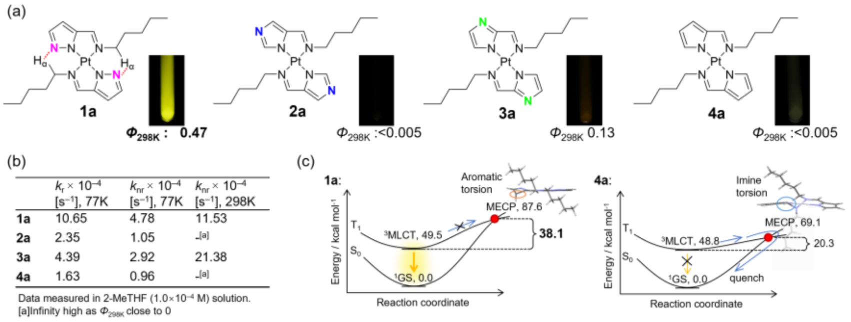
Experimental and Theoretical Investigation of Molecular Design of *trans*-Bis(iminoazolate)platinum(II) Complexes with Strong Emission

([1]*Graduate School of Engineering Science, Osaka University*) ○Shufang Huang,[1] Soichiro Kawamorita,[1] Shuichi Suzuki,[1] Takeshi Naota[1]

Keywords: Phosphorescence; Platinum; Intramolecular Hydrogen Bonding; Density Functional Theory Calculation; Minimum Energy Crossing Point

An effective strategy for designing highly emissive phosphorescent transition metal complexes is to use rigid ligand frameworks, which minimize non-radiative decay. Platinum complexes with rigid ligands, such as 2,2'-bipyridine and 2-phenylpyridine, show high phosphorescent quantum yields, while those with flexible imine ligands are weakly emissive. In the series of *trans*-bisiminoazolate platinum complexes, we previously found that the pyrazole derivative exhibits strong emission, unlike 2-pyrrole, 2-imidazole, and 4-imidazole derivatives, which are non-emissive. In this study, theoretical calculations were performed to understand the strong emission of the iminopyrazolate platinum complex and revealed that intramolecular hydrogen bonding effectively suppresses excited-state deactivation. Based on these findings, novel complexes with enhanced emission efficiency were synthesized by strengthening intramolecular hydrogen bonding.

As shown in Figure 1a, complex **1a** exhibits strong yellow-green emission in 2–MeTHF at 298 K (Φ_{298K} = 0.47), whereas other complexes showed negligible emission. Notably, **1a** shows the lowest k_{nr} of 11.53 × 10^4 s^{-1} at 298 K than **2a**–**4a** (Figure 1b). Theoretical analysis revealed that **1a**'s intramolecular hydrogen bonding can stabilize the excited state and increase the energy of minimum energy crossing point (MECP), the intersection of S_0 and T_1 states (Figure 1c), effectively suppressing irradiative decay. Furthermore, a series of complexes **1** with various functional groups attached to the imine were designed and synthesized. These complexes, with varying $CH_\alpha \cdots N$ distances, exhibited a clear inverse proportional relationship between the T_1–MECP energy gap, heat resistance (ratio of Φ_{298K}/Φ_{77K}), and k_{nr} at 298K, demonstrating a intramolecular $CH_\alpha \cdots N$ distance–dependent emission.



	k_r × 10^{-4} [s^{-1}], 77K	k_{nr} × 10^{-4} [s^{-1}], 77K	k_{nr} × 10^{-4} [s^{-1}], 298K
1a	10.65	4.78	11.53
2a	2.35	1.05	-[a]
3a	4.39	2.92	21.38
4a	1.63	0.96	-[a]

Data measured in 2-MeTHF (1.0×10^{-4} M) solution.
[a]Infinity high as Φ_{298K} close to 0

Figure 1. (a) Chemical structures and photographs under UV irradiation of **1a**–**4a**. (b) k_r/k_{nr} at 77K and 298K (c) Schematic representation of configurations and energies of S_0, T_1 and MECP for complexes **1a** and **4a**.