**Modulation of Solid-State Aggregation of Square-Planar Pt(II) Based Emitters:
Enabling Highly Efficient Deep-Red/Near Infrared Electroluminescence**

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Design of square-planar Pt(II) complexes with highly efficient solid-state near infrared (NIR) luminescence for electroluminescence is attractive but challenging. This study presents the fine-tuning of excited state properties and application of a series of isoquinolinyl pyrazolate Pt(II) complexes that are modulated by steric demanding substituents. It reveals that the bulky substituents do not always disfavor metallophilic Pt $\cdots$ Pt interactions. Instead, π - π stacking among chelates, which are fine-tuned by the associated substituents, also exerts strong influence to the MMLCT transition character. Theoretical calculation indicate that Pt $\cdots$ Pt contacts become more relevant in the trimers rather than dimers, especially in their T₁ states, associated with a change from mixed ³LC/³MLCT transition in the monomer/dimer to mixed ³LC/³MMLCT transition character in the trimer. Electroluminescence devices affording intense deep-red/NIR emission (near 670 nm) with unprecedentedly high external quantum efficiency over 30% are demonstrated. This work provides deeper insights into formation MMLCT transition of square-planar Pt(II) complexes and efficient molecular design for deep-red/NIR electroluminescence.

1. Introduction

Materials with efficient luminescence in solid states are the subject of ever-increasing interest from both scientific and industrial point of views.^[1-4] Organic light-emitting diodes (OLEDs) which employ various kind of emissive materials have already earned a pivotal position for both full-color flat-panel display and solid-state lighting applications.^[5,6] To date, a variety of light-emitting materials, including both organic and organometallic luminophores, have been contrived for organic electroluminescence

(EL) devices, and their excited state energy gaps can be fine-tuned from blue,^[7,8] green^[9,10] and even to orange-red^[11,12] regions of the visible spectrum and with nearly unitary photoluminescence quantum yield (PLQY). Inspired by the dramatic progresses of light-emitting diode technologies, much effort has been diverted to the researches on deep-red to near infrared (NIR) OLEDs, because of their unique applications in optical communication, night-vision readable displays, and photodynamic therapy.^[13–16] However, only a few materials were reported to show efficient deep-red to NIR emissions.^[17–20] This represents a highly challenging objective because of the prediction of “energy gap law”, which stated that the non-radiative decay rate constant increases exponentially with decreasing optical energy gap (ΔE_{opt}).^[21] One potential strategy to red-shift the excited state energy to deep-red/NIR region is to use square-planar Pt(II) complexes with strong aggregation in solid state, for which one representative example has exhibited emission peak max. at 740 nm and with PLQY as high as 81%; thereafter, superior performance with maximum external quantum efficiency (EQE) of up to $24 \pm 1\%$ was achieved.^[22] Recently, Zhou and co-workers also reported a series of deep-red and NIR light-emitting pyrimidine-based Pt(II) complexes with PLQY up to 74% and OLEDs that showed emission max. at 724 nm and with max. EQE of 16.7%.^[23]

Generally speaking, Pt(II) metal complexes are notable to its planar molecular geometry originated from the d^8 electronic configuration, which allows extensive intermolecular metallophilic contact along the sterically undemanding z -axis via d - d orbital interaction (**Scheme 1**). This feature endows Pt(II) complexes to exhibit rich

dimer/aggregate photophysical properties; i.e. a remarkably red-shifted emission in comparison to those of monomeric species.^[24] The corresponding processes are denoted as metal-metal-to-ligand charge transfer (MMLCT) transitions, in which the electron is excited from a filled Pt···Pt antibonding d_{σ^*} orbital to a vacant π^* orbital of chelate. The gap of MMLCT excited states have strong dependence on the Pt···Pt interaction; i.e. shortened the metal-metal separation and lowered the MMLCT transition energy.^[25] The metallophilic interactions can further manifest themselves as dimers, trimers, oligomers or even one-dimensional stacked structure with Pt···Pt separation shorter than the sum of van der Waals radii.^[26–29] Metallophilic Pt···Pt interactions are known to be comparable to the bond strength of hydrogen bonding, but are much weaker than that of typical covalent and ionic bonding.^[30] This means that these relatively weakened metallophilic bonding can be easily disturbed by both steric effect and other intra- or inter-molecular interactions, such as solvation, π – π stacking, both hydrogen and halogen bonding interactions, etc.^[31–34] It also indicated that metallophilic interactions often coexist with other intermolecular forces that, in turn, would stabilize or destabilize the metal···metal interactions. Therefore, understanding the structure-property relationship of Pt(II) complexes and mastering the metallophilic interactions via manipulation of packing motifs in solid state would significantly promote the development of deep-red/NIR OLEDs.

Herein, we presented the excited-state properties and actual application of a series of isoquinolinyl pyrazolate Pt(II) complexes that were modulated by steric-demanding substituents such as 2,6-dimethylphenyl (dmp) and 2,6-diisopropylphenyl

(dip) as illustrated in Scheme 1. We also discovered that these bulky substituents do not always disfavor metallophilic Pt···Pt interactions. Instead, π – π stacking among chelates, which were fine-tuned by the associated substituents, also exerts strong influence to the MMLCT transition character. This allows us to realize highly efficient OLEDs with peaking wavelength over 670 nm and max. EQE as high as 30%.

2. Results and Discussion

2.1. Syntheses and characterization

Five Pt(II) metal complexes **1–5** (Scheme 1) bearing isoquinolinyl pyrazolate chelates were prepared according to their literature precedent, to which the detailed synthetic protocols are shown in the Supporting Information. It is notable that the homoleptic Pt(II) metal complexes **1**, **2** and **3** were prepared by direct treatment of two eq. of pyrazole chelate with Pt(DMSO)₂Cl₂ in presence of Na₂CO₃.^[26] In contrast, the heteroleptic counterparts **4** and **5** were obtained by coordination of one chelate to K₂PtCl₄ in forming a dichloride intermediate, followed by addition of the second pyrazolate chelate.^[35] All isolated Pt(II) metal complexes were fully characterized by mass spectrometry, elemental analyses, and ¹H and ¹⁹F NMR spectroscopies.

High-quality single crystals of **1** were successfully obtained from slow cooling of a hot solution of *p*-xylene. Single crystal X-ray structural analysis was executed in confirming their molecular structure as well as the packing arrangement in the solid state. As illustrated in Figure S1, complex **1** showed a planar coordination configuration with both isoquinolinyl pyrazolate chelates held by double inter-ligand C–H···N

hydrogen bonding, to which the N $\cdots$ H distance is measured to be 2.18 Å, showing H-bonding distance comparable to its literature precedents.^[35,36] Moreover, the molecules aligned along the [010] direction with a slipped, parallel arrangement. Strong π - π stacking is confirmed by the shortened interlayer separation of 3.52 Å. In this case, inter-ligand π - π stacking becomes predominant and, thus the vertical intermolecular separation is limited by the sum of van der Waals radii of carbon atoms of aromatic ligands. However, the Pt $\cdots$ Pt distance is measured to be 5.03 Å, giving insignificant MMLCT characteristics in the crystal structures. In fact, this lengthened Pt $\cdots$ Pt interaction is confirmed by the orange color observed for the single crystals under excitation, which is in sharp contrast to the red color displayed by the corresponding vacuum deposited thin film (TF), which is expected to exhibit a relatively shortened intermolecular Pt $\cdots$ Pt separation.

Moreover, all isoquinolinyl pyrazolates formed planar ensembles around Pt(II) metal and, hence, are expected to possess strengthened π - π stacking interaction between individual molecule in both crystalline solid and TF. Moreover, CF₃-substituted pyrazolate also plays a key role in promoting intermolecular interaction. To name a few, the CF₃ substituents are able to increase both the electron mobility^[37,38] and crystallinity of functionalized samples,^[11,39] while the pyrazolate fragment can enhance the inter-ligand H-bonding between its sp² hybridized N atom and C-H moiety of adjacent isoquinolinyl entity (vide supra),^[40] further consolidate the planarity and metal-chelate bond strength of Pt(II) complexes (Scheme 1). Furthermore, the packing in solid state can be systematic modified by introduction of bulky substituents (i.e. dmp

or dip) at the 6-position of isoquinolinyl fragment, as represented by the prototype Pt(II) metal complex **1**. This structural modification afforded two additional homoleptic (**2** and **3**) and two heteroleptic Pt(II) metal complexes (**4** and **5**), showing structural and photophysical characters that are dependent to their substituents.

2.2. Photophysical Properties

Figure S1 shows the UV-vis absorption and PL spectra of all Pt(II) complexes **1–5** in CH₂Cl₂ (10⁻⁵ M), and the related photophysical data are summarized in **Table 1**. All of them display essentially identical absorption and emission spectra, indicating that the bulky 6-substituents on isoquinolinyl fragment have negligible influences to their electronic structures of well separated molecules in solution. More specifically, the absorption bands at around 290 nm with high extinction coefficients (ϵ , ~7900–9100 M⁻¹ cm⁻¹) are ascribed to ligand-centered pyrazolate $\rightarrow$ isoquinoline intra-ligand π – π^* transitions,^[26] while the less intense absorption bands located at around 380–460 nm (less than 1000 M⁻¹ cm⁻¹) are originated from the mixed ligand-centered (LC) π – π^* and metal-to-ligand charge transfer (MLCT) transitions.^[41,42] Furthermore, these Pt(II) complexes exhibit bright orange emission in degassed CH₂Cl₂ with PLQY in the range of 25.8 to 37.9%. Phosphorescence from combined ³LC/³MLCT process is confirmed by the well-resolved PL profiles with observed lifetimes in microsecond regions (τ_{obs} = 10.8–15.9 μ s), which also indicates the lack of excimer or even aggregated states in solution.

In sharp contrast, the photophysical properties of sublimed powder (SP) of **1–5** (denoted as SP1 to SP5) behaved very different from those observed in solution. The related photophysical parameters are summarized in Table 1. The samples SP1, SP2 and SP4 appear as yellow and orange and exhibit absorption onset extended to ~600 nm, while SP3 and SP5 appear as deep-red, showing an absorption profile extending to ~650 nm (**Figure 1a**). Hence, the more red-shifted absorption of SP3, SP4 and SP5 that occurred from 600 to 650 nm should be considered as the MMLCT transition, while the absorption bands below 600 nm for both SP1 and SP2 are dominated by intra-ligand $\pi-\pi^*$ or charge transfer characters. The emission spectra also follow a similar pattern; i.e. those with blue-shifted absorption onset exhibited structured emission profile, while those with lower energy onset of absorption have showed much red-shifted, featureless emission. To our surprise, SP1 shows the essentially identical PL profile in comparison to the solution spectrum, while SP2 showed slightly increased contribution from the longer wavelength emission component, but all other samples, i.e. SP3, SP4 and SP5, exhibited predominantly lower-energy, structureless emissions. These photophysical characteristics are distinctive from the common excimer systems,^[43] in which all bulky substituents introduced into the system, should have a strong detrimental effect to the Pt...Pt interaction that promoted the MMLCT transition characteristics.

For further investigating this behavior, transient PL decay spectra of all Pt(II) complexes **1–5** in SP state were recorded and shown in Figure 1b. As can be seen, SP1 and SP2 showed the longest τ_{obs} of 4.98 and 3.61 μs , respectively, which are in good agreement with the structured profile observed and the LC dominated excited state

character. SP3 and SP5 exhibit much short-lived τ_{obs} of less than 250 ns, a result of the MMLCT dominated transition character. Moreover, SP4 displays a deep-red emission with peak maximum at 670 nm with τ_{obs} of 0.59 μs , together with a relatively weak, higher-energy shoulder at 570 nm and with more elongated τ_{obs} of 2.48 μs , respectively. This behavior is consistent with the co-existence of both LC and MMLCT excited state character in SP4 upon excitation.

It is also notable that the PLQY of SP samples increase as the ΔE_{opt} decrease (Figure 1c). For example, SP3 and SP5 showed the highest and second highest PLQY of 91.3 and 68.7% with the smallest and second smallest ΔE_{opt} of 1.89 and 1.90 eV, respectively, while SP1 exhibits the lowest PLQY of 10.2% as it possessed the largest ΔE_{opt} of 2.16 eV. Hence, the lower lying excited state of this class of Pt(II) complexes are strongly coupled with both the reduced τ_{obs} and improved PLQY.^[22,44,45] Combined with above observations, it implied that more efficient MMLCT transitions are obtained in both Pt(II) complexes **3** and **5** with dual and single dip-substituted isoquinoliny chelate, respectively.

Absorption and PL spectra for TF of **1–5** prepared by vacuum deposition (500 Å, deposition rate $\sim 1 \text{ Å s}^{-1}$) on fused silica (denoted as TF1 to TF5) are shown in **Figure 2a**. Besides the higher energy absorption bands that are comparable to those recorded in solution (*vide supra*), a newly emerged MMLCT transition is clearly observed in the region of 490–600 nm for all the TF samples, which is also similar to the previously reported data.^[22,44] The MMLCT absorption transitions exhibited small oscillator strengths with low ε , which are often difficult to be resolved from more

intense LC and MLCT transitions.^[46] It is worth noting that TF1 exhibits the most prominent MMLCT transition band, not observed in solution, but overlapped with the absorption onset of SP1 to certain degree. This intensified MMLCT character can be attributed to the formation of the Pt···Pt metallophilic interaction.^[32,47] To our surprise again, totally distinctive from the emission spectra of SP samples in Figure 1a, all spectra of TF1–5 demonstrate homologous Gaussian pattern, with peak max. ranging from 672 to 691 nm as shown in Figure 2a. Taking **1** as an example, its emission dramatically changes from a vibronic coupled profile with first peak max. at 604 nm in SP1, to a featureless pattern with peak max. at 672 nm in TF1. The corresponding PLQY is also boosted from 10.2 to 80.5% in the meantime. This change in photophysical data is probably induced by the enhanced Pt···Pt metallophilic interaction that existed in TF1 but not in SP1.

Generally speaking, sublimation involves a fast mass transport process, during which all volatile molecules in vacuum are deposited on substrate surface rapidly. In contrast, the vacuum deposited TF was prepared under high vacuum and the molecules are slowly deposited (kept at $\sim 1.0 \text{ \AA s}^{-1}$) under a thermodynamic controlled manner. Therefore, it existed a better packing arrangement in TFs, which would improve the likelihood of better intermolecular Pt···Pt interaction. We also believed that these TF samples may possess at least three closely associated Pt(II) molecules bearing both the strong intermolecular π – π stacking and Pt···Pt metallophilic interaction, simply because that the crystal structural analyses on **1** has already showed that the most stable arrangement of dimers possesses only the intermolecular π – π stacking, but no Pt···Pt

metallophilic interaction. After then, the concomitant MMLCT transitions of aggregated species in the TF give formation of the observed red-shifted emission.^[48] Furthermore, all TF samples show monoexponential decay (Figure 2b) with τ_{obs} lower than 700 ns and radiative rate constants (k_r) as high as 10^7 s^{-1} . These submicrosecond τ_{obs} with high k_r further support the triplet $^3\text{MMLCT}$ transition detected in all TF samples. These observations highlight a distinctive excited state characters and will be investigated in subsequent theoretical investigations.

The MMLCT transition can be further confirmed by the temperature-dependent spectroscopy, as shown in Figure 2c–d and Figure S3–6. We take TF1 as an example, it indicated that upon cooling from 300 to 80 K, its broadband emission corresponding to the MMLCT experiences a bathochromic shift from 674 to 705 nm (Figure 2c), during which the τ_{obs} also increased from 0.26 to 1.72 μs (Figure 2f). Additionally, the emission bandwidth becomes narrowed as temperature decreases, with the full-width at half-maximum (FWHM) reduced from 104 nm at 300 K to 74 nm at 80 K (Figure 2e). These changes of excited-state properties are due to a decrease of Pt···Pt distance by virtue of lattice contraction upon cooling, which are also in accordance to the MMLCT assignment,^[49] or can be attributed to the delocalized carrier.^[50] Note that although other TF samples show similar spectral behaviors versus temperature, subtle differences still existed. For example, a higher energy shoulder at 590 nm appeared in the spectrum of TF2 at 170 K and downwards (Figure S3a), while measurement of emission lifetime for this band exhibited a bi-exponential τ_{obs} , to which one long lifetime component is notably distinctive from that of main peak (Figure S3c–d). This

behavior is similar to that observed in SP4, which is assignable to the co-existence of both ^3LC and $^3\text{MMLCT}$ transition processes.

2.3. GIXD Studies

TFs of Pt(II) complexes **1–5** were deposited on (100) surface of silicon wafer using thermal vacuum deposition and the averaged metric parameters of crystallites were investigated by grazing-incidence X-ray diffraction (GIXD) studies using synchrotron radiation facility of NSRRC. All TFs showed weak and diffused GIXD signals (Figure 3 and Figure S7), indicative of low crystallinity, which can be confirmed by the small grain sizes (correlation lengths) along the three lattice axes (**Table 2**). The extents of molecular stacking, i.e. correlation lengths along *c*-axis, are minimal and decrease with lower molecular symmetry and larger substituents. The average numbers of stacking molecular planes in the crystallites are 5, 2, 3, 2, and 4 for **1–5** respectively. Electron density maps (EDMs) were calculated from the 2D GIXD patterns and depicted in **Figure 3**. These EDMs reveal the electron density projection in *ab*- and *ac*-planes. From these EDMs, molecular dimensions as well as molecular plane packing patterns in the *ab*- and *ac*-planes can be deduced by assuming van der Waals contacts of neighboring molecules. The representative packing patterns along *ab*- and *ac*-planes in Figure 3 are drawn and can be fairly compared. The EDMs resolved molecular lengths and widths are in accordance with the pattern and size of substitution. Pt(II) complex **3** is found to be with the largest length while complex **1** is of the smallest length and width. It is noted that complexes **2** and **3** show layer inter-digitation in *ac*-plane,

ascribed to the possibly staggered packing of bulky dmp and dip groups of stacked complexes, which can also be clearly visualized in molecular plane overlap in the *ab*-plane projection of molecular packing. In all TFs, the Pt(II) molecular planes are roughly perpendicular to the substrate with the tilting angles of 17, 26, 11, 18, and 16° for **1**–**5** respectively. The similar tilting angles for **1**, **4**, and **5** result in comparable Pt···Pt distances of 0.45–0.48 nm. On the other hand, the relative larger and smaller tilting angles for **2** and **3** respectively lead to the corresponding longer (0.51 nm) and shorter (0.41 nm) Pt···Pt distances. The longer Pt···Pt separation observed in **2** is an averaged value and may suggest the existence of closely packed dimers (or trimers) that are separated by the longer Pt···Pt separation among these aggregated units.^[26] The π – π stacking distances are in the range of 0.33–0.38 nm. The shortest π – π stacking distance of 0.33 nm for **3** may be attributed to the higher molecular symmetry for more efficient stacking and the largest substituents for interlocked stacking. For the vacuum deposited TF samples, **3** shows a significantly shorter Pt···Pt distance than others, which is in accordance with the measured considerably red-shifted emission. Within the averaged crystallite, **2** is with the longest Pt···Pt distance and the minimal number of stacking molecules, in accordance to the least red-shifted optical behavior.

2.4. DFT and TD-DFT Calculations

To gain further insights into the electronic structures and photophysical properties of the investigated isoquinolinyl pyrazolate Pt(II) complexes, density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were performed (see the

computational details in the experimental section). We aimed first to understand the observed red-shifted peaks in the UV-vis absorption and emission spectra of the aggregated species in the TF. Pt(II) complexes **1–3** and **5** were selected for these studies.

The geometries in the ground (S_0) and the first triplet excited (T_1) states of monomers, dimers, and trimers of **1–3** and **5** were optimized (Figure S8–10 and Table S2–3 in Supporting Information). All monomer Pt(II) complexes adopt square-planar geometries. The Pt-N bond lengths are all very similar for the monomers.

In the case of dimers and trimers, the geometries of different conformers in the S_0 and T_1 potential energy surfaces were optimized. Figures S9 and S10 collect: i) the geometries of all the optimized conformers, ii) their Pt···Pt distances, and iii) their relative energies, for dimers and trimers respectively. Several conformers are found to be close-lying both in the S_0 and T_1 potential energy surfaces (e.g., within 0–2 kcal/mol), and thus, assuming a Boltzmann population. These results highlight that there is some degree of conformational flexibility for dimers and trimers at room temperature. Two main intermolecular forces drive the dimer and trimer assembly: intermolecular π – π stacking interactions and Pt···Pt contacts. The former interaction is predominant in all investigated dimer species, regardless whether we consider the S_0 or the T_1 optimized geometries. The interlayer distances range between 3.3 and 3.6 Å (see Figure S9). For example, the computed interlayer distance of the lowest-energy dimer of **1** is 3.59 Å, which is in perfect agreement with the data of X-ray structural analyses. The metallophilic interactions are more evident in the trimer structures, and especially in the case of the T_1 optimized geometries.^[51] For example, let us evaluate the case of the

optimized T_1 excited state structures of **1** (see **Figure 4a**). The lowest-energy conformer of the dimer of **1** displays an interlayer distance of 3.56 Å. This distance turns significantly shorter in the lowest-energy conformer **1(a)** of the trimer (2.94 Å), where the metallophilic contacts become more evident.

Figure S11 depicted the computed UV-vis absorption spectra for **1–3** and **5** in their monomer, dimer and trimer forms. These results are summarized in Table S4. Exemplary the UV-vis absorption spectra arising from the lowest-energy S_0 conformer of the monomer, and for several dimer and trimer conformers of **1** are shown in Figure 4b. The orbitals involved in the electronic transitions as well as the spin density plots of **1** are plotted in **Figure 5**. Figures S12–15 collect the orbitals and spin density plots for **2**, **3** and **5**. The calculated absorption maxima of monomers are located at 333, 334, 332, and 332 nm which reasonably agree with the experimental values of 349, 350, 351, and 350 nm for **1–3** and **5**, respectively. More in details, the absorption band around 290 nm is ascribed predominantly to ligand-centered pyrazolate $\rightarrow$ isoquinoline intra-ligand $\pi\text{--}\pi^*$ transitions and the absorption band around 420 nm is mainly originated from the mixed LC and MLCT transitions. Importantly, the simulated UV-vis absorption spectra of dimers and trimers are red-shifted, compared with those of monomers (see Figure 4b for **1** and Figure S11 for the rest of complexes). A further inspection of the results for **1** highlight that the trimer conformer **1(c)** exhibiting the shortest Pt $\cdots$ Pt contacts (i.e., 3.31 Å, c.f. Figure 4a) in the S_0 state leads to the most red-shifted absorption bands among all possible conformers. The analysis of the electronic transitions involved in those peaks highlights the prominent MMLCT

character of those bands (see e.g., the orbitals involved for this specific trimer in Figure 5). This piece of evidence further supports the assignment of the experimentally observed red-shifted absorptions to electronic transitions with significant MMLCT character. It is worth noting that this trend is not only observed for **1** but can also be observed in other Pt(II) complexes. Overall, the results confirmed that the red-shifted absorption and emission are induced by a better packing arrangement in trimers, which improves the possibility of a better intermolecular metallophilic interaction leading to enhanced MMLCT character of the resulting excited states. The calculations also reflect that those states are easily accessible for some of the trimers, but less likely for the dimers. Concerning emission processes, the character of lowest triplet excited state changes from mixed $^3\text{LC}/^3\text{MLCT}$ character in the monomer and dimer to a mixed $^3\text{LC}/^3\text{MMLCT}$ state in the case of the trimer (see Figure 5 for **1** and Figure S14–15 for the rest of complexes). Importantly, and in agreement with the experimental evidence, the predicted emission maxima are red-shifted in the case of the $^3\text{LC}/^3\text{MMLCT}$ -based emissions (compare for instance in Table S4 the predicted emission maxima of 842 nm arising from the lowest energy trimer conformer **1(a)** versus 749 nm obtained for the dimer conformers **1(b/c)**). Conversely, the emission maxima of monomers are located at 636, 635, 635, and 774 nm for **1–3** and **5**, respectively, corresponding to emission arising from mixed $^3\text{LC}/^3\text{MLCT}$ states (see Table S4). Dimers and trimers emission peaks are generally red-shifted with respect to the monomers. In opposition to trimer-emission, dimer-emission resembles more to the monomer emission, since their responsible emissive states are also of $^3\text{LC}/^3\text{MLCT}$ character. In a nutshell, depending

on the supramolecular aggregation we can fine-tune the emission properties. For instance, if a dimer arrangement predominates (such as in the case of the most stable crystal phase of **1**), we predominantly observe the blue-shift emission bands of mixed $^3\text{LC}/^3\text{MLCT}$ character. Contrarily, the red-shifted emissions from a $^3\text{LC}/^3\text{MMLCT}$ state might be driven by a given supramolecular arrangement that favors trimer forms and higher aggregates, and shorter metallophilic contacts. Further photophysical results also support our hypothesis, which was depicted in Supporting Information (Figure S16).

It is worth noting that, although GIXD data showed that the Pt(II) complexes packed in a slip manner, which is different from the vertical trimer discussed in our simulated model. We supposed that there should be some kind of conformational freedom in TF, considering to the small energetic differences between the different conformers of dimers and trimers. The vertical aggregation is expected to provide reduced Pt $\cdots$ Pt interaction and, hence, greater contribution from the $^3\text{MMLCT}$ transition process. This could be the case as revealed in Figure 3, where complex **3** shows the smallest tilting angle. Accordingly, higher degree of $^3\text{MMLCT}$ contribution is expected in **3** rather than in **2**, which is in accordance with observed photophysical data.

2.5. Electroluminescence Performances

Motivated by the excellent photophysical properties of all solid TF, we then moved one step further to fabricate light-emitting devices by using **1–5** as a nondoped emission layer (EML). Accordingly, a set of devices was prepared with a structure of ITO/TPAC

(40 nm)/mCP (10 nm)/EML (30 nm)/TPBI (60 nm)/LiF (1 nm)/Al (100 nm), denoted as device **a1–a5**, respectively; ITO (indium tin oxide) and Al acted as anode and cathode, TAPC (*N*-(4-(1-(4-(di-*p*-tolylamino)phenyl)cyclohexyl)phenyl)-3-methyl-*N*-(*p*-tolyl)aniline), mCP (1,3-bis(*N*-carbazolyl)benzene), TPBI (1,3,5-tris(phenyl-2-benzimidazolyl)-benzene) and LiF served as hole-transporting, electron-blocking, electron-transporting, electron-injection layers, respectively (**Figure 6a**).

The EL properties of device **a1–a5** are shown in Figure 6b–c, and the related parameters are listed in Table 3. Although the studied complexes have the same light-emitting core structure, their packing mode and electronic properties are expected to be modulated by their substituents (*vide supra*) and would eventually influence their EL performances. Taking **2** as an example, while **a2** shows similar EL spectra to others, its max. EQE is only 12.2%, which is much lower than those of **a1**, **a4** and **a5** (27.1, 28.2 and 21.6%, respectively). Owing to the existence of dmp substituted chelates in **2**, the poor electrical property of the EML in **a2** should be responsible for the inferior EL performances. Therefore, it is not surprised that **a2** has relatively high V_1 and V_{100} (voltage measured at 1 and 100 cd m⁻², respectively) of 5.3 and 7.1 V, respectively (**Figure 7a**). The situation becomes worse in **a3** due to the existence of dip substituents in **3**, to which the isopropyl substituents are considered to be an even better insulator. The carrier transport of **a3** is so poor that the excitons cannot fully recombine within EML, giving blue colored EL emission from adjacent layer (Figure 6c). In sharp contrast, **a1** shows excellent performances with max. EQE of 27.1% because of its good carrier transport by virtue of both strong π – π stacking and lack of any aryl substituents

on emitters. We further optimized the OLED structure by inserting a 20 nm layer of 4,4',4''-tri-9-carbazolyltriphenylamine (TCTA) between TAPC/mCP to improve the hole injection/transport as well as electron blocking capacity (Figure 6a), denoted as device **b1–b5**. The efficiencies are much improved in b-type devices (Figure S18); most of them demonstrated higher max. EQE and decreased driving voltages (Figure 7a), especially for **b2**. Considering the much stabilized HOMO and LUMO of the emitters, the TPBI layer is further replaced by a tri[2,4,6-trimethyl-3-(3-pyridyl)phenyl]borane (3TPYMB) layer with deeper HOMO and LUMO levels (Figure 6a), denoted as device **c1 to c5**; their EL performances are shown in Figure 7b–d. For **2**, **4** and **5**, their EL performances are performed perfectly with c-type device structure. Although the driving voltages become the lowest and the extrinsic EL band observed in **a3** and **b3** disappears, the efficiency of **c3** failed to increase, which should be limited by the intrinsically poor charge-transporting property of **3**. Interestingly, **1** performs well even in the simplest device structure **a1**, thanks to its good electrical properties as well as short τ_{obs} in TF. Note that **4** shows the best EL performance among all the complexes ($\text{EQE}_{\text{max}} > 30\%$ in device **c4**). Considering heteroleptic **4** bears only one dmp group, its relatively reduced steric hindrance provided both good charge-transporting property and efficient MMLCT transition in TF4, leading to excellent EL performances.

Overall, device **b1**, **c2**, **c4** and **c5** emit highly intense deep-red EL with peak wavelength at 677, 675, 666 and 670 nm, respectively. These EL spectra showed the expected $^3\text{MMLCT}$ emission with longer wavelength tail extended into the NIR region;^[45] in which the photons with wavelength longer than 700 nm account for ~30%

of the total radiation. Although high-efficiency OLEDs showing similar EL spectra have been reported by employing thermally activated delayed fluorescence (TADF) emitters,^[18,19,52,53] most of them required doped EMLs to avoid emission quenching and serious efficiency roll-off. Our OLEDs with a non-doped EML architecture delivered unprecedentedly max. EQEs of 27.4, 22.7, 30.4 and 28.5% for **b1**, **c2**, **c4** and **c5**, respectively. Even at high brightness of 1000 cd m⁻², the EQEs are still high up to 18.7, 21.2, 25.1 and 27.8%, respectively, demonstrating the superiority of our square-planar Pt(II) emitters in deep-red/NIR EL application.

3. Conclusion

In conclusion, we present a clear picture for the formation MMLCT transition for strong deep-red/NIR emission from a series of isoquinoliny pyrazolate Pt(II) complexes. The principle, which involves the fine-tuning of molecular packing arrangement and exciton character by modulating steric-demanding substituents, provides a useful tool for manipulating the MMLCT transition needed for efficient low-energy radiation processes. We also discovered that these bulky substituents do not always disfavor metallophilic Pt···Pt interactions. Instead, π - π stacking among chelates, which were controlled by the associated substituents, also exerts strong influence to the MMLCT transition character. From detailed analysis of EDM generated from GIXD of vacuum deposited samples, the most and least red-shifted optical behaviors of **3** and **2** respectively can be rationalized by the shortest and longest Pt···Pt distances of **3** and **2** respectively, in addition to the minimal molecular stacking of **2**. We also provide an

elaborated theoretical calculation using dimer/trimer model and suggests that trimer and higher-level oligomer are more likely to generate MMLCT emission. This result is consistent with the observation that only the π - π stacking interaction was observed in the single crystal X-ray structural analysis of the parent Pt(II) complex **1**. Moreover, a change from mixed $^3\text{LC}/^3\text{MLCT}$ character in both the monomers and dimers to mixed $^3\text{LC}/^3\text{MMLCT}$ character is suggested in the trimers. It is also showed that **1**, **2**, **4** and **5** can deliver intense deep-red/NIR EL with peak wavelength at 677, 675, 666 and 670 nm respectively, and unprecedented high EQE up to 27.4, 22.7, 30.4 and 28.5%, respectively. Despite TF3 exhibits a superior PLQY of 96.8% and a short τ_{obs} of 0.39 μs , its corresponding EL performances are the lowest due to its insulating dip substituents, which deserves careful consideration in the future design of NIR emitters.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Scheme 1. Molecular orbital diagram illustrating the Pt···Pt interaction and formation of MMLCT transition (left panel) and the proposed molecular design of square-planar Pt(II) complexes (right panel).

Figure 1. a) Absorption and PL spectra (insets show the corresponding powder samples under ambient (left) and 365-nm UV irradiation (right), respectively), b) transient PL decay profiles and c) PLQY/optical energy gaps of the sublimed powders of 1–5.

Figure 2. a) Absorption and PL spectra of **1–5** (inset: PL photographs of solid thin film of **1**) and b) transient PL decay profiles of corresponding thin film at room temperature. Photophysical properties of thin film of **1** at various temperatures: c) exciton spectra; d) emission spectra; e) plot of peak wavelength-temperature-full width at half maximum; f) transient PL decay profiles.

Figure 3. Molecular packing of crystallites in thin films of **1–5** ((a)–(e)) resolved by GIXD: EDMs along ab and ac planes, unit-cell packing arrangements drawn to scale along ab and ac planes (from left to right). Green and red arrow indicated the direction of $\pi\pi$ stacking interaction and Pt...Pt vector.

Figure 4. a) Optimized geometries (B3LYP/6-31G(d)) of selected conformers of monomer, dimer and trimer of **1** at the S_0 and T_1 states and b) convoluted TD-B3LYP/6-31G(d) UV-vis absorption spectra for **1**.

Figure 5. Contour plots of HOMO and LUMO at the S_0 and T_1 optimized geometries, and spin density plots at the T_1 optimized geometries (UB3LYP/6-31G(d)).

Figure 6. a) Device architectures of the fabricated OLEDs. b) EQE-Luminance plots and c) EL spectra (measured at 1000 cd m^{-2}) of the a-type OLEDs.

Figure 7. a) Max. EQE and driving voltages (V_1 , V_{100} for voltages at 1 and 100 cd m⁻², respectively) among a-, b-, c-type device structures. b) Current density-voltage, c) luminance-voltage and d) EQE-luminance of c-type devices (inset: EL spectra and photograph of an operating device 4c).

Table 1. Photoluminescence properties of the studied Pt(II) complexes 1–5.

Emitter	λ_{em} [nm] ^{a)}			PLQY [%] ^{b)}			τ_{obs} [μ s] ^{c)}		
	solu.	SP	TF	solu.	SP	TF	solu.	SP	TF
1	561, 605, 656 (sh)	563, 604, 660, 725 (sh)	672	34.6	10.2	80.5	14.8	4.98 ^{d)}	0.27
2	563, 608, 655 (sh)	575, 615, 665, 729 (sh)	673	25.8	17.7	66.9	10.8	3.61 ^{d)}	0.61
3	563, 606, 657 (sh)	673	691	37.9	91.3	96.8	15.6	0.24 ^{e)}	0.39
4	560, 607, 660 (sh)	570 (sh), 670	678	29.1	33.3	88.4	13.3	0.59 ^{e)}	0.47
5	562, 606, 656 (sh)	675	687	28.1	68.7	75.3	15.9	0.20 ^{e)}	0.44

^{a)}Wavelength of emission peak max., ^{b)}PL quantum yield and ^{c)}observed lifetime measured in degassed CH₂Cl₂ solution (10⁻⁵ M⁻¹), sublimed powder (SP) and solid thin film (TF), respectively; data recorded at ^{d)}the first peak max. and ^{e)}the max. peak, respectively.

Table 2. GIXD crystallographic data of vacuum deposited thin film of Pt(II) complexes 1–5.

Parameter	1	2	3	4	5
a [nm]	2.40	1.57	1.75	2.44	2.72
b [nm]	1.22	1.30	1.73	1.26	1.44
c [nm]	0.45	0.51	0.41	0.48	0.46
β [°]	110.2	111.0	114.4	108.6	110.2
Pt...Pt separation [nm]	0.45	0.51	0.41	0.48	0.46
vertical π - π separation [nm]	0.36	0.35	0.33	0.38	0.37
grain size [100] [nm]	12.1	3.29	5.41	7.30	4.01
grain size [010] [nm]	4.73	1.83	3.18	1.92	2.70
grain size [001] [nm]	1.79	0.49	0.79	0.56	1.60
tilting angle to substrate normal [°]	17	26	11	18	16

Table 3. EL performances of the devices based on Pt(II) complexes 1–5.

Device ^{a)}	V_i [V] ^{b)}	λ_{EL} [nm] ^{c)}	CIE index ^{c)}	CE [cd A ⁻¹] ^{d)}	PE [lm W ⁻¹] ^{d)}	EQE ^{d)} [%] ^{d)}
a1	4.0	674	(0.68, 0.31)	7.0, 5.9, 4.8	4.9, 3.1, 1.8	27.1, 18.6, 15.2
a2	5.3	670	(0.67, 0.33)	5.9, 5.6, 4.8	2.9, 2.5, 1.6	12.2, 11.7, 9.5
a3	5.6	673	(0.65, 0.33)	7.1, 2.8, 1.7	3.8, 1.1, 0.5	11.1, 7.5, 4.7
a4	5.2	671	(0.68, 0.33)	9.2, 7.9, 7.1	5.1, 3.9, 2.5	28.2, 20.0, 18.1
a5	5.4	668	(0.67, 0.31)	7.4, 7.1, 6.2	3.9, 3.1, 1.9	21.6, 20.5, 17.3
b1	4.1	677	(0.70, 0.31)	18.8, 6.4, 5.4	12.7, 3.1, 1.9	27.4, 22.1, 18.7
b2	5.3	679	(0.67, 0.33)	9.4, 7.4, 7.1	5.2, 3.3, 2.4	21.0, 18.7, 17.2
b3	5.2	686	(0.66, 0.31)	3.1, 3.0, 2.8	1.7, 1.3, 0.9	10.8, 10.4, 8.7
b4	4.8	672	(0.69, 0.32)	11.3, 8.0, 7.6	6.8, 3.8, 2.7	25.2, 22.7, 20.3
b5	5.1	676	(0.68, 0.31)	10.6, 7.1, 6.7	6.3, 3.2, 2.2	24.8, 23.3, 22.0
c1	3.9	662	(0.67, 0.31)	4.6, 1.8, 0.6	3.6, 0.7, 0.2	11.2, 5.1, 1.3
c2	4.7	675	(0.66, 0.32)	9.8, 9.6, 9.5	6.0, 5.0, 4.2	22.7, 22.4, 21.2
c3	4.5	680	(0.68, 0.32)	4.0, 3.1, 2.7	2.6, 1.6, 1.0	10.7, 9.8, 7.5
c4	4.2	666	(0.68, 0.32)	12.1, 10.4, 10.0	8.5, 6.1, 4.7	30.4, 26.7, 25.1
c5	4.4	670	(0.68, 0.31)	9.5, 9.2, 9.3	5.3, 4.9, 4.1	28.5, 28.1, 27.8

^{a)}Device a: ITO/TPAC (40 nm)/mCP (10 nm)/EML (30 nm)/TPBI (60 nm)/LiF (1 nm)/Al (100 nm), Device b: ITO/TPAC (40 nm)/TCTA (20 nm)/mCP (10 nm)/EML (30 nm)/TPBI (60 nm)/LiF (1 nm)/Al (100 nm), Device c: ITO/TPAC (40 nm)/TCTA (20 nm)/mCP (10 nm)/EML (30 nm)/3TPYMB (60 nm)/LiF (1 nm)/Al (100 nm); ^{b)}Turn-on voltage measured at 1 cd m⁻²; ^{c)}data measured at 1000 cd m⁻²; ^{d)}performances at 100 and 1000 cd m⁻², respectively.

A series of deep-red/near infrared phosphorescent square-planar isoquinolinyl pyrazolate Pt(II) complexes modeled by steric-demanding substituents is designed and demonstrates high photoluminescence quantum efficiencies and short excited-state lifetimes. This allows highly efficient deep-red/near infrared organic electroluminescence with external quantum efficiency as high as 30% and peak wavelength of ca. 670 nm.

Keywords: isoquinolinyl pyrazolate Pt(II) complex, NIR phosphorescent emitter, OLED, solid-state aggregation, trimer

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Modulation of Solid-State Aggregation of Square-Planar Pt(II) Based Emitters: Enabling Highly Efficient Deep-Red/Near Infrared Electroluminescence

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Supporting Information

Modulation of Solid-State Aggregation of Square-Planar Pt(II) Based Emitters: Enabling Highly Efficient Deep-Red/Near Infrared Electroluminescence

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1. Experimental Procedures

General Procedures: All reactions were conducted under nitrogen and monitored by TLC with pre-coated silica gel plates (Merck, 0.20 mm with fluorescent indicator UV254). Compounds were visualized with UV irradiation at 254 or 365 nm. Flash column chromatography was carried out using silica gel obtained from Merck (230–400 mesh). Commercially available reagents were used without further purification, and solvents were distilled from appropriate drying agents prior to use. Mass spectra were obtained on a JEOL SX-102A instrument operating in electron impact (EI) or fast atom bombardment (FAB) mode. ^1H and ^{19}F NMR spectra were recorded on a Bruker-400 or Varian Mercury-400 instrument; chemical shifts are quoted with respect to the internal standard tetramethylsilane. Elemental analysis was carried out with a Heraeus CHN-O Rapid Elementary Analyzer. Absorption was recorded on a PE Lambda 750 UV/Vis/NIR spectrophotometer. All the emission related measurements were conducted by Edinburgh FLS980 spectrophotometer. The emission lifetimes were conducted using a picosecond pulsed diode laser (375 nm, EPL-375). The solutions were degassed using freeze-pump-thaw technique before photoluminescence (PL) measurements. PL quantum yields of solid-state samples were measured with an integrating sphere, while those of solution

samples were determined using 4-dicyanomethylene-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran in DMSO (80%) as a reference.^[1] The thin films for PL measurement were prepared with a deposition rate of $1 \text{ \AA s}^{-1}$. The temperature-dependent photophysical properties of thin films were acquired in an Oxford optistatDN cryostat situated in the cell compartment of the Edinburgh FLS980 spectrophotometer. 10-nm thin films of the new compounds were prepared on an ITO glass substrate for highest occupied molecular orbital (HOMO) determination via ultraviolet photoelectron spectroscopy with a VG ESCALAB 220i-XL surface analysis system using a He-discharge lamp as a excitation source with He-I photons of 21.2 eV under a vacuum better than 10^{-9} torr. The lowest unoccupied molecular orbital (LUMO) levels were then estimated by $\text{LUMO} = \text{HOMO} + \text{optical energy gap}$, where the optical energy gap was measured from absorption onset. Single crystal X-ray diffraction measurements were carried out on an Oxford Gemeni S Ultra diffractometer with Cu K_{α} radiation at 173 K.

Grazing-incidence X-ray diffraction (GIXD) measurement: GIXD was performed at beamline 01C2 of Taiwan Light Source at National Synchrotron Radiation Research Center (NSRRC), Taiwan. All studied thin films were deposited on the Si substrate (300 $\text{\AA}$, deposition rate $\sim 1 \text{ \AA s}^{-1}$), and the GIXD data were collected using a 2D image plate (Mar345) and 12 keV X-ray beam with wavelength of 1.033 $\text{\AA}$. The incidence angle of X-ray beam was $\sim 0.2^{\circ}$ for GIXD.

Electron density map (EDM): Fourier reconstruction of the electron density maps were carried out using the general formula for 2D electron density as $\rho(x, y) = \sum_{hk} \sqrt{I(hk)} \exp [2\pi i(hx + ky) + i\varphi(hk)]$, where $\varphi(hk)$ are phases of structure factor (equal to 0 or π) and $I(hk)$ is intensity of Bragg peaks obtained from the GIXD patterns after background subtraction and correlation

of Lorentz and polarization factors, respectively. Because of the low crystallinity of the deposited films, only averaged metric parameters of crystallites were investigated. The correct phase can be determined on the basis of physical merits of the reconstructed EDM, aided by other information on the system coming from e.g. other spectra or molecular simulation. The data employed for reconstruction of EDMs are listed in Table S1. The electron density projections in both the *ab*- and *ac*-planes are revealed. The π - π and Pt $\cdots$ Pt distances measured by GIXD were estimated by averaging the electron density of EDM-*ab* and EDM-*ac*, which may quite different from the absolute values observed in single crystal.

Device fabrication and measurement: ITO glass substrates with a sheet resistance of $15\ \Omega\ \text{sq}^{-1}$ was first cleaned with 10% Decon 90 detergent solution and rinsed with deionized water before roughly drying by pure N_2 flow. Before use, the substrates experienced 1-hour baking in an oven ($120\ ^\circ\text{C}$) and a subsequent 15-min UV-ozone treatment and then were loaded into a deposition chamber with a base vacuum of 10^{-6} Torr. The deposition rates for organic, LiF and Al layers were controlled to be 1, 0.1 and $5\ \text{\AA}\ \text{s}^{-1}$, respectively. Current density-voltage characteristics were recorded on a programmable Keithley 2400 power. Luminance and electroluminescence spectra were recorded by a Spectrascan PR650 photometer (Photo Research) and PMA-12 photonic multichannel analyzer (Hamamatsu). Device measurements were performed under an ambient condition without encapsulation.

Computational details: All calculations for **1–3** and **5** were carried out by using density functional theory (DFT) and time-dependent DFT (TD-DFT). The geometries optimizations of **1–3** and **5** in the singlet ground state (S_0) were optimized using the restricted Becke's three-parameter hybrid exchange functional combined with the Lee-Yang-Parr correlation functional

(B3LYP),^[2-4] in combination with 6-31G(d) atomic basis set for all non-metal atoms. Relativistic effects were included for the metal Pt atoms by using ECP-60-mwb pseudopotential.^[5] For all open-shell calculations, the geometries optimizations of **1-3** and **5** in the lowest triplet state (T_1) were performed by unrestricted B3LYP (UB3LYP) method with the same basis set. To study the packing interaction, the dimeric and trimeric **1-3** and **5** were carried out through the Grimme approach using atom pair-wise additive schemes using dispersion-corrected B3LYP-D3 method to elucidate the dispersion effects for non-bonding interaction.^[6] Calculations of vertical excitation energies were done from the optimized structures of S_0 and T_1 states using TD-B3LYP with low-lying singlet-singlet/triplet and triplet-triplet/singlet transition. The solvent effect was taken into account by the polarized continuum model (PCM)^[7] in dichloromethane (CH_2Cl_2) media. All optimized structures were confirmed to be local minima by normal mode analysis with all positive frequencies. The absorption spectra and the orbital contributions were generated with GaussSum package.^[8] All calculations were performed using Gaussian 16 program package.^[9]

2. Synthesis

Synthesis of 1-acetylisquinoline (L1-1)

A solution of iron(II) sulfate heptahydrate (43 mg, 0.15 mmol), para-acetaldehyde (5.14 mL, 38.7 mmol), *tert*-butyl hydroperoxide (1.86 mL of 70 wt. % solution in water, 19.4 mmol), isoquinoline (1.0 g, 7.7 mmol) and trifluoroacetic acid (0.59 mL, 7.7 mmol) in MeCN (40 mL) was heated to reflux for 12 h. The solvent was removed by evaporation under vacuum. The

residue was dissolved in ethyl acetate and neutralized with Na₂CO₃ solution. The organic phase was washed with brine and dried over Na₂SO₄, the solvent was removed under vacuum to give a crude product. Purification by SiO₂ column chromatography eluting with ethyl acetate and hexane (1:6) afforded a yellow oil (1.17 g, 88%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ 8.96 (d, J = 8.0 Hz, 1H), 8.58 (d, J = 5.6 Hz, 1H), 7.86 (d, J = 7.34 Hz, 1H), 7.81 (d, J = 5.6 Hz, 1H), 7.73–7.66 (m, 2H), 2.84 (s, 3H).

Synthesis of 1-(3-(trifluoromethyl)-1*H*-pyrazol-5-yl)isoquinoline (L1)

L1-1 (2.0 g, 11.68 mmol) was slowly added to a stirred suspension of NaOEt (1.2 g, 17.5 mmol) in dry THF (50 mL) at 0 °C. The resultant solution was stirred for 1 hour at RT. Ethyl trifluoroacetate (2.1 mL, 17.5 mmol) was added dropwise at 0 °C and the mixture was refluxed for 12 h. After then, the content was quenched with 2N HCl until pH 5–6 and extracted three times with ethyl acetate. The combined organic phase was washed with brine, dried over Na₂SO₄, and concentrated under vacuum to yield the crude 1,3-dione. To the crude 1,3-dione was added hydrazine monohydrate (2.9 mL, 58.4 mmol) and *p*-toluenesulfonic acid (0.2 g, 1.17 mmol) in 50 mL of EtOH and refluxed for 1 day. The solvent was removed by evaporation under vacuum. The residue was dissolved in ethyl acetate and neutralized with Na₂CO₃ solution. The organic phase was washed with brine and dried over Na₂SO₄, the solvent was removed under vacuum to give a crude product. It was then purified by SiO₂ column chromatography and eluting with a mixture of ethyl acetate and hexane (1:3). Recrystallization from a mixed solution of CH₂Cl₂ and hexane gave a white solid (2.46 g, 80%). ¹H NMR (400 MHz, CDCl₃, 298K): δ 8.90 (d, J = 8.0 Hz, 1H), 8.56 (d, J = 13.6 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 10.4 Hz, 1H), 7.64 ~ 7.60 (m, 2H), 6.82 (s, 1H). ¹⁹F NMR (376 MHz, CDCl₃, 298K): δ 64.48 (s, 3F). EI MS: m/z 263.1 [M + H]⁺.

Synthesis of (2,6-dimethylphenyl)boronic acid

To a 100 mL two-neck bottle was added 2-bromo-1,3-dimethylbenzene (5 g, 27.0 mmol) under nitrogen. Dry THF (50 mL) was added and the solution was cooled to -78°C . After the addition of *n*-BuLi (16.2 mL, 2.5 M in *n*-hexane), the solution was stirred at -78°C for 1 h, and then trimethyl borate (4.61 mL, 40.5 mmol) dissolved in 10 mL of dry THF was added. The solution was allowed to warm to RT overnight. After that the reaction was quenched with 2N HCl (10 mL). The solvent was removed under vacuum. The residue was dissolved in ethyl acetate and neutralized with saturated Na_2CO_3 solution. The organic phase was washed with brine and dried over Na_2SO_4 , and the solvent was removed under vacuum. Recrystallization from hexane gave a white solid (2.71 g, 67%). ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 7.16 (t, $J = 7.5$ Hz, 1H), 6.99 (d, $J = 7.5$ Hz, 2H), 4.59 (s, 2H), 2.38 (s, 6H).

Synthesis of 1-(6-bromoisoquinolin-1-yl)ethanone (L2-1)

A solution of iron(II) sulfate heptahydrate (33 mg, 0.12 mmol), para-acetaldehyde (3.9 mL, 28.84 mmol), *tert*-butyl hydroperoxide (2.0 mL of 70 wt % solution in water, 14.42 mmol), 6-bromoisoquinoline (1.2 g, 5.77 mmol) and trifluoroacetic acid (0.44 mL, 5.77 mmol) in MeCN (40 mL) was heated to reflux for 12 h. The solvent was removed by evaporation under vacuum.

The residue was dissolved in ethyl acetate and neutralized with Na₂CO₃ solution. The organic phase was washed with brine and dried over Na₂SO₄, the solvent was removed under vacuum to give a crude product. Purification by SiO₂ column chromatography eluting with ethyl acetate and hexane (1:6) afforded a yellow oil (1.02 g, 71%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ 8.87 (d, J = 9.2 Hz, 1H), 8.59 (d, J = 8.6 Hz, 1H), 8.02 (s, 1H), 7.74–7.70 (m, 2H), 2.84 (s, 3H).

Synthesis of 1-(6-(2,6-dimethylphenyl)isoquinolin-1-yl)ethanone (L2-2)

To a 100 mL two-neck bottle was added L2-1 (1.0 g, 4.0 mmol), (2,6-dimethylphenyl)boronic acid (0.9 g, 6.0 mmol), Ba(OH)₂·8H₂O (6.31 g, 20 mmol) and Pd(PPh₃)₄ (462 mg, 0.4 mmol) under nitrogen. Degassed 1,4-dioxane and water (v/v, 3:1, 60 mL) was added and heated to reflux for 12 h. The solvent was removed under vacuum. The residue was dissolved in ethyl acetate and neutralized with Na₂CO₃ solution. The organic phase was washed with brine and dried over Na₂SO₄, and the solvent was removed under vacuum. Then, the residue was purified using SiO₂ column chromatography eluting with ethyl acetate and hexane (1:6). Recrystallization from CH₂Cl₂ and hexane gave a white solid (0.97 g, 88%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ 9.01 (d, J = 8.8 Hz, 1H), 8.60 (d, J = 5.6 Hz, 1H), 7.81 (d, J = 5.6 Hz, 1H), 7.64 (s, 1H), 7.51 (d, J = 8.8 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H), 7.14 (d, J = 7.5 Hz, 2H), 2.89 (s, 3H), 2.02 (s, 6H).

Synthesis of 6-(2,6-dimethylphenyl)-1-(3-(trifluoromethyl)-1H-pyrazol-5-yl)isoquinoline (L2)

L2-2 (1.0 g, 3.63 mmol) was slowly added to a stirred suspension of NaOEt (0.37 g, 5.45 mmol) in dry THF (50 mL) at 0 °C. The resultant solution was stirred for 1 hour at RT. Ethyl

trifluoroacetate (0.65 mL, 5.45 mmol) was added dropwise at 0 °C and the mixture was refluxed for 12 h. After then, the content was quenched with 2N HCl until pH 5–6 and extracted three times with ethyl acetate. The combined organic phase was washed with brine, dried over Na₂SO₄, and concentrated under vacuum to yield the crude 1,3-dione. To the crude 1,3-dione was added hydrazine monohydrate (0.89 mL, 18.2 mmol) and *p*-toluenesulfonic acid (62 mg, 0.36 mmol) in 50 mL of EtOH and refluxed for 1 day. The solvent was removed by evaporation under vacuum. The residue was dissolved in ethyl acetate and neutralized with Na₂CO₃ solution. The organic phase was washed with brine and dried over Na₂SO₄, the solvent was removed under vacuum to give a crude product. It was then purified by SiO₂ column chromatography and eluting with a mixture of ethyl acetate and hexane (1:4). Recrystallization from a mixed solution of CH₂Cl₂ and hexane gave a white solid (1.07 g, 80%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ 12.11 (br, 1 H, NH), 8.59–8.56 (m, 2 H), 7.72 (m, 2 H), 7.55 (d, *J* = 8.6 Hz, 1 H), 7.29 (s, 1 H), 7.25 (t, *J* = 7.5 Hz, 1 H), 7.17 (d, *J* = 7.5 Hz, 2 H), 2.05 (s, 6 H). ¹⁹F NMR (376 MHz, CDCl₃, 298 K): δ 62.13 (s, 3F). EI MS: *m/z* 367.2 [M + 1]⁺.

L3-1

L3-2

L3

Synthesis of (2,6-diisopropylphenyl)boronic acid

To a 100 mL two-neck bottle was added 2-bromo-1,3-diisopropylbenzene (5 g, 21.0 mmol) under nitrogen. Dry THF (50 mL) was added and the solution was cooled to -78 °C. After the

addition of *n*-BuLi (12.5 mL, 2.5 M in *n*-hexane), the solution was stirred at -78 °C for 1 h, and then trimethyl borate (3.55 mL, 31.2 mmol) dissolved in 10 mL of dry THF was added. The solution was allowed to warm to RT overnight. After that the reaction was quenched with 2N HCl (10 mL). The solvent was removed under vacuum. The residue was dissolved in ethyl acetate and neutralized with saturated Na₂CO₃ solution. The organic phase was washed with brine and dried over Na₂SO₄, and the solvent was removed under vacuum. Recrystallization from hexane gave a white solid (3 g, 70%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ 7.31 (t, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 7.7 Hz, 2H), 4.62 (s, 2H), 2.89 (hept, *J* = 6.8 Hz, 2H), 1.26 (d, *J* = 6.8 Hz, 12H).

Synthesis of 1-(6-bromoisoquinolin-1-yl)ethanone (L3-1)

A solution of iron(II) sulfate heptahydrate (33 mg, 0.12 mmol), para-acetaldehyde (3.9 mL, 28.8 mmol), *tert*-butyl hydroperoxide (2.0 mL of 70 wt.% solution in water, 14.4 mmol), 6-bromoisoquinoline (1.2 g, 5.77 mmol) and trifluoroacetic acid (0.44 mL, 5.77 mmol) in MeCN (40 mL) was heated to reflux for 12 h. The solvent was removed by evaporation under vacuum. The residue was dissolved in ethyl acetate and neutralized with Na₂CO₃ solution. The organic phase was washed with brine and dried over Na₂SO₄, the solvent was removed under vacuum to give a crude product. Purification by SiO₂ column chromatography eluting with ethyl acetate and hexane (1:6) afforded a yellow oil (1.02 g, 71%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ 8.87 (d, *J* = 9.2 Hz, 1H), 8.59 (d, *J* = 8.6 Hz, 1H), 8.02 (s, 1H), 7.74–7.70 (m, 2H), 2.84 (s, 3H).

Synthesis of 1-(6-(2,6-diisopropylphenyl)isoquinolin-1-yl)ethanone (L3-2)

To a 100 mL two-neck bottle was added L3-1 (1.00 g, 4.0 mmol), (2,6-diisopropylphenyl)boronic acid (1.06 g, 5.21 mmol), Ba(OH)₂·8H₂O (6.31 g, 20 mmol) and

$\text{Pd(PPh}_3)_4$ (462 mg, 0.39 mmol) under nitrogen. Degassed 1,4-dioxane and water (v/v, 3:1, 60 mL) was added and heated to reflux for 12 h. The solvent was removed under vacuum. The residue was dissolved in ethyl acetate and neutralized with Na_2CO_3 solution. The organic phase was washed with brine and dried over Na_2SO_4 , and the solvent was removed under vacuum. Then, the residue was purified using SiO_2 column chromatography eluting with ethyl acetate and hexane (1:6). Recrystallization from CH_2Cl_2 and hexane gave a white solid (1.05 g, 79%). ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 8.99 (d, J = 8.8 Hz, 1H), 8.62 (d, J = 5.6 Hz, 1H), 7.82 (d, J = 5.6 Hz, 1H), 7.68 (s, 1H), 7.54 (d, J = 8.8 Hz, 1H), 7.40 (t, J = 7.8 Hz, 1H), 7.26 (s, 2H), 2.90 (s, 3H), 2.52 (hept, J = 6.8 Hz, 2H), 1.07 (d, J = 6.8 Hz, 12H).

Synthesis of 6-(2,6-diisopropylphenyl)-1-(3-(trifluoromethyl)-1*H*-pyrazol-5-yl)isoquinoline (L3)

L3-2 (1.0 g, 3.02 mmol) was slowly added to a stirred suspension of NaOEt (0.31 g, 4.53 mmol) in dry THF (50 mL) at 0 °C. The resultant solution was stirred for 1 hour at RT. Ethyl trifluoroacetate (0.55 mL, 4.53 mmol) was added dropwise at 0 °C and the mixture was refluxed for 12 h. After then, the content was quenched with 2N HCl until pH 5–6 and extracted three times with ethyl acetate. The combined organic phase was washed with brine, dried over Na_2SO_4 , and concentrated under vacuum to yield the crude 1,3-dione. To the crude 1,3-dione was added hydrazine monohydrate (0.74 mL, 15.1 mmol) and *p*-toluenesulfonic acid (52 mg, 0.3 mmol) in 50 mL of EtOH and refluxed for 1 day. The solvent was removed by evaporation under vacuum. The residue was dissolved in ethyl acetate and neutralized with Na_2CO_3 solution. The organic phase was washed with brine and dried over Na_2SO_4 , the solvent was removed under vacuum to give a crude product. It was then purified by SiO_2 column chromatography and eluting with a mixture of ethyl acetate and hexane (1:4). Recrystallization from a mixed

solution of CH_2Cl_2 and hexane gave a white solid (1.02 g, 80%). ^1H NMR (400 MHz, d_6 -acetone, 298 K): δ 13.53 (br, 1H, NH), 8.69 (d, J = 8.8 Hz, 1H), 8.68 (d, J = 5.2 Hz, 1H), 7.94 (d, J = 4.4 Hz, 1H), 7.92 (s, 1H), 7.64 (d, J = 8.8 Hz, 1H), 7.52 (s, 1H), 7.41 (d, J = 7.6 Hz, 1H), 7.30 (d, J = 8.0 Hz, 2H), 2.57 (hept, J = 6.8 Hz, 2H), 1.09 (d, J = 6.8 Hz, 12H). ^{19}F NMR (376 MHz, d_6 -acetone, 298 K): δ 62.32 (s, 3F). EI MS: m/z 423.2 $[\text{M} + \text{H}]^+$.

Synthesis of $[\text{Pt}(\text{L1})_2]$ (**1**)

A mixture of $\text{Pt}(\text{DMSO})_2\text{Cl}_2$ (100 mg, 0.24 mmol), L1 (131 mg, 0.50 mmol) and Na_2CO_3 (251 mg, 2.42 mmol) in 30 mL of THF was refluxed overnight. Then, excess of H_2O was added to induce precipitation. Filtration and washing with H_2O and diethyl ether afforded a yellow solid (161 mg, 95%). Color changed to orange after sublimation; yield: 120 mg, 75%. ^1H NMR (500 MHz, $\text{DMSO}-d_6$): δ 10.56 (d, J = 7.0 Hz, 2H), 8.96 (d, J = 9.0 Hz, 2H), 8.18 (d, J = 8.0 Hz, 2H), 8.14 (d, J = 6.5 Hz, 2H), 8.05 (t, J = 8.0 Hz, 2H), 7.96 (s, 2H), 7.92 (t, J = 7.0 Hz, 2H). ^{19}F NMR (470 MHz, $\text{DMSO}-d_6$): δ 59.5 (s, 6F). FD MS: m/z 719.1 $[\text{M} + 1]^+$. Anal. Calcd. for $\text{C}_{26}\text{H}_{14}\text{F}_6\text{N}_6\text{Pt}$: C, 43.40; H, 1.96; N, 11.68. Found: C, 43.50; H, 2.07; N, 11.65.

Crystallographic data of Pt(II) complex **1** was deposited to Cambridge Crystallographic Data Centre with code CCDC 1967832. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of $[\text{Pt}(\text{L2})_2]$ (**2**)

A mixture of $\text{Pt}(\text{DMSO})_2\text{Cl}_2$ (100 mg, 0.24 mmol), L2 (183 mg, 0.50 mmol) and Na_2CO_3 (251 mg, 2.42 mmol) in 30 mL of THF was refluxed overnight. Excess H_2O was then added to induce precipitation. Filtration and washing with H_2O and diethyl ether in sequence afforded a yellow solid (215 mg, 98%). Color changed to orange after sublimation; yield: 173 mg, 80%. ^1H NMR

(500 MHz, DMSO- d_6): δ 10.55 (d, J = 6.5 Hz, 2H), 8.99 (d, J = 9.0 Hz, 2H), 8.11 (d, J = 6.5 Hz, 2H), 7.99 (s, 2H), 7.93 (s, 2H), 7.69 (d, J = 9.0 Hz, 2H), 7.27 (t, J = 7.5 Hz, 2H), 7.22 (d, J = 7.5 Hz, 4H), 2.07 (s, 12H). ^{19}F NMR (470 MHz, DMSO- d_6): δ 59.5 (s, 6F). FD MS: m/z 927.4 $[\text{M} + 1]^+$. Anal. Calcd. for $\text{C}_{42}\text{H}_{30}\text{F}_6\text{N}_6\text{Pt}$: C, 54.37; H, 3.26; N, 9.06. Found: C, 54.54; H, 3.65; N, 9.08.

Synthesis of $[\text{Pt}(\text{L3})_2]$ (3)

A mixture of $\text{Pt}(\text{DMSO})_2\text{Cl}_2$ (100 mg, 0.24 mmol), L3 (210 mg, 0.50 mmol) and Na_2CO_3 (251 mg, 2.42 mmol) in 30 mL of THF was refluxed overnight. Excess H_2O was then added to induce precipitation. Filtration and washing with H_2O and diethyl ether in sequence afforded a purple solid (225 mg, 91%). Color changed to red after sublimation; yield: 192 mg, 85%. ^1H NMR (500 MHz, DMSO- d_6): δ 10.59 (d, J = 7.0 Hz, 2H), 9.03 (d, J = 8.5 Hz, 2H), 8.18 (d, J = 6.5 Hz, 2H), 8.02 (d, J = 11.5 Hz, 4H), 7.72 (d, J = 8.0 Hz, 2H), 7.45 (t, J = 8.0 Hz, 2H), 7.32 (d, J = 7.5 Hz, 4H), 2.53 (hept, J = 7.0 Hz, 4H), 1.09 (d, J = 7.0 Hz, 24 H). ^{19}F NMR (470 MHz, DMSO- d_6): δ -59.5 (s, 6F). FD MS: m/z 1039.4 $[\text{M} + 1]^+$. Anal. Calcd. for $\text{C}_{50}\text{H}_{46}\text{F}_6\text{N}_6\text{Pt}$: C, 57.74; H, 4.96; N, 8.08. Found: C, 57.86; H, 4.93; N, 8.24.

Synthesis of $[\text{Pt}(\text{L1})(\text{L2})]$ (4)

L1 (200 mg, 0.76 mmol) was slowly added to a stirred suspension of K_2PtCl_4 (331 mg, 0.8 mmol) in 2N HCl (30 mL) at RT for 12 h. The yellow solid was filtered and washed with H_2O and diethyl ether; yield: 297 mg, 74%. To this yellow solid (200 mg, 0.38 mmol) was added L2 (146 mg, 0.4 mmol) in 30 mL of 2-methoxyethanol and the mixture was refluxed overnight. After cooled to RT, excess H_2O was added to induce precipitation. Filtration and washing with H_2O and diethyl ether afforded an orange solid (177.1 mg, 57%). After sublimation; yield: 134

mg, 76%. ^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ 10.54 ~ 10.49 (m, 2H), 8.97 (dd, $J=9.0, 4.0$ Hz, 1H), 8.88 (dd, $J=9.0, 4.0$ Hz, 1H), 8.16 ~ 8.14 (m, 1H), 8.09 ~ 8.02 (m, 3H), 7.98 (d, $J=4.0$ Hz, 1H), 7.91 ~ 7.87 (m, 3H), 7.76 (dd, $J=8.5$ Hz, 1H), 7.27 (t, $J=8.0$ Hz, 1H), 7.22 (d, $J=8.0$ Hz, 2H), 2.07 (s, 6H). ^{19}F NMR (470 MHz, $\text{DMSO-}d_6$): δ 59.48 (s, 3F), 59.49 (s, 3F). FD MS: m/z 823.2 $[\text{M} + 1]^+$. Anal. Calcd. for $\text{C}_{34}\text{H}_{22}\text{F}_6\text{N}_6\text{Pt}$: C, 49.58; H, 2.69; N, 10.20. Found: C, 46.81; H, 2.23; N, 11.01.

Synthesis of $[\text{Pt}(\text{L1})(\text{L3})]$ (5)

L1 (200 mg, 0.76 mmol) was slowly added to a stirred suspension of K_2PtCl_4 (331 mg, 0.8 mmol) in 2N HCl (30 mL) at RT for 12 h. The yellow solid was filtered and washed with H_2O and diethyl ether; yield: 297 mg, 74%. To this yellow solid (200 mg, 0.38 mmol) was added L3 (168 mg, 0.4 mmol) in 30 mL of 2-methoxyethanol and the mixture was refluxed overnight. After cooled to RT, excess H_2O was added to induce precipitation. Filtration and washing with H_2O and diethyl ether afforded a red solid (179.2 mg, 54%). After sublimation; yield: 155 mg, 86%. ^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ 10.55 (d, $J=3.5$ Hz, 1H), 10.53 (d, $J=3.5$ Hz, 1H), 8.99 (d, $J=8.5$ Hz, 1H), 8.92 (d, $J=8.5$ Hz, 1H), 8.17 (d, $J=8.0$ Hz, 2H), 8.13–8.09 (m, 2H), 8.05 (t, $J=7.0$ Hz, 1H), 8.00 (s, 1H), 7.95 (s, 1H), 7.91 (m, 2H), 7.69 (d, $J=8.5$ Hz, 1H), 7.45 (t, $J=8.0$ Hz, 1H), 7.31 (d, $J=8.0$ Hz, 2H), 2.55 (hept, $J=7.0$ Hz, 2H), 1.09 (d, $J=7.0$ Hz, 12H). ^{19}F NMR (470 MHz, $\text{DMSO-}d_6$): δ 59.51 (s, 3F), 59.53 (s, 3F). FD MS: m/z 879.1 $[\text{M} + 1]^+$. Anal. Calcd. for $\text{C}_{38}\text{H}_{30}\text{F}_6\text{N}_6\text{Pt}$: C, 51.88; H, 3.44; N, 9.55. Found: C, 52.05; H, 3.22; N, 9.50.

3. Crystallographic Data for Complex 1

Figure S1. Molecular structure and packing diagram of Pt(II) complex 1.

4. Photophysical Properties of CH₂Cl₂ solution

Figure S2. Absorption and PL spectra of 1–5 in CH₂Cl₂ solution (10⁻⁵ M).

5. Temperature-Dependent Photophysical Properties of Solid Thin Films

Figure S3. Temperature-dependent photophysical properties of solid thin film of **2**. a) emission spectra; b) excitation spectra; transient PL decay profiles monitored at c) peak maximum and d) 590 nm, respectively.

Figure S4. Temperature-dependent photophysical properties of solid thin film of **3**. a) emission spectra; b) excitation spectra c) transient PL decay profiles monitored at peak maximum.

Figure S5. Temperature-dependent photophysical properties of solid thin film of **4**. a) emission spectra; b) excitation spectra c) transient PL decay profiles monitored at peak maximum.

Figure S6. Temperature-dependent photophysical properties of solid thin film of **5**. a) emission spectra; b) excitation spectra c) transient PL decay profiles monitored at peak maximum.

6. GIXD Data

Figure S7. The ab (left) and ac (right) index of GIXD patterns of Pt(II) complexes **1** (a), **2** (b) and **3** (c), **4** (d), **5** (e).

Table S1(a). GIXD data for Pt(II) complex 1.

(h k)	I(hk)	ϕ	(h k)	I(hk)	ϕ	(h k)	I(hk)	ϕ	(h k)	I(hk)	ϕ
(2 0)	100	0	(4 0)	5.83	0	(6 0)	4.55	0	(0 1)	11.0	0
(1 1)	9.87	0	(5 1)	4.60	0	(4 2)	4.49	0	(0 4)	8.45	0
(1 4)	6.98	0	(2 4)	5.53	0						
(h l)	I(hl)	ϕ	(h l)	I(hl)	ϕ	(h l)	I(hl)	ϕ	(h l)	I(hl)	ϕ
(2 0)	100	0	(4 0)	5.83	0	(6 0)	4.87	0	(0 1)	4.02	0
(4 -1)	4.18	0									
$a = 24.0 \text{ \AA}; b = 12.2 \text{ \AA}; c = 4.61 \text{ \AA}$											
$\alpha = 90^\circ; \beta = 110.2^\circ; \gamma = 90^\circ$											

Table S1(b). GIXD data for Pt(II) complex 2.

(h k)	I(hk)	ϕ	(h k)	I(hk)	ϕ	(h k)	I(hk)	ϕ	(h k)	I(hk)	ϕ
(0 1)	100	0	(1 0)	53.0	π	(2 0)	43.3	0	(3 0)	36.0	0
(4 0)	30.9	0									
(h l)	I(hl)	ϕ	(h l)	I(hl)	ϕ	(h l)	I(hl)	ϕ	(h l)	I(hl)	ϕ
(0 1)	41.1	0	(1 0)	100	0	(2 0)	37.9	0	(3 0)	33.7	0
(4 0)	31.5	0									
$a = 15.7 \text{ \AA}; b = 13.0 \text{ \AA}; c = 5.27 \text{ \AA}$											
$\alpha = 90^\circ; \beta = 111.0^\circ; \gamma = 90^\circ$											

Table S1(c). GIXD data for Pt(II) complex 3.

(h k)	I(hk)	ϕ	(h k)	I(hk)	ϕ	(h k)	I(hk)	ϕ	(h k)	I(hk)	ϕ
(0 1)	100	0	(1 0)	53.0	π	(2 0)	22.1	0	(3 0)	17.1	0
(4 0)	10.3	0									
(h l)	I(hl)	ϕ	(h l)	I(hl)	ϕ	(h l)	I(hl)	ϕ	(h l)	I(hl)	ϕ
(0 1)	17.0	0	(1 0)	100	0	(2 0)	21.9	0	(3 0)	13.7	0
(4 0)	15.1	0									
$a = 17.5 \text{ \AA}; b = 17.3 \text{ \AA}; c = 4.47 \text{ \AA}$											
$\alpha = 90^\circ; \beta = 114.4^\circ; \gamma = 90^\circ$											

Table S1(d). GIXD data for Pt(II) complex 4.

(h k)	I(hk)	ϕ	(h k)	I(hk)	ϕ	(h k)	I(hk)	ϕ	(h k)	I(hk)	ϕ
(2 0)	100	0	(4 0)	20.7	0	(6 0)	18.3	0	(8 0)	13.6	0
(0 1)	32.2	0	(1 1)	30.4	0	(3 1)	20.0	0	(5 1)	18.0	0
(7 1)	13.8	0	(2 3)	17.6	0	(4 3)	16.9	0	(6 3)	13.3	0
(0 4)	17.5	0	(1 4)	17.0	0						
(h l)	I(hl)	ϕ	(h l)	I(hl)	ϕ	(h l)	I(hl)	ϕ	(h l)	I(hl)	ϕ
(2 0)	100	0	(4 0)	20.9	0	(6 0)	18.5	0	(8 0)	14.6	0
(0 1)	17.5	0	(4 1)	13.7	0	(4 -1)	17.5	0	(8 -1)	13.4	0
$a = 24.4 \text{ \AA}; b = 12.6 \text{ \AA}; c = 4.90 \text{ \AA}$											
$\alpha = 90^\circ; \beta = 108.6^\circ; \gamma = 90^\circ$											

Table S1(e). GIXD data for Pt(II) complex **5**.

(h k)	I(hk)	ϕ	(h k)	I(hk)	ϕ	(h k)	I(hk)	ϕ	(h k)	I(hk)	ϕ
(2 0)	100	0	(6 0)	4.66	0	(8 0)	3.96	0	(0 1)	4.88	0
(1 1)	8.95	0	(5 1)	4.71	0						
(h l)	I(hl)	ϕ	(h l)	I(hl)	ϕ	(h l)	I(hl)	ϕ	(h l)	I(hl)	ϕ
(2 0)	100	0	(6 0)	31.7	0	(8 0)	25.9	0	(0 1)	29.6	0
(4 -1)	28.2	0									
$a = 27.2 \text{ \AA}; b = 14.4 \text{ \AA}; c = 4.64 \text{ \AA}$											
$\alpha = 90^\circ; \beta = 109.3^\circ; \gamma = 90^\circ$											

7. Optimized Molecular Geometry of Monomers

Figure S8. Optimized molecular geometry of all Pt(II) monomers in S_0 and T_1 states computed at B3LYP/6-31G(d) level.

8. Optimized Molecular Geometry of Dimers

Figure S9. S₀ and T₁ optimized geometries of dimeric Pt(II) complexes 1–3 and 5 computed at B3LYP-D3/6-31G(d) level.

9. Optimized Molecular Geometry of Trimers

Figure S10. S₀ and T₁ optimized geometries of trimeric Pt(II) complexes **1–3** and **5** computed at B3LYP-D3/6-31G(d) level.

10. List of Computed Data

Table S2. Selected bond distances and dihedral angles of the studied Pt(II) monomers in the S_0 and T_1 states computed at B3LYP/6-31G(d) level.

	1		2		3		5	
	S_0 state	T_1 state	S_0 state	T_1 state	S_0 state	T_1 state	S_0 state	T_1 state
Distance [Å]								
Pt–N1	2.075	2.049	2.075	2.048	2.075	2.048	2.074	2.046
Pt–N2	2.025	2.003	2.025	2.004	2.025	2.004	2.025	2.020
Pt–N3	2.075	2.049	2.075	2.048	2.075	2.048	2.075	2.074
Pt–N4	2.025	2.003	2.025	2.004	2.025	2.004	2.025	2.021
Bond angle [°]								
N1PtN2	77.44	78.36	77.45	78.37	77.45	78.37	77.45	78.46
N3PtN4	77.44	78.36	77.45	78.37	77.46	78.37	77.44	77.61
N1PtN4	102.55	101.63	102.54	101.62	102.54	101.62	102.55	102.44
N2PtN3	102.55	101.63	102.54	101.62	102.53	101.62	102.54	101.48
Dihedral angle [°]								
C1C2C3C4	3.465	2.919	3.283	2.738	3.284	2.797	3.122	5.928
C5C6C7C8	3.466	2.918	3.261	2.774	3.350	2.787	3.611	4.486

Table S3. Equilibrium distance of Pt···Pt interlayer separation (R_e in Å) of studied Pt(II) dimers and trimers in the S_0 and T_1 states computed at B3LYP-D3/6-31G(d) level.

Pt(II) complex	Dimer		Trimer			
	S_0 state	T_1 state	S_0 state		T_1 state	
	R_e [Å]	R_e [Å]	R_{e1} [Å]	R_{e2} [Å]	R_{e1} [Å]	R_{e2} [Å]
1(a)	3.382	3.331	3.312	3.312	2.941	2.941
1(b)	3.590	3.558	3.516	3.512	3.530	3.526
1(c)	3.590	3.558	3.516	3.562	3.519	3.552
2(b)	3.446	3.446	3.566	3.479	3.564	3.446
2(c)	3.684	3.684	3.357	3.382	3.292	3.380
3(b)	3.370	3.352	3.732	3.317	3.737	3.308
3(c)	3.647	3.593	3.778	3.331	3.749	3.337
5(a)	3.389	3.352	3.461	3.432	2.960	2.968
5(b)	3.569	3.565	3.626	2.281	3.027	2.978
5(c)	3.605	3.634	3.365	3.627	3.317	3.625

Table S4. TD-B3LYP/6-31G(d) lowest-energy electronic transitions in nm at the S_0 (absorption) and T_1 (emission) optimized geometries. Oscillator strengths (f) and molecular orbital contributions for the first excited state (S_1 or T_1) are included.

Pt(II) complex	Absorption			Emission		
	λ_{max} [nm]	f	MOs Contribution of S_1	λ_{emiss} [nm]	MOs Contribution of T_1	
Monomer	1	281, 333, 427	0.067	HOMO $\rightarrow$ LUMO (93%)	636	HOMO $\rightarrow$ LUMO (66%)
	2	286, 334, 424	0.076	HOMO $\rightarrow$ LUMO (93%)	635	HOMO $\rightarrow$ LUMO (66%)
	3	284, 332, 428	0.076	HOMO $\rightarrow$ LUMO (93%)	635	HOMO $\rightarrow$ LUMO (66%)
	5	284, 332, 432	0.072	HOMO $\rightarrow$ LUMO L (93%)	774	HOMO $\rightarrow$ LUMO (83%)
Dimer	1(a)	344, 462	0.0440	HOMO $\rightarrow$ LUMO (88%)	678	HOMO $\rightarrow$ LUMO (69%)
	1(b)	331, 457	0.0488	HOMO $\rightarrow$ LUMO (90%)	749	HOMO $\rightarrow$ LUMO (69%)
	1(c)	295, 333, 442	0.0377	HOMO $\rightarrow$ LUMO (93%)	749	HOMO $\rightarrow$ LUMO (69%)
	2(b)	344, 462	0.0440	HOMO $\rightarrow$ LUMO (88%)	678	HOMO $\rightarrow$ LUMO (69%)
	2(c)	337, 443	0.0488	HOMO $\rightarrow$ LUMO (90%)	749	HOMO $\rightarrow$ LUMO (60%)
	3(b)	340, 459	0.0377	HOMO $\rightarrow$ LUMO (93%)	749	HOMO $\rightarrow$ LUMO (65%)
	3(c)	339, 438	0.0481	HOMO $\rightarrow$ LUMO (90%)	759	HOMO $\rightarrow$ LUMO (71%)
	5(a)	335, 453	0.0307	HOMO $\rightarrow$ LUMO (65%)	638	HOMO $\rightarrow$ LUMO (67%)
	5(b)	344, 446	0.0310	HOMO $\rightarrow$ LUMO (66%)	786	HOMO $\rightarrow$ LUMO (72%)
	5(c)	339, 447	0.0361	HOMO $\rightarrow$ LUMO (67%)	777	HOMO $\rightarrow$ LUMO (77%)
Trimer	1(a)	365, 464, 541	0.0617	HOMO $\rightarrow$ LUMO (98%)	842	HOMO $\rightarrow$ LUMO (98%)
	1(b)	359, 451	0.0390	HOMO $\rightarrow$ LUMO (81%)	755	HOMO $\rightarrow$ LUMO (64%)
	1(c)	361, 447	0.0389	HOMO $\rightarrow$ LUMO (81%)	788	HOMO $\rightarrow$ LUMO (60%)
	2(b)	367, 460	0.0334	HOMO $\rightarrow$ LUMO (85%)	776	HOMO $\rightarrow$ LUMO (59%)
	2(c)	363, 518	0.0409	HOMO $\rightarrow$ LUMO (97%)	757	HOMO-1 $\rightarrow$ LUMO (55%)
	3(b)	404, 460	0.0225	HOMO $\rightarrow$ LUMO (61%)	785	HOMO $\rightarrow$ LUMO (60%)
	3(c)	403, 459	0.0235	HOMO $\rightarrow$ LUMO (73%)	770	HOMO-4 $\rightarrow$ LUMO (30%)
	5(a)	367, 449	0.0330	HOMO $\rightarrow$ LUMO (96%)	801	HOMO $\rightarrow$ LUMO (49%)
	5(b)	361, 453	0.0371	HOMO $\rightarrow$ LUMO (51%)	833	HOMO $\rightarrow$ LUMO (98%)
	5(c)	363, 455	0.0290	HOMO $\rightarrow$ LUMO (96%)	757	HOMO $\rightarrow$ LUMO (58%)

11. Simulated Absorption of Monomers, Dimers, and Trimers

Figure S11. Absorption of monomers, dimers, and trimers of studied Pt(II) complexes 1–3 and 5 computed at TD-B3LYP and TD-B3LYP-D3/6-31G(d) level.

12. HOMO and LUMO of Monomers

 S_0 state T_1 state

Figure S12. Contour plots of HOMO and LUMO in S_0 and T_1 states of monomeric Pt(II) complexes 1–3 and 5 computed at B3LYP/6-31G(d) level.

13. HOMO and LUMO of Dimers

 S_0 state T_1 state

Figure S13. Contour plots of HOMO and LUMO in S_0 and T_1 states of dimeric Pt(II) complexes 1–3 and 5 computed at B3LYP-D3/6-31G(d) level.

14. HOMO and LUMO of Trimers

 S_0 state T_1 state

Figure S14. Contour plots of HOMO and LUMO in S_0 and T_1 states of trimeric Pt(II) complexes 1–3 and 5 computed at B3LYP-D3/6-31G(d) level.

15. Spin Density Distrubution

Figure S15. Spin density in the T_1 state of studied Pt(II) complexes 1–3 and 5 computed at B3LYP-D3/6-31G(d) level.

16. Photophysical Properties of the Blended Films of Complex 1

Figure S16 shows the steady-state PL spectra and transient PL decay profiles for a series of complex **1**'s doped films (2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole) as the host). Two main intermolecular forces drive the dimer and trimer assembly: intermolecular π - π stacking interactions and Pt $\cdots$ Pt contacts. In powder state, Pt(II) complex **1** demonstrates strong π - π stacking and structural PL spectra comparable (c.f. Figure 1 and Figure S2), despite of the fact that π - π stacking can also lead to red-shifted, structureless emission in organic compounds. On the other hand, in film state the Pt $\cdots$ Pt intermolecular interaction is considered to be the primary reason for the red-shifted intermolecular charge transfer process as shown in Figure S16a, rather than the other intermolecular interaction. Generally speaking, strong intermolecular interaction, i.e. π - π stacking, often induces low PLQY and longer emission lifetime. However, in this case, the PLQY of the doped film increased (Figure S16a inset) and emission lifetime decreased (Figure S16b) monotonously with increasing concentration of **1**, indicative of MMLCT character by metallophilic interaction. Upon the doping concentration gradually increased, the Pt(II) complex must experience a “monomer $\rightarrow$ dimer $\rightarrow$ trimer $\rightarrow$ oligomer” transformation in sequence, corresponding to the transition in formation of “Pt” $\rightarrow$ “Pt $\cdots$ Pt” $\rightarrow$ “Pt $\cdots$ Pt $\cdots$ Pt” $\rightarrow$ “Pt $\cdots$ Pt $\cdots$ Pt assemblies ...”. When the concentration of **1** is extremely low (0.5 wt%), the complex is considered to be an isolated molecule with negligible Pt $\cdots$ Pt interaction. Therefore, the PL spectrum of the 0.5 wt% blended film is similar to that of the diluted solution of **1**, accompanied by a long emission lifetime ($> 20 \mu\text{s}$). Upon increasing the concentration of **1** to 10 wt%, a redshifted, structureless emission band emerged, together with simultaneous increase of the corresponding PLQY. Although this redshifted band turned more dominant at concentration of 5 and 10 wt%, it still exhibited the long-lived

$^3\text{LC}^3\text{MLCT}$ transition characteristics, as evidenced by their bi-exponential PL decay profiles (Figure S16b). This PL spectrum at the early stage of doping process (a concentration between 0.5–10 wt%) should be attributed to the dimer (“Pt···Pt”), before the formation of trimer or higher oligomers. Therefore, the dimer does not show evident MMLCT-like emission, which is in accordance with the calculation results. In contrast, further increase of the concentration of **1** to ≥ 20 wt% did not significantly change the PL profiles, but afforded a shorted-lived mono-exponential PL decay with $\tau_{\text{obs}} < 1$ μs , implying dominant MMLCT character. In this case, shortened intermolecular metallophilic contact is more evident, leading to trimer or even oligomer as projected by calculation.

Figure S16. a) Steady-state PL spectra and PLQYs (inset), and b) transient PL decay profiles of the doped thin films of **1** in (2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole) as the host).

17. UPS Spectra

Figure S17. UPS spectra of thin film deposited on ITO substrates. Enlarged views of a) low and b) high kinetic energy portions.

18. Performances of b-Type Device

Figure S18. EL characteristics of b-type devices with a structure of ITO/TPAC (40 nm)/TCTA (20 nm)/mCP (10 nm)/EML (30 nm)/TPBI (60 nm)/LiF (1 nm)/Al (100 nm): a) J - V - L plots. b) EL spectra at 1000 cd m⁻². c) EQE-luminance plots.

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