Electronic Supplementary Information (ESI)

Creation of Cationic Iridium(III) complexes with aggregation-induced phosphorescent emission (AIPE) property by increasing rotation groups on carbazole peripheries

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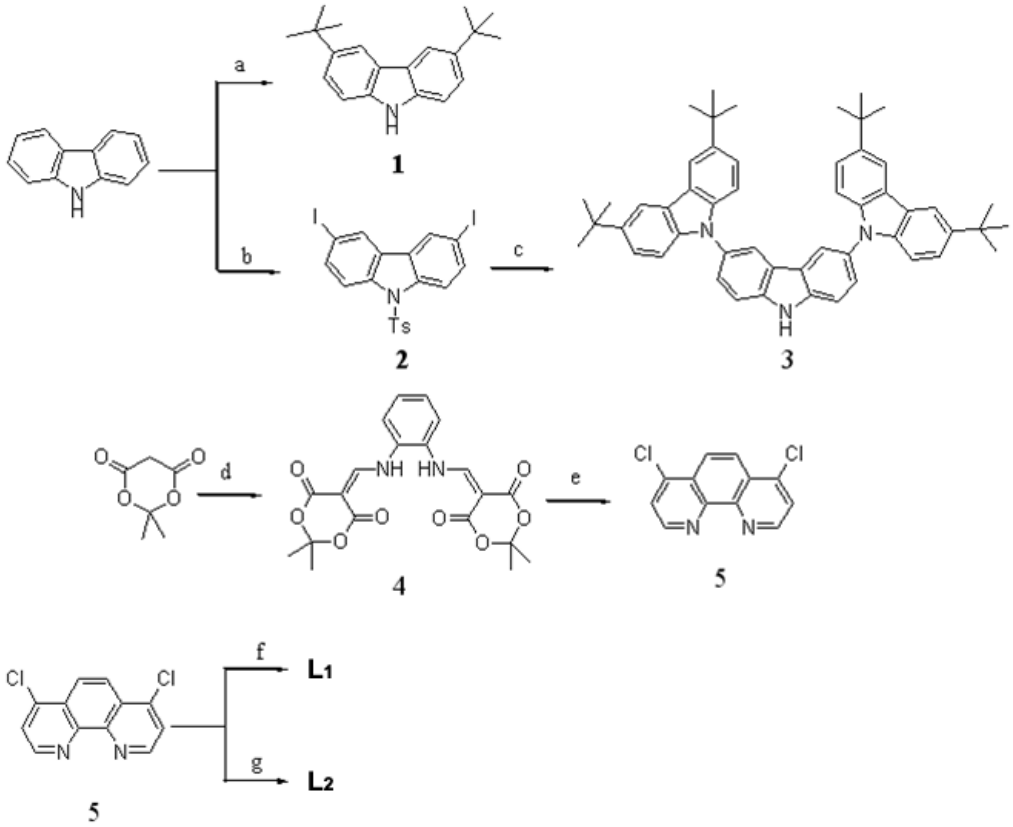
Experimental Section

Synthetic Procedures and Charaterization

The Scheme **S1** shows the general synthesis route of all intermediates (**1**–**5**), $\mathbf{L_1}$ and $\mathbf{L_2}$**.** 3,6-di-tert-butyl-carbazole (**1**), 3, 6, 3'', 6''-Tetrakis-tert-butyl-9H-[9, 3'; 6', 9''] tercarbazole (**3**) and 4, 7-dichloro-1, 10-phenanthroline (**5**) were prepared according to the literatures.[1] Then, the nucleophilic aromatic substitution reactions were used to synthesize the ligands $\mathbf{L_1}$ and $\mathbf{L_2}$[2]. The ^{1}H NMR spectra of them were recorded using a Bruker Avance 500 MHz spectrometer relative to tertramethylsilane as internal standard.



Scheme S1 Synthesis of $\mathbf{L_1}$ and $\mathbf{L_2}$**.** Reagents and conditions: a) 2-cholro-2-methylpropane, $AlCl_3$, DCM, 0^{o}C-RT; b) KI, KIO_3, CH_3COOH, 80 ^{o}C ,then NaH, Tosylchloride, RT; c) CuO_2, DAMC, 150 ^{o}C, then KOH, DMSO, reflux; d) o-phenylhenediamine, 100 ^{o}C; e) diphenyl ether, reflux; f) NaH, **1**, THF, reflux; g) NaH, **3**, THF, 50 ^{o}C.

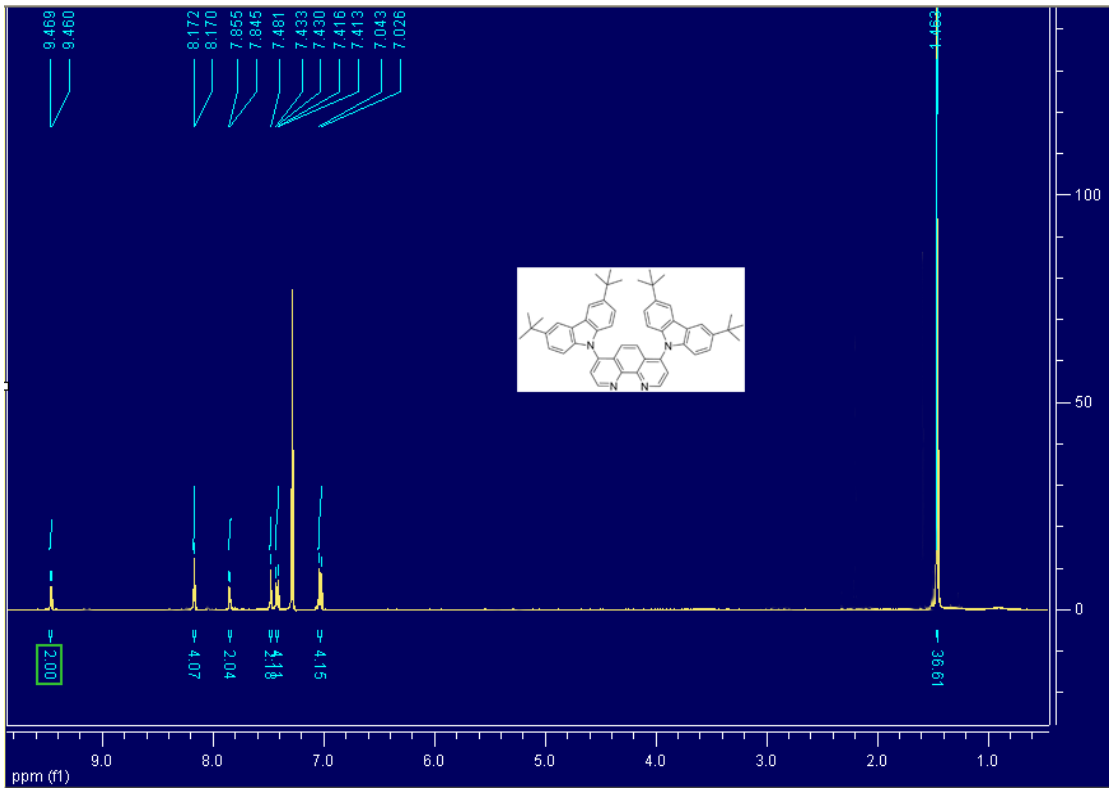


Fig. S1 ^{1}H NMR spectrum of $\mathbf{L_1}$ in $CDCl_3$.

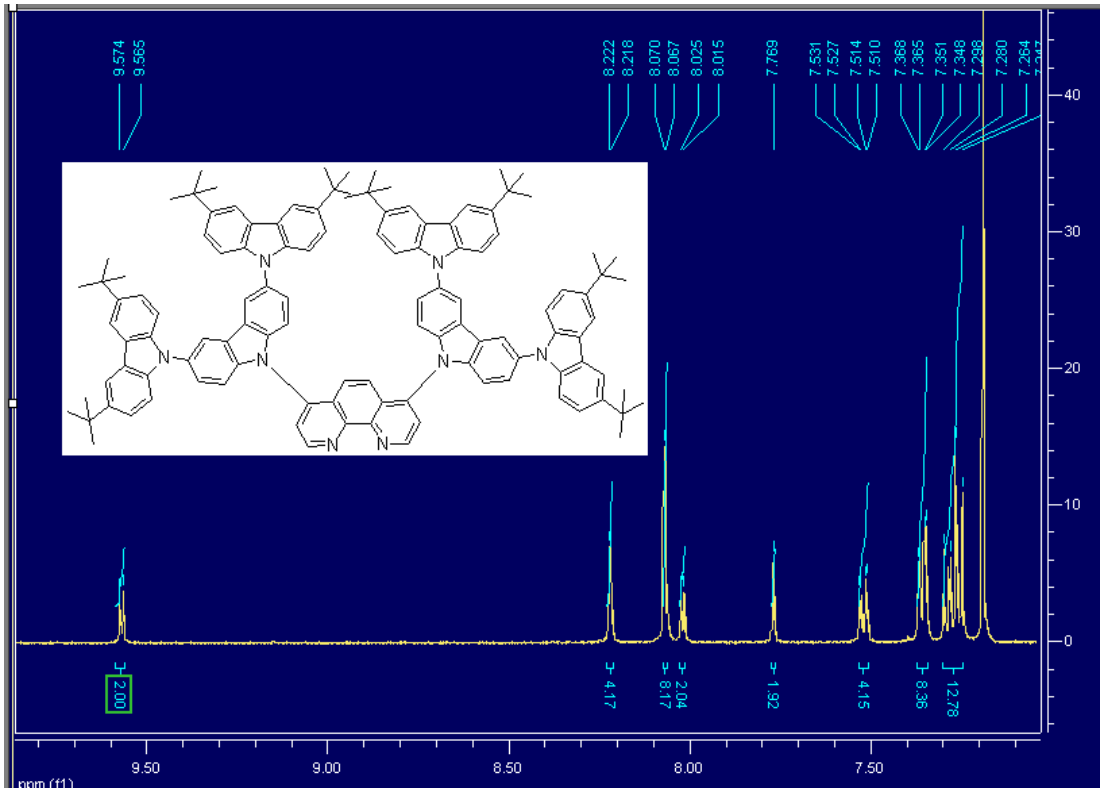


Fig. S2 ^{1}H NMR spectrum of $\mathbf{L_2}$ in $CDCl_3$.

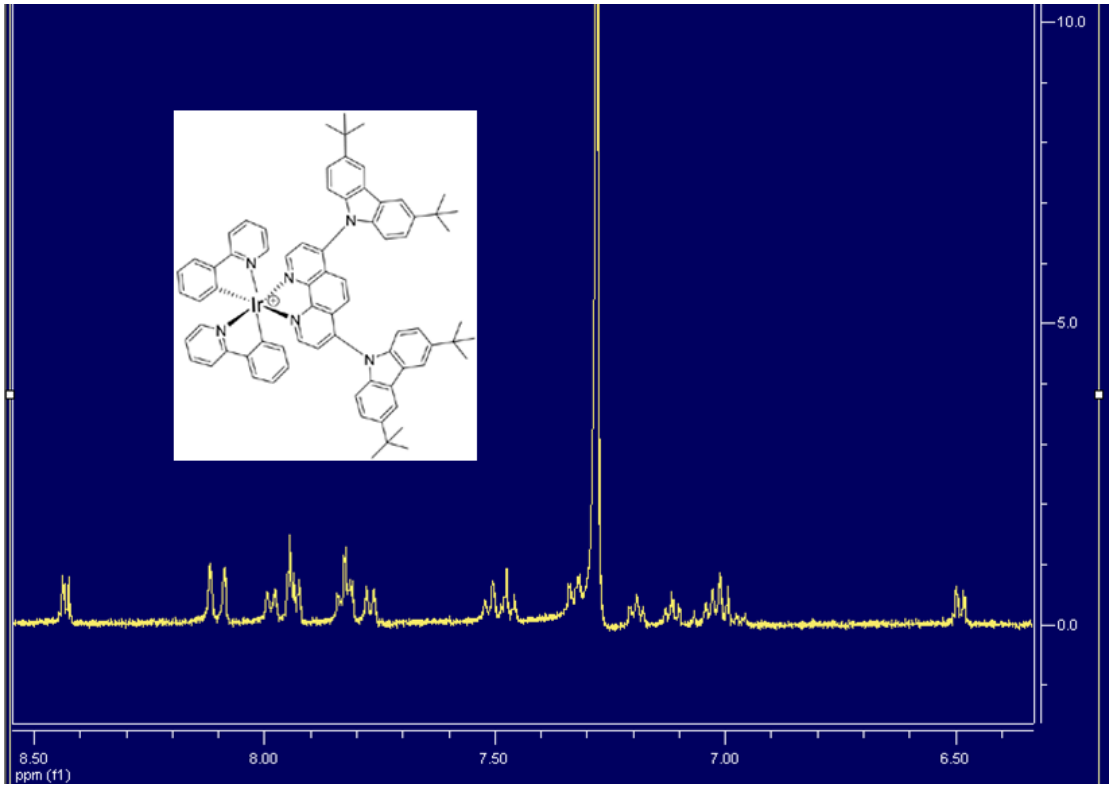


Fig. S3 ^{1}H NMR spectrum of complex **1** in $CDCl_3$.

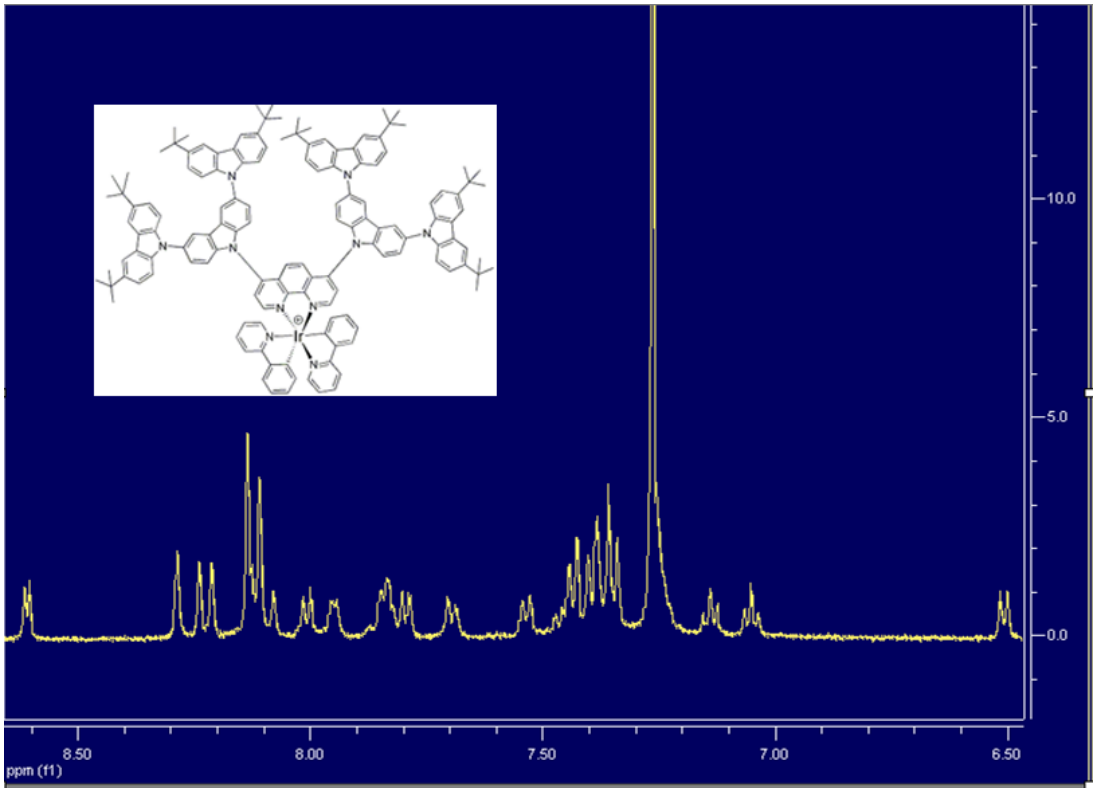


Fig. S4 ^{1}H NMR spectrum of complex **2** in $CDCl_3$.

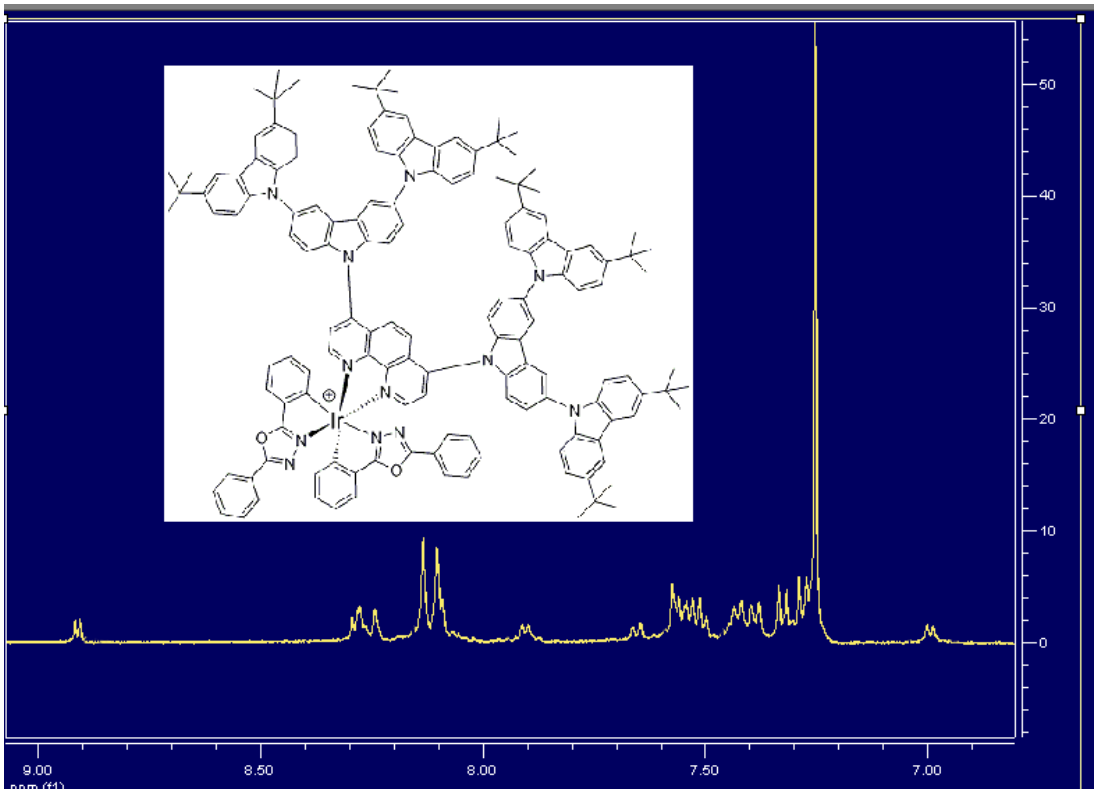


Fig. S5. ^{1}H NMR spectrum of complex **3** in $CDCl_3$.

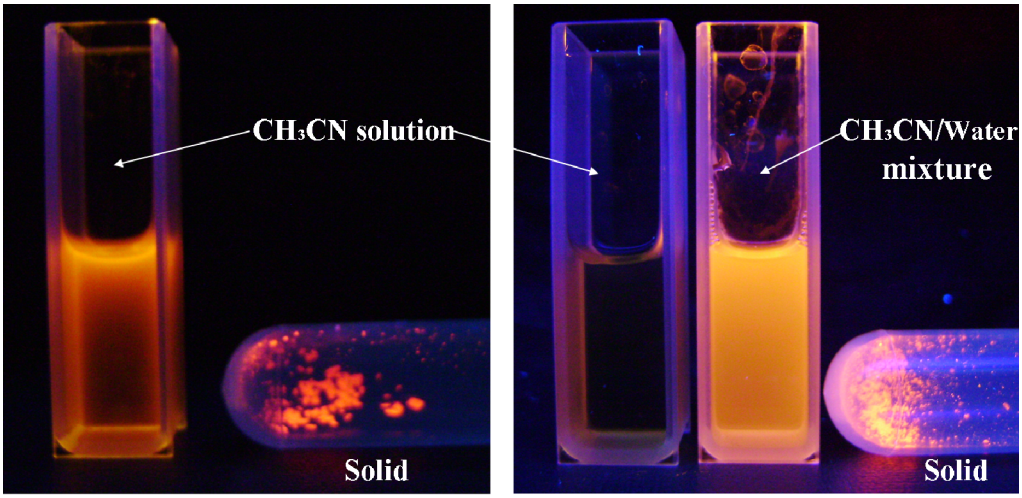


Fig. S6 The luminescent photographs of complexes **1** and **2** in different states.

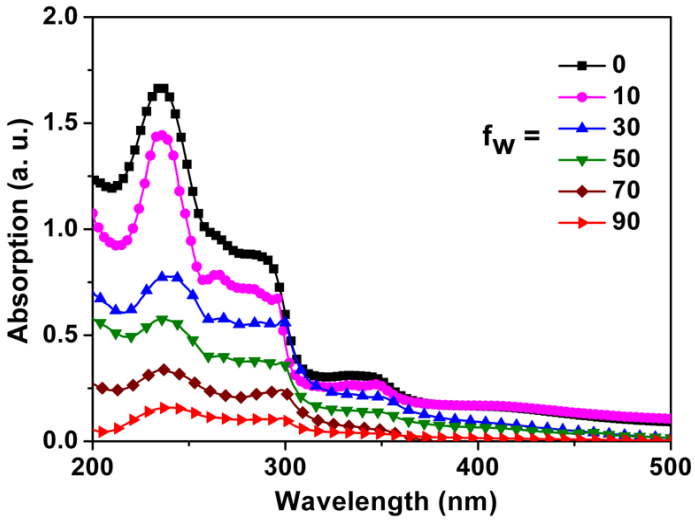


Fig. S7 Luminescent photographs of complex **2** in various solvents at a concentration of 1×10^{-5} M and powder under the 365 nm UV-light

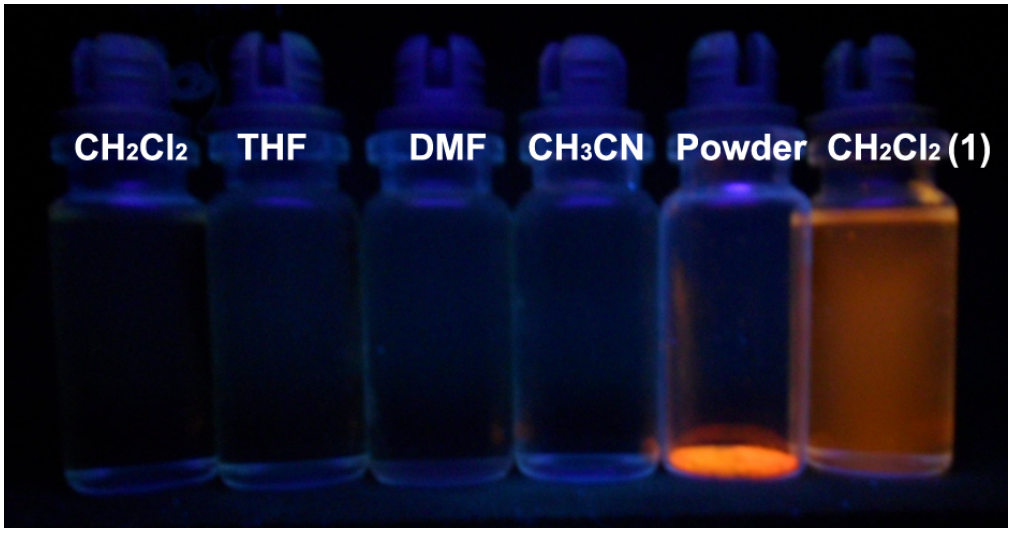


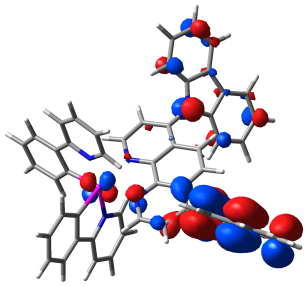
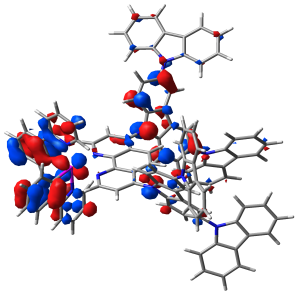
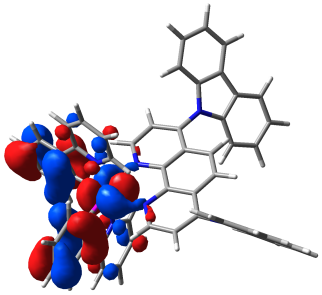
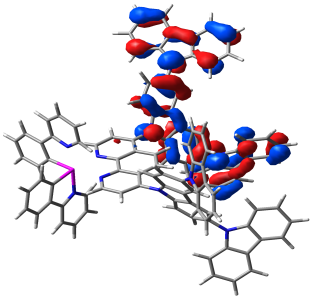
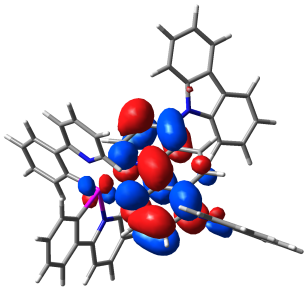
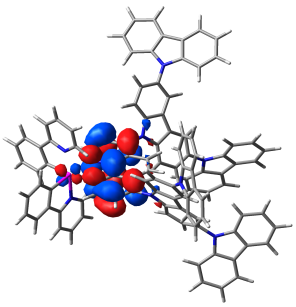
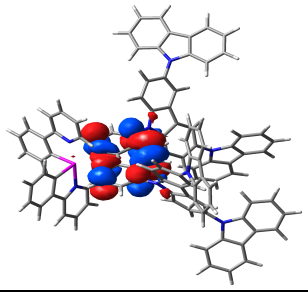
Fig. S8 Luminescent photographs of complex **2** in various solvents at a concentration of 1×10^{-5} M and powder under the 365 nm UV-light.

Table S1 The calculated energy levels of the lower-lying transitions of complexes **1** and **2**.

Complex	States	Assignment	λ (nm)	f	Nature
1	T1	H-1→L (10%) H→L (69%)	606	0	ILCT MLCT/LLCT

		H-9→L (17%)			MLCT/LLCT
2	T1	H→L (67%)	640	0	ILCT
		H→L+1 (10%)			ILCT

Fig. S9 Selected frontier orbitals of complexes **1** and **2**.

complex **1**	complex **2**
HOMO-1	HOMO-9
	
HOMO	HOMO
	
LUMO	LUMO
	
	LUMO+1
	

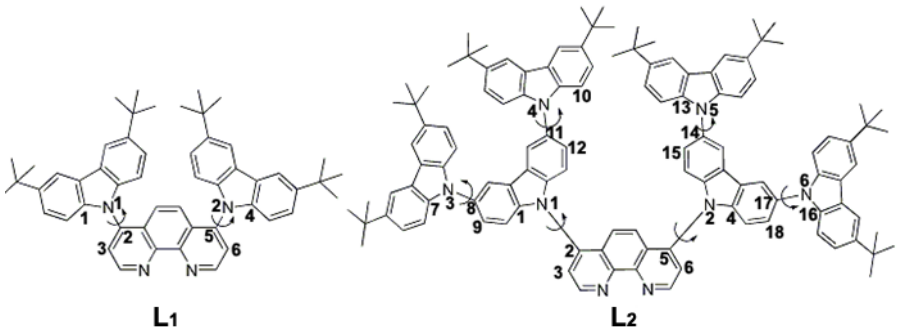


Table S2 Dihedral angle (deg) modifications from S_0 to T_1 as calculated by DFT approach for complexes **1** and **2**.

complex **1**			complex **2**		
Dihedral angles	S_0	T_1	Dihedral angles	S_0	T_1
C1–N1–C2–C3	47.7	53.7	C1–N1–C2–C3	47.4	62.7
C4–N2–C5–C6	48.2	57.2	C4–N2–C5–C6	48.4	63.1
			C7–N3–C8–C9	54.1	52.2
			C10–N4–C11–C12	54.2	52.2
			C13–N5–C14–C15	54.3	52.1
			C16–N6–C17–C18	53.7	51.8

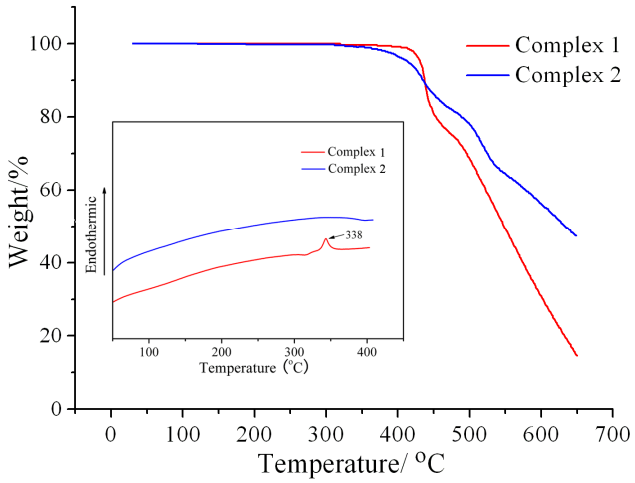


Fig. S10 The TGA and DTA curves of complexes **1** and **2**.

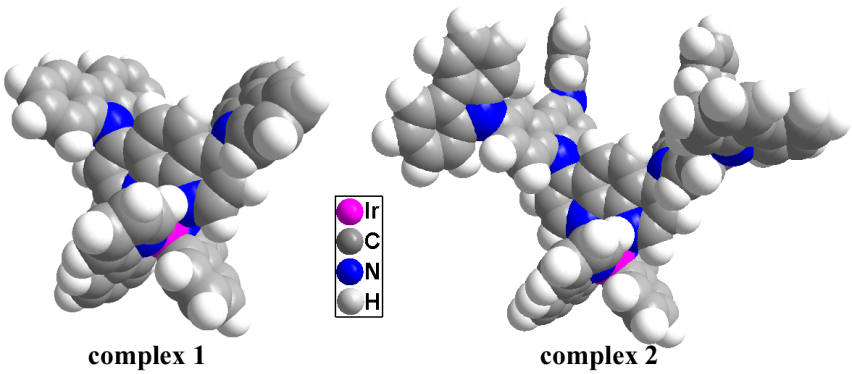


Fig. S11 The space-filling models of complexes **1** and **2**

References

1. (a) F. A. Neugebauer, and H. Fisher, *Chem. Ber*., **1972**, 105, 2686; (b) A. Kimoto, J. S. Cho, M. Higuchi, and K. Yamamoto, *Macromolecules.,* **2004**, 37, 5531.

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