

Dinuclear Pt^{II} Complexes with Strong Blue Phosphorescence for Operational Stable Organic Light-Emitting Diodes with EQE up to 23% at 1000 cd m⁻²

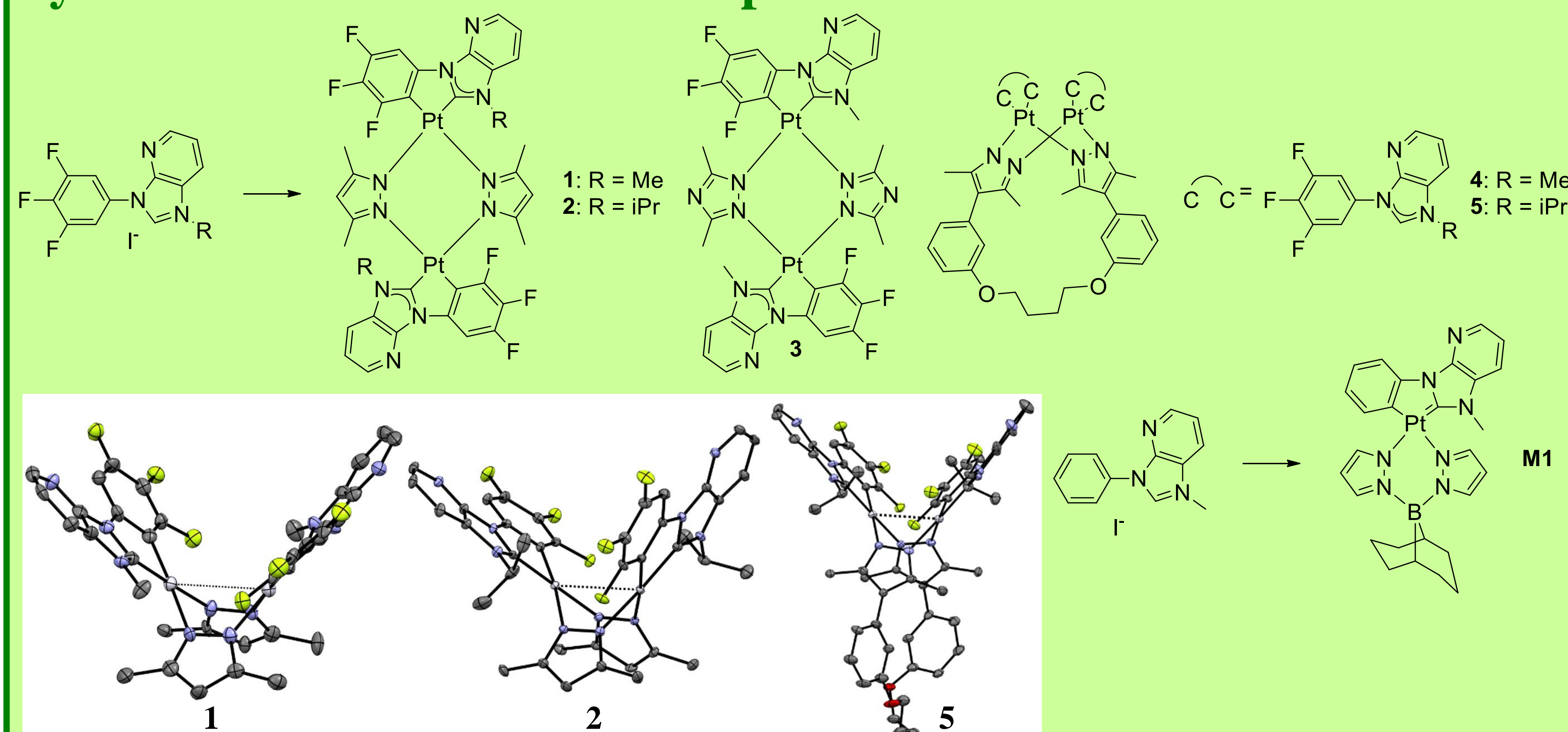
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Introduction

The development of high performance blue phosphorescent organic light-emitting diodes (PhOLEDs) has attracted a surge of interest in recent years. To develop stable blue emitting Pt^{II} complexes, the C[∧]C* ligand is usually used due to its strong σ -donating carbene carbon atom. Dinuclear Pt^{II} complexes can undergo photo-induced structural changes (PSC) from open form to closed form at the ³MMLCT excited state. We aimed to harness the high energy excited state of dinuclear Pt^{II} complexes in the open form in order to realize blue emission with a large k_r . Herein, we describe the synthesis and characterization of a series of pyrazole and triazole bridged C[∧]C* cyclometalated Pt^{II} complexes.

Synthesis of dinuclear Pt^{II} complexes

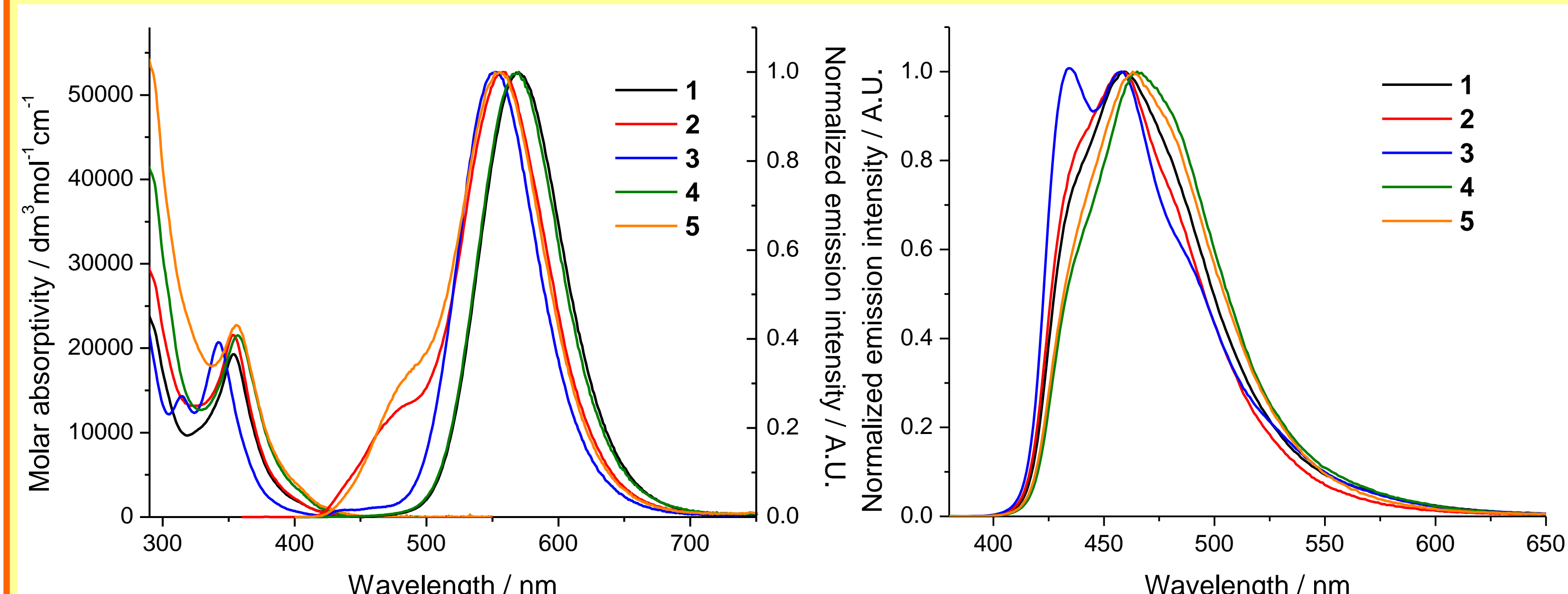


- Only one isomer was obtained for each complex
- High decomposition temperature (defined at 2% weight loss) of up to 447 °C

Table 1. Photophysical and electrochemical data of complexes 1–5

	Absorption		Emission		E_T (eV) ^[c]
	λ_{abs} [nm] (ϵ [10 ³ dm ³ mol ⁻¹ cm ⁻¹]) ^[a]		toluene	4 wt% in PMMA thin film	
1	298(sh, 18.9), 399(sh, 2.1)	354(19.3), 570	λ_{em} [nm] (Φ ; τ [μ s]; k_r [10 ⁵ s ⁻¹]) ^[b]	λ_{em} [nm] (Φ ; τ [μ s]; k_r [10 ⁵ s ⁻¹]) ^[b]	2.99
2	296(sh, 26.2), 393(sh, 3.1)	353(21.6), 478(sh), 557	(0.77; 2.2; 3.5)	(0.91; 1.5; 6.1)	2.99
3	314(14.3), 408(br, 0.4)	343(20.7), 437(sh), 460(sh), 552	(0.62; 1.8; 3.4)	(0.94; 1.8; 5.2)	3.01
4	300(sh, 31.0), 412(br, 1.9)	357(21.5), 568	(0.64; 1.9; 3.4)	(0.78; 3.3; 2.4)	2.98
5	295(sh, 50.2), 405(br, 3.4)	356(22.8), 480(sh), 555	(0.81; 1.9; 4.3)	(0.95; 1.3; 7.3)	2.99
			(0.65; 1.6; 4.1)	(0.94; 1.5; 6.3)	2.99

[a] Determined in a degassed toluene solution at 2×10^{-5} M at 293 K. “br” stands for broad and “sh” stands for shoulder. [b] Emission quantum yields of solution and thin-film samples were measured with a Hamamatsu C11347 Quantaury-QY Absolute PL quantum yield spectrometer. [c] Determined from the onset of thin film emission.

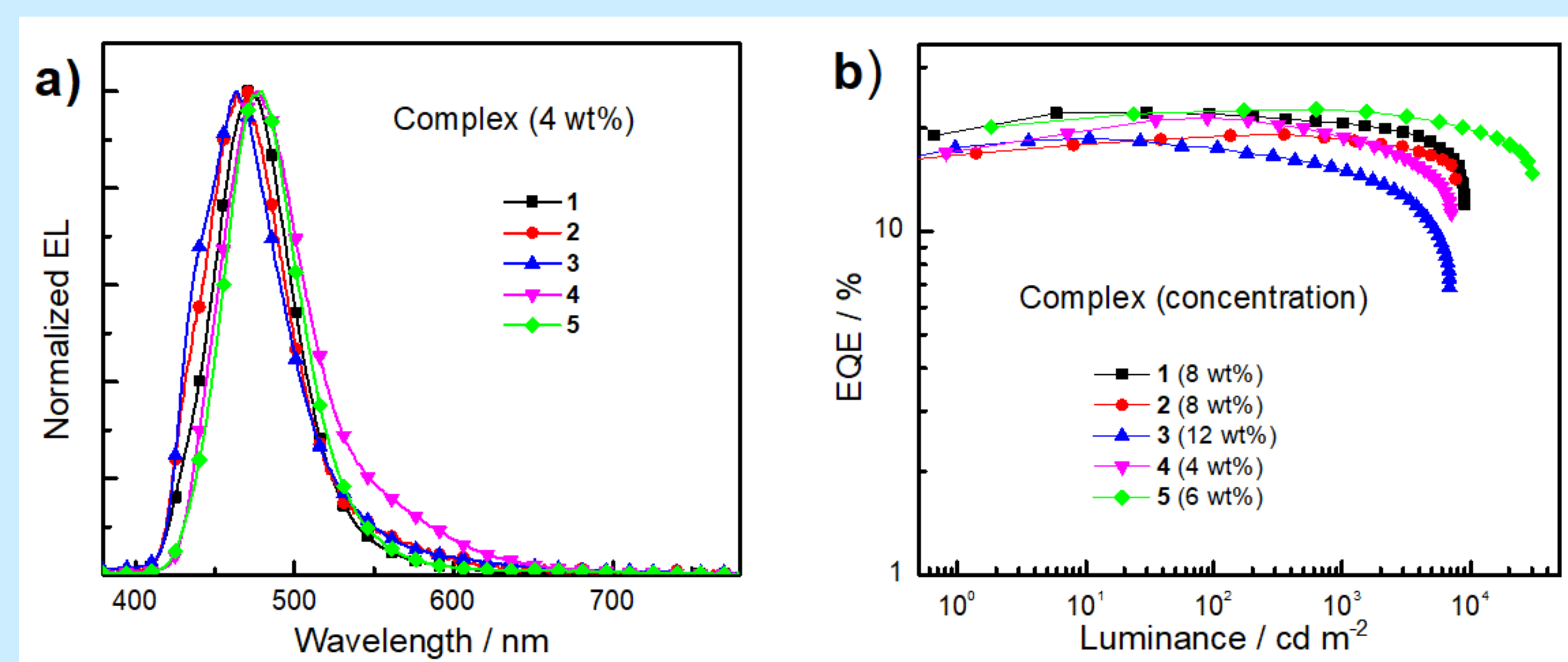


UV-vis absorption and emission spectra of 1–5 in degassed toluene (2×10^{-5} M) at r.t. Normalized emission spectra of 1–5 in PMMA thin film (4 wt%) at r.t.

Excited state nature Evaluation

For both complexes **M1** and **1**, the occupied orbital(s) of the S_2 excited state is(are) mainly derived from the Pt(d_z^2) orbital, and the SOC (spin-orbit coupling) matrix element between the S_2 and the T_1 excited state is relatively large ($\langle S_2 | H_{SOC} | T_1 \rangle$ are 674 and 412 cm⁻¹ for **M1** and **1**, respectively); however, these SOC values are contrary to the conventional wisdom that a dinuclear transition metal complex should have a larger SOC than its mononuclear counterpart. The markedly enhanced k_r of **1**, on the other hand, is due to the much larger transition dipole moment of the $S_2 \rightarrow S_0$ transition of **1**, as reflected in the oscillator strength (f) ($f(S_2 \rightarrow S_0) = 0.0265$ and 0.152 for **M1** and **1**, respectively). The more-than-five-fold increase in f is due to the molecular structure of **1** (the open form) which allows mixing of the $\pi(C^{\wedge}C^*)$ orbitals with the Pt(d_z^2) orbitals, whereas the corresponding metal orbital is nearly orthogonal to the $C^{\wedge}C^*$ plane, resulting in little overlap between the transition orbital pairs and a smaller transition dipole moment for the mononuclear complex. Thus, the much enhanced k_r in the pyrazole-bridged dinuclear Pt^{II} complex is because of its open form molecular structure that can give rise to a ¹MLCT excited state having both high metal character (resulting in large SOC) and a large transition dipole moment.

OLEDs performance



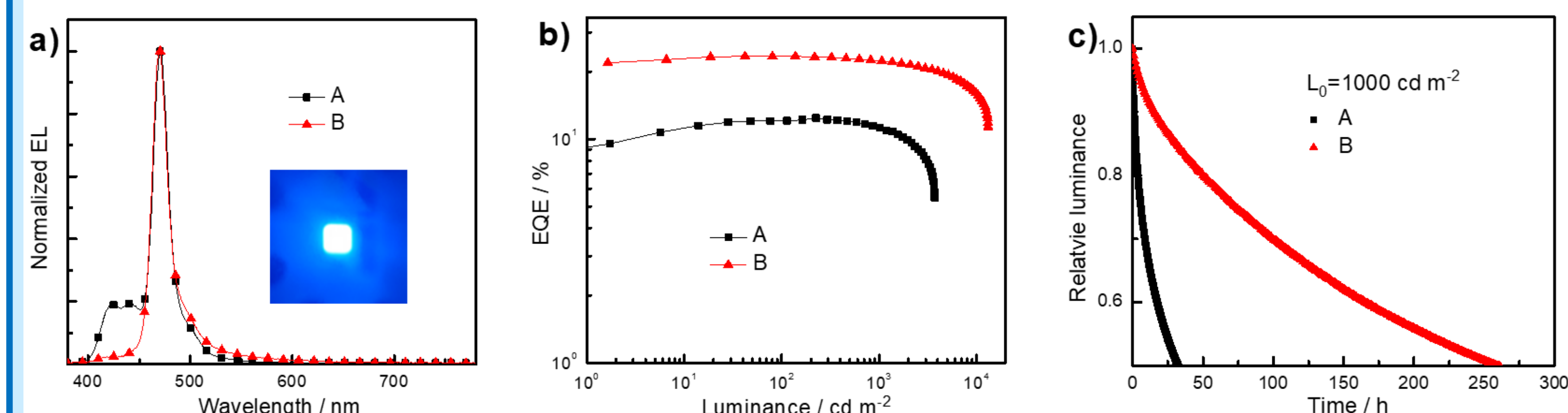
Normalized EL spectra of OLEDs with 1–5 at 4 wt% doping concentration and b) EQE-luminance characteristics of OLEDs with 1–5 at their optimized doping concentration

Hyper OLEDs performance

Table 2. Key performance parameters of devices A and B

Device	L ^[a] (cd m ⁻²)	CE ^[b] (cd A ⁻¹)	PE ^[c] (lm W ⁻¹)	EQE ^[d] (%)	EQE at 1000 cd m ⁻² (%)	CIE ^[e] (x, y)	λ_{max} ^[f] (nm)	FWHM ^[g] (nm)
A:v-DABNA wt%)	(1.0 3720	8.48	6.48	12.4	11.2	0.13, 0.09	470	18
B:5 (10 wt%):v- DABNA (1.0 wt%)	13200	23.0	21.1	23.4	22.4	0.13, 0.12	469	18

[a] Maximum luminance. [b] Maximum current efficiency. [c] Maximum power efficiency. [d] Maximum external quantum efficiency. [e] CIE coordinates at 1000 cd m⁻². [f] Maximum of EL spectrum at 1000 cd m⁻². [g] Full-width-at-half-maximum of EL spectrum at 1000 cd m⁻².



a) Normalized EL spectra, b) EQE-luminance characteristics and c) relative luminance-operational time of devices A and B. Inset of a): photograph of device B.

References:

- (1) K. W. Lo, G. S. M. Tong, G. Cheng, K. H. Low, C.-M. Che, *Angew. Chem. Int. Ed.* **2022**, *61*, e202115515

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