Evidence for enhanced dipolar interactions between Pt centers in binuclear phosphorescent complexes

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ABSTRACT

Transient studies are used to examine the radiative decay dynamics in a series of phosphorescent platinum binuclear complexes. The complexes studied consist of square planar \(2\text{-}(4\text{-}6\text{-}\text{difluorophenyl})\text{pyridinato-N,C}^2\text{Pt}\) units bridged by either pyrazole or thiopyridine ligands. We observe an increase in radiative lifetime as temperature is reduced from 300 K to 4 K when the binuclear complexes, named 1, 2 and 3 with Pt–Pt spacings 3.19 Å, 3.05 Å, and 2.83 Å, respectively, are doped into a p-bis(triphenylsilylyl)benzene wide energy gap host. The lifetimes for 1, 2 and 3 are \(\tau = 6.3 \pm 0.1\) µs, \(\tau = 2.3 \pm 0.1\) µs, and \(\tau = 2.0 \pm 0.1\) µs at \(T = 295\) K, respectively. At \(T = 4\) K, those values increase to \(\tau = 8.6 \pm 0.1\) µs, \(\tau = 14.4 \pm 0.1\) µs, and \(\tau = 17.0 \pm 0.1\) µs, suggesting that the neighboring heavy metal centers in compounds 2 and 3 have significant orbital overlap. A three-level zero-field splitting model yields the lowest triplet energy splittings of 28 ± 3 cm\(^{-1}\), 142 ± 9 cm\(^{-1}\), and 113 ± 10 cm\(^{-1}\) for compounds 1, 2 and 3, respectively.

1. Introduction

Spin–orbit coupling between singlet and triplet states in organic molecules is known to be an effective means to promote rapid, radiative triplet emission. When this process is electrically excited, it results in electrophosphorescent emission in organic light emitting devices (OLEDs), leading to unity internal quantum efficiency [1]. The typically slow (\(>10^{-6}\) s) and inefficient, room-temperature phosphorescence in organic molecules is enhanced by introducing a heavy metal atom in the molecular complex [2]. The magnitude of the spin–orbit interaction by the presence of the heavy metal atom with atomic number \(Z\), scales as \(Z^5\). The efficient electrophosphorescent OLED was based on platinum(II) octaethylporphyrine (PtOEP) [3], whose emissive state is a mixture of ligand-centered triplet (3LC) and metal–ligand charge transfer (3MLCT) triplet states. A number of other square planar platinum complexes have also been utilized in OLEDs, emitting from a similar mixture of MLCT and LC states [4]. A related class of phosphors comprised of the binuclear Pt complexes, where the emissive state arises from charge transfer involving the metal–metal-to-ligand charge transfer (3MMLCT) interaction. The photophysical properties of this latter class of materials are explored in this work as a function of the Pt–Pt spacing.

Recently, Ma et al. reported a series of phosphorescent pyrazole-ligated cyclometalated platinum(II) complexes [5] with the general formula: \(\text{C}^\text{N}^\text{C}^\text{C}^\text{N}\text{Pt(2-thiopyridyl)}\)\(_2\) (FPt2) with a peak emission at a wavelength of 610 nm has also been studied, and thus the emission spectrum. For example, compounds 1, 2 and 3 in Fig. 1a, with Pt–Pt spacings (1) 3.19 Å, (2) 3.05 Å, and (3) 2.83 Å, lead to efficient phosphorescence in the blue, green and red, respectively, as shown in Fig. 1b [8].

The bridging ligands rigidly link the two metal centers of the three binuclear compounds [9]. For compound 1, the emission spectrum indicates a mixed 3LC/3MLCT excited state [5], proving evidence for a weak interaction between the two metal centers. In addition, broad and featureless emission spectra of compounds 2 and 3 are observed, and assigned to 3MMLCT [10]. This occurs when the metal centers are in close proximity, and their interactions are enhanced. An analogous Pt complex, [(2-(4’6’-difluorophenyl)pyridinato-N,C^2)Pt(2-thiopyridyl)]\(_2\) (Pft2) with a peak emission at a wavelength of \(\lambda = 610\) nm has also been studied, and has a Pt–Pt distance of 2.87 Å, as shown in inset of Fig. 1a [11].

In this Letter, time-resolved photoluminescence of four, Pt-based binuclear complexes are investigated, and large triplet energy splittings of compounds 2, 3 and Pft2 are observed. Theoretical analysis of the phosphorescent properties of the complexes is provided in Section 2. Section 3 includes experimental techniques and details. Results from the transient measurements are...
spectra. For example, \([\text{Rh(bpy)}_3]^3+, \text{[Pt(bpy)}_2]^2+\) have small ZFS of smaller compounds are determined using high resolution optical
ular complexes\[14\]. The ZFS values for most of the transition me-
section 4, and are followed in section 5 with analysis and
simulations based on density function theory (DFT) to interpret
spectral properties, and conclusions are provided in section 6.

2. Theory

Zero-field splitting (ZFS) refers to the difference between other-
wise degenerate triplet states in the absence of an external mag-
netic field \[12,13\]. For most materials, the dipolar interactions
between spins average to zero since the spins are in a rapid isotro-
pic motion in the molecular frame. However, splitting arises where
there is large overlap of the orbitals containing the unpaired spins,
which results in electron exchange and spin quantization. Using
perturbation theory, ZFS has two contributions: a first-order term
resulting from dipolar spin–spin (S · S) coupling, and second-order
L · S coupling which is dominant in high Z transition metal mole-
cular complexes \[14\]. The ZFS values for most of the transition met-
al compounds are determined using high resolution optical
spectra. For example, \([\text{Rh(bpy)}_3]^3+, \text{[Pt(bpy)}_2]^2+\) have small ZFS of
only \(-0.1\ \text{cm}^{-1}\), while the splitting of \([\text{Os(bpy)}_3]^2+\) reaches
211 \text{ cm}^{-1} due to its increased metal character \[15\].

Alternatively, details of the energetics of ZFS can be obtained by
studying temperature dependent photoluminescence decay
 dynamics \[16\]. Assuming a Boltzmann distribution among the
field-split sublevels, the transition rate follows \[17\]:

\[ k_{\text{therm}} = k_1 + k_2 e^{-\Delta E_2/k_B T} + k_3 e^{-\Delta E_3/k_B T} \]

\[ k_{\text{therm}} = 1 + e^{-\Delta E_2/k_B T} + e^{-\Delta E_3/k_B T} \]

(1)

where \(\Delta E_2\) and \(\Delta E_3\) are the energy differences between triplet
sublevels 3 and 1, and 2 and 1, respectively, as shown in the pro-
posed energy level scheme of Fig. 1c. Also, \(T\) is the temperature,
\(k_0\) is Boltzmann’s constant, and \(k_1, k_2\) and \(k_3\) are decay rates from
the three sublevels. This equation is simplified at low temperature,
where

\[ k_{\text{therm}}^{\text{LT}} = k_1 \]

since the population is frozen into the lowest sublevel 1. Fur-
thermore, at high temperature, where \(\Delta E_2, \Delta E_3 \ll kT\), Eq. (1) simplifies to

\[ k_{\text{therm}}^{\text{HT}} = (k_1 + k_2 + k_3)/3 \]

(3)

3. Experimental

Each metalorganic phosphor was codeposited at 8 wt\% with the
large energy gap host, \(p\)-bis(triphenylsilyl)benzene (UGH2) \[18\]
ono a clean Si substrate by thermal evaporation in a vacuum.
chamber with a base pressure of $10^{-7}$ Torr. The large energy gap of UGH2 ensures that exciton formation by optical pumping occurs directly on the guest phosphor molecules. The thickness of the organic layer was fixed at 180 nm.

Samples were mounted in a cryostat where the temperature was varied from 4 K to 295 K. Photoluminescence (PL) was excited using a N$_2$ laser with a wavelength of $\lambda = 337$ nm at a 10 Hz repetition pulse rate. The 18 $\mu$J pulse with a duration of 0.7 ns

Fig. 3. Temperature dependence of the integrated photoluminescence intensity of compounds (a) 2 and (b) 3 doped into UGH2 at 8 wt%. Data were taken between $T = 295$ K and 12 K.

Fig. 4. Radiative lifetimes of compounds (a) 1, (b) 2, (c) 3 and (d) FPt2 at room temperature ($T = 295$ K) and 4 K (30 K for FPt2) after pulsed photoexcitation using a N$_2$ laser at a 10 Hz repetition pulse rate, and at a wavelength of $\lambda = 337$ nm. Dots are experimental data and solid lines are fits. Compounds 2, 3 and FPt2 exhibit strong temperature dependent decay. The curves are normalized for comparison. The structure of FPt2 is shown in the inset of (d).
was focused on the sample to a 1.5 mm diameter spot. The resulting PL was focused into a streak camera (Hamamatsu C4334) that monitored the time-resolved spectral decay.

4. Results

The PL spectra for three compounds as solid solutions in UGH2, are shown in Fig. 1b. For compound 1, the emission spectrum shows vibronic features that are typical for $^3LC/MLCT$ mixed excited states. A fit of the spectrum of compound 1 to its three vibronic components is shown in Fig. 2. In contrast, compounds 2 and 3 show broad and featureless emission spectra, similar to those of excimers [19]. Emission from 2 and 3 results from a $^3\text{d}r^*\pi^*$ state, where the $r^*$ orbital is formed by the two occupied $d_{z^2}$ orbitals of the co-facial Pt centers [5]. The integrated PL intensities for compounds 2 and 3 doped in UGH2 are provided in Fig. 3, showing no temperature dependence.

The dimer properties of the complexes can be understood in terms of their phosphorescent decay transients. In Fig. 4, we show the phosphorescent decay at $T = 4$ K and 295 K after pulsed photoexcitation for compounds 1–3 and FPt2. For FPt2, we observed significant non-linearities in the transients, suggesting the presence of non-radiative loss channels, such as triplet–triplet (T–T) annihilation [20]. In this case, the phosphorescent emission intensity follows:

$$L(t) = \frac{L(0)}{(1 + K \tau)e^{t/\tau} - K\tau},$$  \hspace{1cm} (4)

where

$$K = \frac{1}{2}k_{\text{TR}}[^3M(0)].$$ \hspace{1cm} (5)

Here, $[^3M(0)]$ is the initial triplet excited state concentration, $\tau$ is the natural phosphorescent recombination lifetime, $k_{\text{TR}}$ is the rate of triplet annihilation, and $L(t)$ is the luminescence intensity at time $t$. The radiative lifetime is measured between room temperature to $T = 30$ K, yielding $\tau = 2.0 \pm 0.1$ $\mu$s and $\tau = 12.0 \pm 0.1$ $\mu$s at these extremes, respectively. We note that the low triplet mobility prevents rapid diffusion of excitons to the dopant from nearby host sites, contributing along with ZFS, to the longer lifetime for FPt2 at $T < 30$ K, and hence those data are not included in the analysis.

For compound 1, the lifetime shows only a slight temperature dependence, ranging from $\tau = 6.3 \pm 0.1$ $\mu$s at $T = 295$ K, to $\tau = 8.6 \pm 0.1$ $\mu$s at $T = 4$ K. However, the lifetimes of compounds 2, 3 and FPt2 all exhibit a pronounced dependence on temperature, as listed in Table 1 and illustrated in Fig. 5.

5. Discussion

As shown in Fig. 4, the emissive decay rate increases with temperature, while the PL intensity for compounds 2 and 3 remains constant. This is evidence for the thermal population [21] of the higher emitting sublevels $E_2$ and $E_3$, as suggested in Eq. (1). Now, the relationship between the non-radiative and radiative emission rates is determined from the PL efficiency via

$$\eta_{\text{PL}} = \frac{k_{\text{R}}}{k_{\text{R}} + k_{\text{NR}}}.$$ \hspace{1cm} (6)

Since the integrated PL intensity in Fig. 3 shows no temperature dependence, we therefore conclude that either $k_{\text{R}} \gg k_{\text{NR}}$ and the

<table>
<thead>
<tr>
<th>Temperature</th>
<th>1 ($\mu$s)</th>
<th>2 ($\mu$s)</th>
<th>3 ($\mu$s)</th>
<th>FPt2 ($\mu$s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T = 295$ K</td>
<td>$6.3 \pm 0.1$</td>
<td>$2.3 \pm 0.1$</td>
<td>$2.0 \pm 0.1$</td>
<td>$2.0 \pm 0.1$</td>
</tr>
<tr>
<td>$T = 4$ K</td>
<td>$8.6 \pm 0.1$</td>
<td>$14.4 \pm 0.1$</td>
<td>$17.0 \pm 0.1$</td>
<td>$12.0 \pm 0.1^a$</td>
</tr>
</tbody>
</table>

$^a$ $T = 30$ K for this measurement.
observed temperature dependence in lifetime is only due to changes in \( k_R \) (i.e., \( \eta_R \approx 1 \)) or that the ratio, \( k_{eq}/k_R \), is temperature independent. The latter possibility only occurs in the unlikely event that the Arrhenius parameters are identical for \( k_R \) and \( k_{eq} \) in both 2 and 3, and thus we favor the former explanation.

Fig. 5 shows Arrhenius plots of the temperature dependent decay rate measurements (filled triangles) for compounds 1–3. Eqs. (1)–(3) are used to fit the data (open circles) and obtain the corresponding ZFS values. Thus, \( \Delta E_{31} = 142 \pm 9 \text{ cm}^{-1} \) and \( \Delta E_{31} = 113 \pm 10 \text{ cm}^{-1} \) for compounds 2 and 3, respectively, which are considerably larger than that of 1, with \( \Delta E_{31} = 28 \pm 3 \text{ cm}^{-1} \). The complete fitting parameters are listed in Table 2. Note that for compound 1, the energy splitting is small. In this case, the condition of \( \Delta E_{31} > kT \) required for the approximation in Eq. (3) is not valid at \( T = 4 \text{ K} \). Hence, to check the result, the fits yielding \( \Delta E_{31}, \Delta E_{31} \), and \( k_2 \), were used directly in Eq. (1) to obtain a non-radiative rate \( k_{\text{nr}} = 0.10 \pm 0.02 \text{ s}^{-1} \approx k_1 \) to within the error range of the data.

To further understand the experimental results, we estimated the metal participation in the triplet state, which is expected to influence the magnitude of the ZFS. The calculated orbital distribution is shown in Fig. 6. No pronounced change in spin density takes place at the pyridyl ring, whereas the triplet spin density surfaces at the Pt–Pt center for compounds 2 and 3 are double that of 1. The spin densities normalized to that on the ligand are listed in Table 3. Indeed, twice the electron density resides on the Pt centers in compounds 2 and 3 compared to 1.

Based on the point dipole model [14], L–S coupling is enhanced as dipoles are brought into close proximity, as in compounds 2, 3, and FP2. According to Fig. 6, compounds therefore show a significant overlap of the d-orbitals of the individual metal atoms that allows for strong interactions, thus lifting the triplet energy degeneracy and leading to a pronounced ZFS.

We consider a simple model based on the DFT simulation to roughly estimate the relative magnitudes of the ZFS in compounds 2 and 3 compared to their mononuclear counterpart, compound 1. For simplicity, we assume that the lowest unoccupied molecular orbital (LUMO) is localized at the center of the pyridyl ring, while the highest occupied molecular orbital (HOMO) is centered on the platinum atoms. A uniform spin density distribution over a sphere of radius \( r_0 \) is assumed for compound 1, and \( 2r_0 \) for compounds 2 and 3, as listed in Table 3. Compounds 2 and 3 are treated together since they have a similar spin density as determined by DFT simulations.

Considering only L–S coupling, and assuming that the Coulomb potential, \( \phi \), arises from a nucleus of charge Ze, then the spin–orbit Hamiltonian follows [22]:

\[
H_{\text{so}} = -\frac{e\hbar^2}{2m_e c^2 r} \frac{d\phi}{dr} \mathbf{L}\mathbf{S} = \zeta(r) \mathbf{L}\mathbf{S},
\]

where

\[
\zeta(r) = \frac{Ze^2 \hbar^2}{2m_e c^2 r^2}
\]

Here, \( e \) is the elementary charge, \( r \) is the distance between the metal center and the unpaired electron of the ligand, and \( m_e \) is the mass of an electron. Then the spin–orbit interaction energy for compound \( i = 1, 2, 3 \) follows \( E_{\text{so}} \propto 1/r_i \). This behavior allows us to calculate the integral over an ideal spherical spin density distribution to yield: \( E_{\text{so}}^3/E_{\text{so}}^1 = 6.3 \). Therefore, we obtain

Table 2
Zero-field splitting energies and transition rates for the binuclear Pt complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta E_{31} ) (cm(^{-1}))</th>
<th>( \Delta E_{31} ) (cm(^{-1}))</th>
<th>( k_1 ) (( \mu s^{-1} ))</th>
<th>( k_2 ) (( \mu s^{-1} ))</th>
<th>( k_3 ) (( \mu s^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>28 ± 3</td>
<td>&lt;4</td>
<td>0.12 ± 0.01</td>
<td>0.11 ± 0.02</td>
<td>0.25 ± 0.02</td>
</tr>
<tr>
<td>2</td>
<td>142 ± 9</td>
<td>31 ± 5</td>
<td>0.07 ± 0.01</td>
<td>0.42 ± 0.08</td>
<td>0.81 ± 0.08</td>
</tr>
<tr>
<td>3</td>
<td>113 ± 10</td>
<td>33 ± 6</td>
<td>0.06 ± 0.01</td>
<td>0.32 ± 0.06</td>
<td>1.12 ± 0.06</td>
</tr>
</tbody>
</table>

Table 3
The spin density at the metal center normalized to that on the ligand

<table>
<thead>
<tr>
<th>Compound</th>
<th>Pt 1</th>
<th>Pt 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.103</td>
<td>0.002</td>
</tr>
<tr>
<td>2</td>
<td>0.198</td>
<td>0.196</td>
</tr>
<tr>
<td>3</td>
<td>0.200</td>
<td>0.206</td>
</tr>
</tbody>
</table>

Fig. 6. Triplet spin density surfaces for compounds 1, 2, and 3. The spin density surface in the triplet state at the Pt–Pt center for compounds 2 and 3 are double to that of compound 1. This indicates a large d\( z^2 \) orbital character in 2 and 3.
\[ \frac{\Delta E_{21}^3}{\Delta E_{11}^3} = \frac{E_{21}^3}{E_{11}^3} = 6.3, \]

which is comparable with experimental results of \( \frac{\Delta E_{21}}{\Delta E_{11}} = 5.1 \pm 0.9 \), and \( \frac{\Delta E_{31}^3}{\Delta E_{11}^3} = 4.1 \pm 0.8 \) for compounds 2 and 3, respectively (see Table 2). The difference between calculation and experiment arises from our estimation of complete LUMO localization at a point in the center of the ligand, in contrast to the actual situation where the electron density is distributed over the pyridyl group. The assumption of a uniform spin density distribution on the HOMO also introduces error, although the difference is relatively minor compared to the approximations made. Hence, we conclude that ZFS is enhanced due to the small Pt–Pt distance characteristic of this set of binuclear complexes.

### 6. Conclusions

We have studied the radiative decay dynamics of a series of Pt binuclear complexes used as phosphorescent dopants in OLEDs. By employing a three-sublevel, non-degenerate triplet spin model, we report large zero-field splitting energies for complexes with strong metal–metal bonds, and have developed a detailed understanding of the photophysics underlying those interactions. A distance of 3 Å or less between the platinum centers allows for significant overlap of the d-orbitals of the individual metal atoms, leading to large ZFS energies.

The photophysical properties of organometallic phosphorescent emitters rely on a strong \( L \cdot S \) coupling dependence on the metal–metal interaction, which controls the magnitude of ZFS of the triplet state. The corresponding ZFS energies reported here are much larger than those in other similar complexes [23]. When applied to OLEDs, the increased metal character of the excited states enhances the intersystem crossing rate [24], and hence increases the internal quantum efficiency of the triplet emission. This understanding may lead to the design of new organic-based transition metal complexes with optimized emission properties for a broad range of practical device applications.

### Acknowledgement

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### References