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Enhancing Phosphorescence in Platinum(II) Complexes through Intramolecular CH–N Interactions

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1. Introduction

Phosphorescent transition-metal complexes have attracted sustained interest owing to their potential applications in organic light-emitting diodes, sensing, and bioimaging. Achieving high photoluminescence quantum yields in such systems is of critical importance. An effective strategy for designing highly emissive complexes is the use of rigid ligand frameworks, such as 2,2'-bipyridine and 2-phenylpyridine, which effectively suppress nonradiative decay and afford strong emission[1]. In contrast, complexes bearing flexible imine-based ligands are generally non-emissive, because of the structural relaxation and facile access to nonradiative decay pathways[2]. We previously found that in a series of *trans*-bis(iminomethylazolato)platinum(II) complexes, the pyrazole derivative exhibits strong phosphorescence, whereas the corresponding pyrrole and imidazole derivatives are weak or non-emissive[3]. This difference was attributed to the formation of intramolecular C–H···N hydrogen bonding between the pyrazole nitrogen and the alkyl C–H group of the opposing ligand, which is expected to suppress nonradiative decay.

In this work, a series of *trans*-bis(5-iminomethylpyrazolato)platinum(II) complexes bearing varied *N*-substituents were synthesized to systematically investigate the structure–phosphorescence relationships. The emission efficiencies exhibit a pronounced substituent dependence. Combined experimental and theoretical analyses reveal that this behavior arises from two structural factors. Molecular planarity controls the nonradiative decay rate (k_{nr}), with highly bent

complexes being weakly emissive or non-emissive. Moreover, intramolecular C–H···N interactions, prominent in planar complexes, modulates both radiative (k_r) and nonradiative processes; stronger interactions enhance k_r while suppressing k_{nr} , resulting in efficient phosphorescence (Fig. 1).

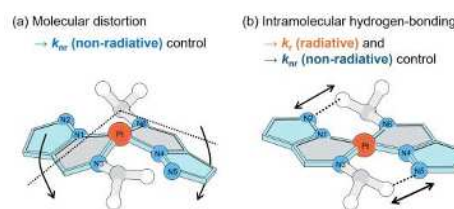


Fig. 1: Schematic illustration of the substituent-dependent control, highlighting (a) molecular distortion and (b) intramolecular hydrogen bonding.

2. Results and discussion

A series of complexes **1a–e** bearing different *N*-substituents on the pyrazolate ligands were synthesized, including polymethylene-bridged (vaulted) structures **1a** ($n = 10$) and **1b** ($n = 12$), as well as non-vaulted analogues bearing an alkyl chain (**1c**), a benzyl group (**1d**), and a trifluoroethyl group (**1e**). Their photoluminescence properties exhibit substituent dependent (Fig. 2). All complexes show yellow emission in 2-MeTHF at 298 K ($\lambda_{298K} = 532$ –542 nm) with quantum yield (Φ_{298K}) increases markedly from 0.04 for **1a** to 0.72 for **1e** at 298 K, corresponding to an approximately 20-fold enhancement. In contrast, comparable emission efficiencies are observed at 77 K ($\Phi_{77K} = 0.64$ –0.72), indicating that the differences at 298 K originate from thermally activated deactivation processes.

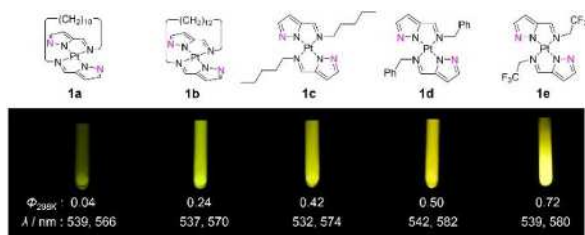


Fig. 2: Molecular structures and photographs of **1a–e** under 365 nm UV irradiation at 298 K (1.0×10^{-4} M in 2-MeTHF)

Emission lifetimes were measured and the k_r and k_{nr} were determined (Fig. 3). At 298 K, k_r increases moderately from $7.3 \times 10^4 \text{ s}^{-1}$ for **1a** to $17.3 \times 10^4 \text{ s}^{-1}$ for **1e**, whereas k_{nr} decreases much more from $114.5 \times 10^4 \text{ s}^{-1}$ to $6.7 \times 10^4 \text{ s}^{-1}$. These results demonstrate that suppression of k_{nr} is the dominant factor governing the enhancement of Φ_{298K} across the series. From **1a** to **1c**, the increase in emission efficiency is dominated by reduced k_{nr} , while for **1c–e**, both increased k_r and decreased k_{nr} contribute comparably.

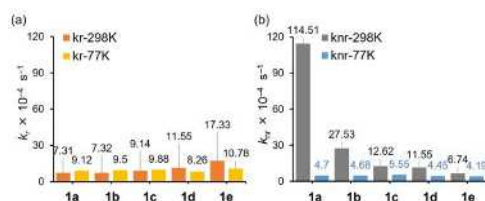


Fig. 3: (a) k_r and (b) k_{nr} of **1a–e** at 298 and 77 K (1.0×10^{-4} M in 2-MeTHF).

To elucidate the structural origin of these trends, DFT calculations were performed to examine molecular planarity and intramolecular hydrogen bonding. The dihedral angle $\angle AB$ defined by the two opposing pyrazole rings was used to quantify molecular distortion. The vaulted complexes show molecular bending ($\angle AB = 21.6^\circ$ for **1a** and 14.0° for **1b**), whereas non-vaulted complexes **1c–e** adopt nearly planar geometries ($\angle AB = 0.04\text{--}0.06^\circ$). Substituent-dependent variations are also observed in the intramolecular C–H $\cdots$ N hydrogen bonding, with

average C–H $\cdots$ N distances decreasing from **1a/1b** (2.474 / 2.482 Å) to **1c–e** (2.447–2.231 Å), consistent with strengthened hydrogen bonding induced by more electron-withdrawing substituents (Fig. 4a). Notably, k_r correlates with the average C–H $\cdots$ N distance (Fig. 4b), indicating enhanced radiative decay upon hydrogen-bond strengthening. In contrast, distinct structural factors govern k_{nr} . For **1a–c**, $\ln(k_{nr})$ correlates with the bending angle $\angle AB$ (Fig. 4c), while within the planar series **1c–e**, $\ln(k_{nr})$ depends primarily on the C–H $\cdots$ N distance (Fig. 4d). These results establish a two-stage structural mechanism for nonradiative decay, dominated by molecular distortion in bent complexes and by intramolecular hydrogen bonding in planar systems.

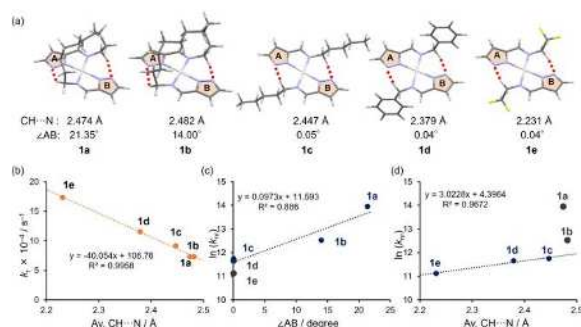


Fig. 4: (a) Optimized S_0 structures. (b) k_r plotted against the C–H $\cdots$ N distance. $\ln(k_{nr})$ plotted against (c) the $\angle AB$ and (d) the C–H $\cdots$ N distance.

To clarify the origin of the substituent-dependent variation in k_{nr} , the excited-state deactivation pathways were analyzed by evaluating the energies of the T_1 state and the minimum-energy crossing point (MECP) between T_1 and S_0 . The energy barrier $\Delta\Delta E_{T_1\text{--}MECP}$ increases monotonically from 13.8 to 19.1 kcal mol^{-1} across **1a–e** (Fig. 5a), indicates progressively hindered access to nonradiative pathways. Consistently, $\Delta\Delta E_{T_1\text{--}MECP}$ exhibits a linear correlation with $\ln(k_{nr})$ (Fig. 5b), confirming that nonradiative decay proceeds via thermally activated access to the MECP. Correlations with key structural parameters were further examined (Fig. 5c,d). For **1a–c**, $\Delta\Delta E_{T_1\text{--}}$

MECP correlates strongly with the bending angle $\angle AB$, and within **1c–e**, $\Delta\Delta E_{T_1\text{--}MECP}$ shows a strong dependence on the C–H $\cdots$ N distance. These results demonstrate that molecular planarity primarily governs k_{nr} by modulating access to the MECP, while intramolecular hydrogen bonding simultaneously enhances k_r and suppresses k_{nr} .

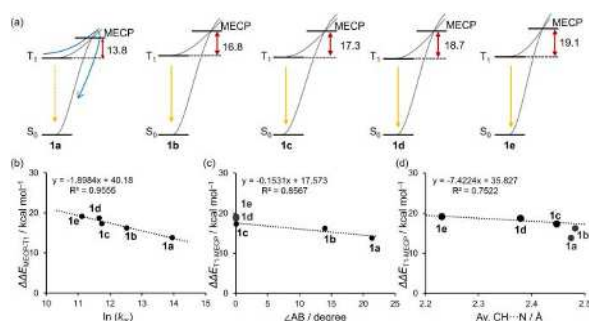


Fig. 5: (a) Energy diagrams of the S₀, T₁, and MECP states. Correlation plots of $\Delta\Delta E_{T_1\text{--}MECP}$ against (b) $\ln(k_{nr})$, (c) $\angle AB$ and (d) C–H $\cdots$ N distance.

3. Conclusion

In this study, a series of *trans*-bis(5-iminomethylpyrazolato)platinum(II) complexes bearing varied *N*-substituents were investigated to elucidate structure–phosphorescence relationships. The photoluminescence efficiency shows a pronounced substituent dependence, varying by more than a factor of 20 across the series. Structural and photophysical analyses reveal that this behavior originates from two key factors: ligand-plane bending in chain-bridged complexes and intramolecular C–H $\cdots$ N hydrogen bonding in planar analogues. Correlations between rate constants, structural parameters, and the T₁–MECP activation energy demonstrate that nonradiative decay is governed by thermally activated access to the MECP, offering clear design guidelines for phosphorescent metal complexes.

References

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