.7 Hz, 6H); <sup>19</sup>F NMR (376 MHz, DMSO- $d_6$ , 273 K)  $\delta$  –68.26 (s, 6F); MS (FD) calcd for C<sub>34</sub>H<sub>40</sub>F<sub>6</sub>N<sub>10</sub>Pt<sub>2</sub> [M<sup>+</sup>] m/z 1092.3, found

1092.1. Anal. Calcd for  $C_{34}H_{40}F_6N_{10}Pt_2$ : C, 37.37; H, 3.69; N, 12.82, Found: C, 37.26; H, 3.61; N, 12.87.

Synthetic Procedure for  $[Pt(pypm)(\mu-F^2)]_2$  (3a),  $[Pt(pypm)(\mu-F^2)]_2$  (3b),  $[Pt(pypm)(\mu-F^2)]_2$  (3b),  $[Pt(pypm)(\mu-F^2)]_2$  (3c),  $[Pt(pypm)(\mu-F^2)]_2$  (3c), [Pt(F<sup>3</sup>)]<sub>2</sub> (3b), and [Pt(pypm)(µ-F<sup>4</sup>)]<sub>2</sub> (3c). A mixture of K<sub>2</sub>PtCl<sub>4</sub> (1.0 mmol) and 5-(pyridin-2-yl)-2-(trifluoromethyl)pyrimidine (pypmH, 1.1 mmol) in a mixture of water and ethoxyethanol was heated to reflux for 36 h. After it was cooled to room temperature, the solution was treated with 30 mL of water. The solid was filtered, thoroughly washed with water, and dried under vacuum to give a black solid. To this black solid were added respectively N,N'-diarylformamidine (F<sup>2</sup>H, F<sup>3</sup>H, and F<sup>4</sup>H, 1.3 mmol), K<sub>2</sub>CO<sub>3</sub> (3 mmol), and 20 mL of 1,2dichloroethane; the mixture was refluxed for 24 h. After that, the solution was evaporated to dryness and the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL). It was next washed with water (50 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated to dryness. The crude product was purified by column chromatography with CH<sub>2</sub>Cl<sub>2</sub> as eluent to give a dark red solid. It was further purified by recrystallization from CH2Cl2 and hexane as well as vacuum sublimation. Crystals of 3a suitable for X-ray diffraction were obtained from a mixture of CH2Cl2 and methanol at room temperature.

Selected spectroscopic data of **3**a: yield 65%; <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ , 273 K)  $\delta$  8.46 (s, 2H), 8.27 (s, 2H), 7.86–7.78 (m, 4H), 7.68 (d, *J* = 5.7 Hz, 2H), 7.44 (d, *J* = 7.8 Hz, 4H), 7.32 (d, *J* = 7.8 Hz, 4H), 7.23 (t, *J* = 7.8 Hz, 4H), 7.14 (t, *J* = 7.8 Hz, 4H), 7.06 (t, *J* = 7.4 Hz, 2H), 6.93 (t, *J* = 7.3 Hz, 2H), 6.61 (td, *J* = 6.2, 2.2 Hz, 2H); <sup>19</sup>F NMR (470 MHz, DMSO- $d_6$ , 273 K)  $\delta$  –68.94 (s, 6F); MS (FD) calcd for C<sub>46</sub>H<sub>32</sub>F<sub>6</sub>N<sub>10</sub>Pt<sub>2</sub> [M<sup>+</sup>] *m*/*z* 1228.2, found 1228.3. Anal. Calcd for C<sub>46</sub>H<sub>32</sub>F<sub>6</sub>N<sub>10</sub>Pt<sub>2</sub>: C, 44.96; H, 2.62; N, 11.40, Found: C, 45.07; H, 2.52; N, 11.36.

Selected X-ray structural data of **3a**:  $C_{47}H_{34}Cl_2F_6N_{10}Pt_2$ ;  $M_r = 1313.92$ ; monoclinic; space group C2/c, a = 21.4155(7) Å, b = 15.8054(6) Å, c = 15.3793(5) Å;  $\beta = 119.1925(11)^\circ$ ; V = 4544.4(3) Å<sup>3</sup>; Z = 4;  $\rho_{calcd} = 1.920$  Mg m<sup>-3</sup>; F(000) = 2520; crystal size 0.220 × 0.203 × 0.187 mm<sup>3</sup>; T = 150(2) K;  $\mu = 6.339$  mm<sup>-1</sup>; 21360 reflections collected, 6619 independent reflections ( $R_{int} = 0.0269$ ), maximum and minimum transmission 0.7460 and 0.5995; restraints/ parameters = 32/326, GOF = 1.071, final R1( $I > 2\sigma(I)$ ) = 0.0198 and wR2(all data) = 0.0467; largest diffraction peak and hole 0.904 and -0.632 e Å<sup>-3</sup>.

Selected spectroscopic data of **3b**: yield 60%; <sup>1</sup>H NMR (500 MHz, DMSO- $d_{6}$ , 273 K)  $\delta$  8.44 (s, 2H), 8.18 (s, 2H), 7.86 (d, J = 5.8 Hz, 2H), 7.83–7.77 (m, 4H), 7.28 (d, J = 8.6 Hz, 4H), 7.19 (d, J = 8.6 Hz, 4H), 7.19 (d, J = 8.6 Hz, 4H), 7.14 (d, J = 8.6 Hz, 4H), 7.09 (d, J = 8.6 Hz, 4H), 6.69 (td, J = 6.0, 2.5 Hz, 2H), 1.22 (s, 18H). 1.17 (s, 18H); <sup>19</sup>F NMR (470 MHz, DMSO- $d_{6}$ , 273 K)  $\delta$  –68.91 (s, 6F); MS (FD) calcd for C<sub>62</sub>H<sub>64</sub>F<sub>6</sub>N<sub>10</sub>Pt<sub>2</sub> [M<sup>+</sup>] m/z 1452.5, found 1452.6. Anal. Calcd for C<sub>62</sub>H<sub>64</sub>F<sub>6</sub>N<sub>10</sub>Pt<sub>2</sub>: C,51.24; H, 4.44; N, 9.64, Found: C, 51.60; H, 4.34; N, 9.56.

Selected spectroscopic data of **3c**: yield 64%; <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ , 273 K)  $\delta$  8.57 (s, 2H), 8.51 (s, 2H), 8.33 (d, J = 5.7 Hz, 2H), 7.91–7.81 (m, 4H), 7.71–7.64 (m, 8H), 7.58 (d, J = 8.7 Hz, 4H), 7.45 (d, J = 8.6 Hz, 4H), 7.09–7.04 (m, 2H); <sup>19</sup>F NMR (470 MHz, DMSO- $d_6$ , 273 K)  $\delta$  –60.09 (s, 6F), –60.27 (s, 6F), –69.08 (s, 6F); MS (FD) calcd for C<sub>50</sub>H<sub>28</sub>F<sub>18</sub>N<sub>10</sub>Pt<sub>2</sub> [M<sup>+</sup>] *m*/*z* 1500.2, found 1500.3. Anal. Calcd for C<sub>50</sub>H<sub>28</sub>F<sub>18</sub>N<sub>10</sub>Pt<sub>2</sub>: C,40.01; H, 1.88; N, 9.33. Found: C, 40.35; H, 1.99; N, 9.26.

**Photophysical Measurements.** Steady-state UV–vis absorption and emission spectra were recorded using the Hitachi (U-4100) spectrophotometer and the Edinburgh (FS920) fluorometer, respectively. The nanosecond time-resolved studies were performed by an Edinburgh FL 900 time-correlated single photon-counting (TCSPC) system with a pulsed hydrogen- or nitrogen-filled lamp as the excitation light source and with an InGaAs detector. Data were fitted with sum of exponential functions using a nonlinear leastsquares procedure in combination with the convolution method. The Raman spectra were collected with an Andor IDus 420 CCD instrument with excitation wavelength 532 nm. All photophysical measurements in this study were performed at room temperature (298 K).

# ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b01754.

General information on calculations and device fabrication, as well as the results of the calculated Raman transition and TD-DFT calculations of the studied Pt(II) metal complexes (PDF)

# **Accession Codes**

CCDC 1920736–1920737 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.

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#### Notes

The authors declare no competing financial interest.

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