Supporting information

Solid state phosphorescence enhancement of Pt^{II}-based emitters via combination of π-Hole(Isocyano Group)··· $d_{z^2}[Pt^{II}]$ and I···Cl Halogen-Bonding Interactions

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S1. X-ray diffraction studies

Table S1.1 Crystal data and structure refinement for **1**·½(1,4-DITFB) adduct.

Identification code	**1**·½(1,4-DITFB)
CCDC code	2290328
Empirical formula	$C_{29}H_{17}ClF_2IN_2Pt$
Formula weight	788.89
Temperature/K	100.02(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.9655(3)
b/Å	4.59870(10)
c/Å	34.1243(7)
α/°	90
β/°	91.549(2)
γ/°	90
Volume/Å^3	2504.51(9)
Z	4
ϱ_{calc}g/cm^3	2.092
μ/mm^{-1}	21.449
F(000)	1484.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.182 to 130
Index ranges	-17 ≤ h ≤ 18, -5 ≤ k ≤ 5, -37 ≤ l ≤ 40
Reflections collected	14691
Independent reflections	4281 [R_{int} = 0.0516, R_{sigma} = 0.0464]
Data/restraints/parameters	4281/0/319
Goodness-of-fit on F^2	1.221
Final R indexes [I>=2σ (I)]	R_1 = 0.0597, wR_2 = 0.1445
Final R indexes [all data]	R_1 = 0.0640, wR_2 = 0.1464
Largest diff. peak/hole / e Å^{-3}	2.31/-1.46

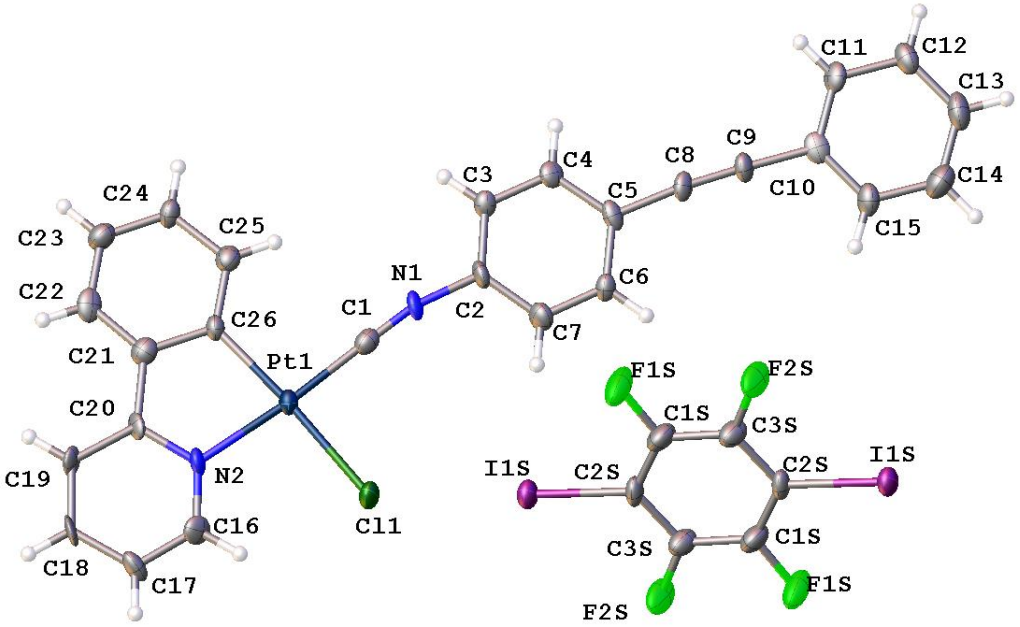


Figure S1.1. Molecular view of **1**·½(1,4-DITFB). Thermal ellipsoids for are drawn at the 50% probability level.

Table S1.2. Selected bond lengths (Å) and angles (°) for **1**·½(1,4-DITFB).

	Length, Å		Angle, °
Pt1–N2	2.077(3)	∠(C26–Pt1–N2)	81.2(5)
Pt1–C26	2.010(12)	∠(N2–Pt1–Cl1)	94.9(3)
Pt1-Cl1	2.396(3)	∠(C1–Pt1–C26)	94.2(5)
Pt1–C1	1.908(14)	∠(N1–C1–Pt1)	178.4(12)
N1–C1	1.147(17)	∠(C1–N1–C2)	168.4(13)
C8–C9	1.211(19)	∠(C5–C8–C9)	174.6(14)

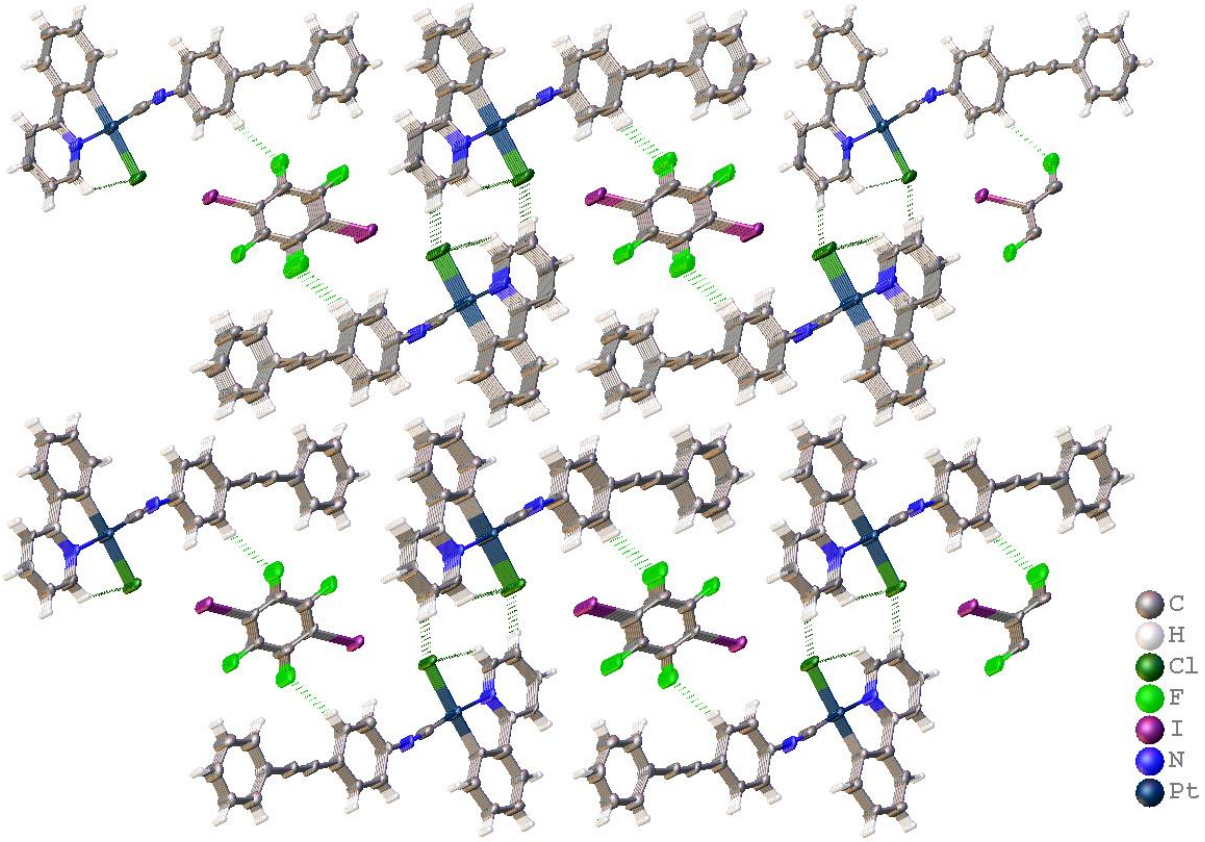


Figure S1.2. A fragment of the crystal packing of **1**·½(1,4-DITFB).

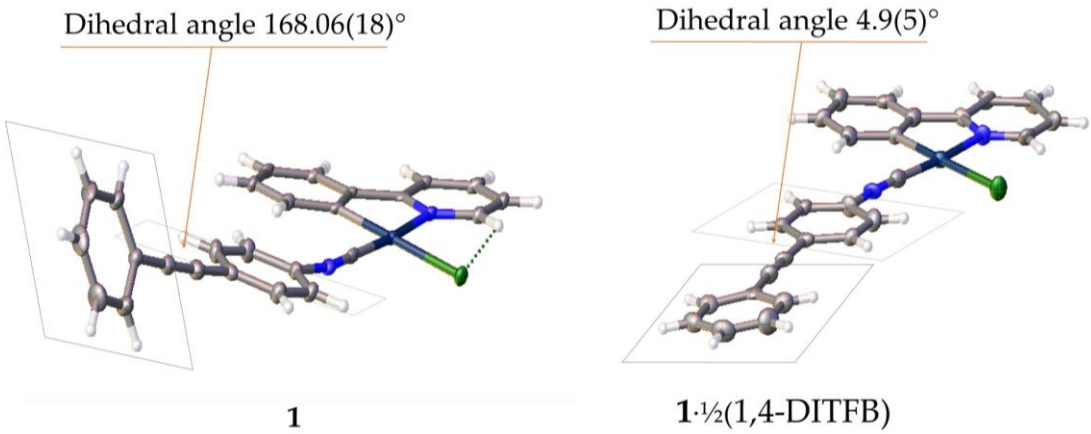


Figure S1.3. Molecule structures of complex **1** in the crystals of pure **1** [58] and adduct **1**·½(1,4-DITFB).

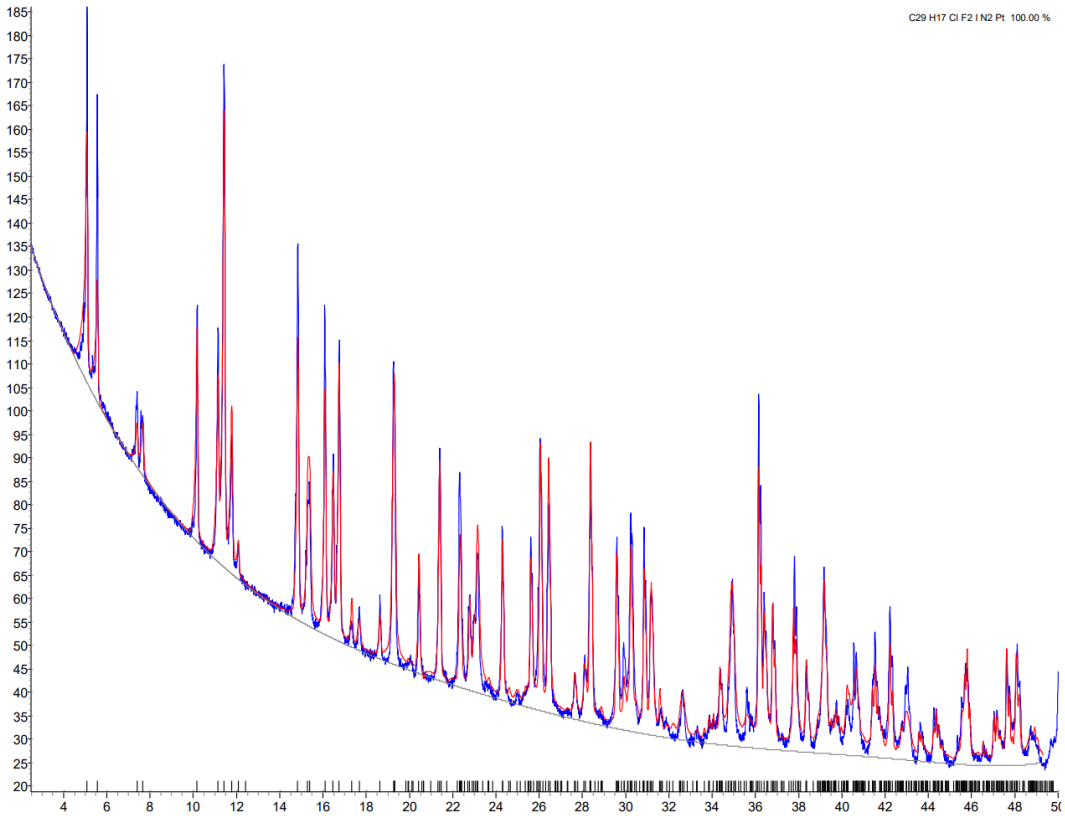
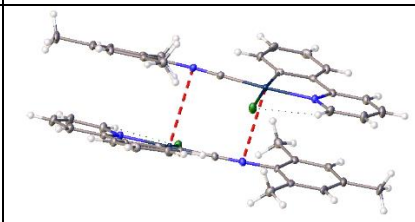
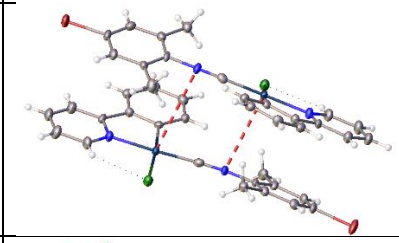
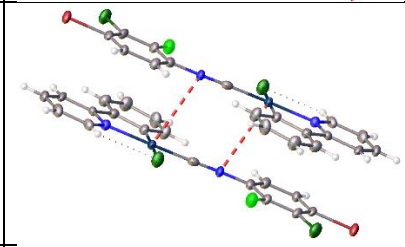
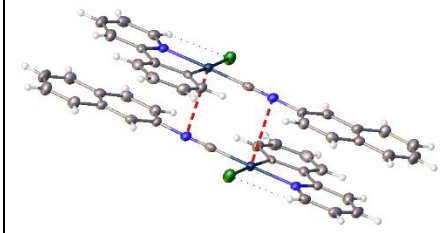
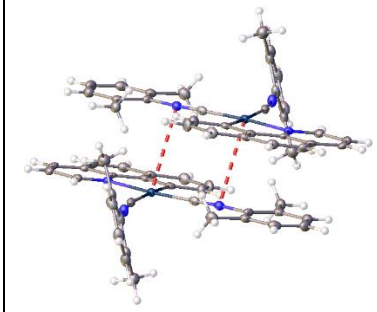
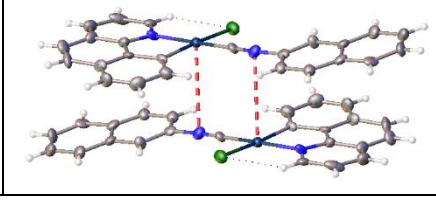
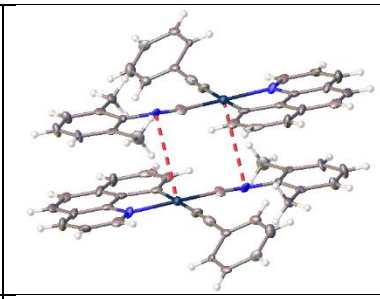
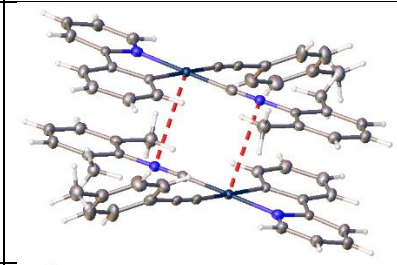
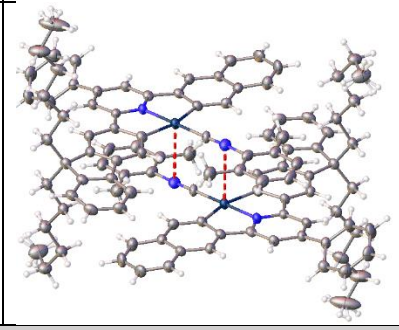


Figure S1.4. The measured powder X-ray diffraction patterns of crystalline **1**·½(1,4-DITFB).

Table S1.3 CSD data analysis.

CCDC code	**Structure**	**Pt•••N$_{iso}$, Å**	**∠(C≡N···Pt)**	Ref.
2044042		3.636(4), 3.832(4)	98.1(3), 93.4(3)	[1]
2075446		3.624(5), 3.938(6)	106.4(4), 95.1(5)	
2078554		3.475(4)	103.2(4)	
2042219		3.501(3)	86.1(3)	
732182		3.62536(5)	94.4034(14)	[2]
792590		3.654(12)	104.5(10)	[3]

893736		3.696(11)	86.0(9)	[4]
1987102		3.523(4)	86.3(3)	[5]
820799		3.62064(7)	82.2962(19)	[6]

Comparison, Å	
Bondi VdW radii	3.30
Batsanov VdW radii	3.65
Alvarez VdW radii	3.95

S2. Theoretical calculations

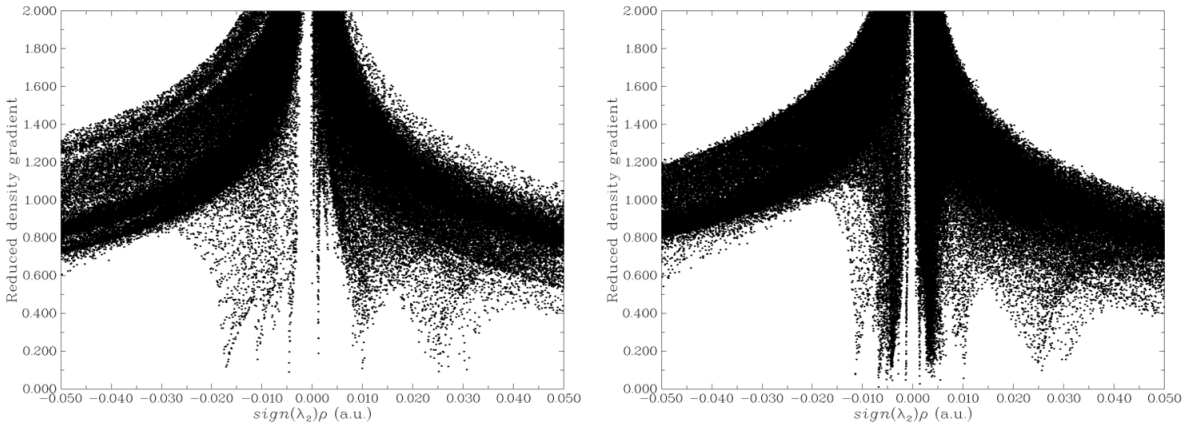


Figure 2.1. RDG(r) – sign[λ_2(**r**)]ρ(**r**) plot for the I···Cl HaB in (left) and N_{CN}···Pt contact (right) in the crystal structure of **1**·½(1,4-DITFB).

ELF and ED/ESP Minima Analysis

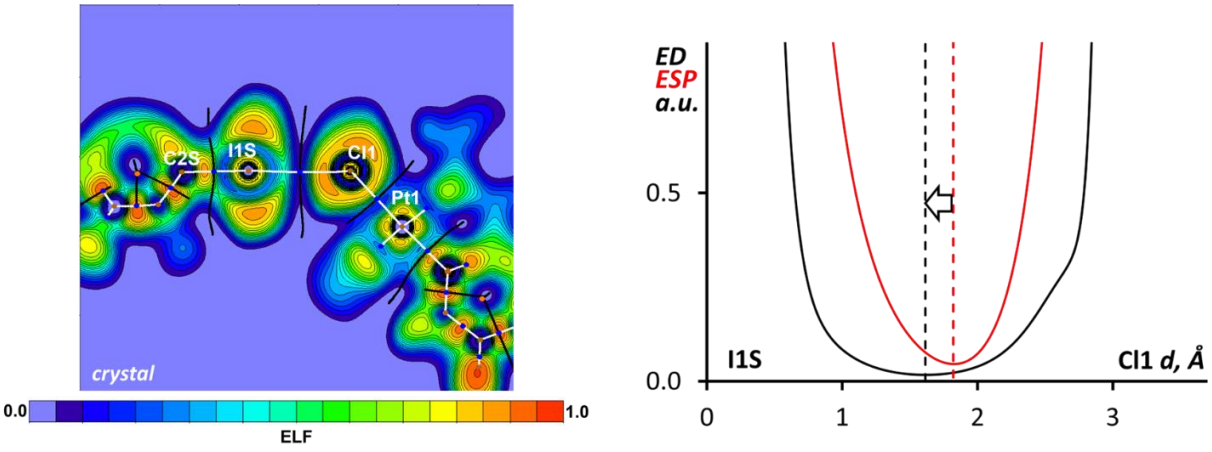


Figure 2.2. Left: ELF projections (contour lines with 0.05 step), bond paths (white lines), zero-flux surface projections (black lines), bond CPs (blue dots), nuclear CPs (brown dots), and ring CPs (orange dots). Right: The ED (black) vs. ESP (red) minima along the bond paths for the I···Cl HaB in the crystal structure of **1**·½(1,4-DITFB).

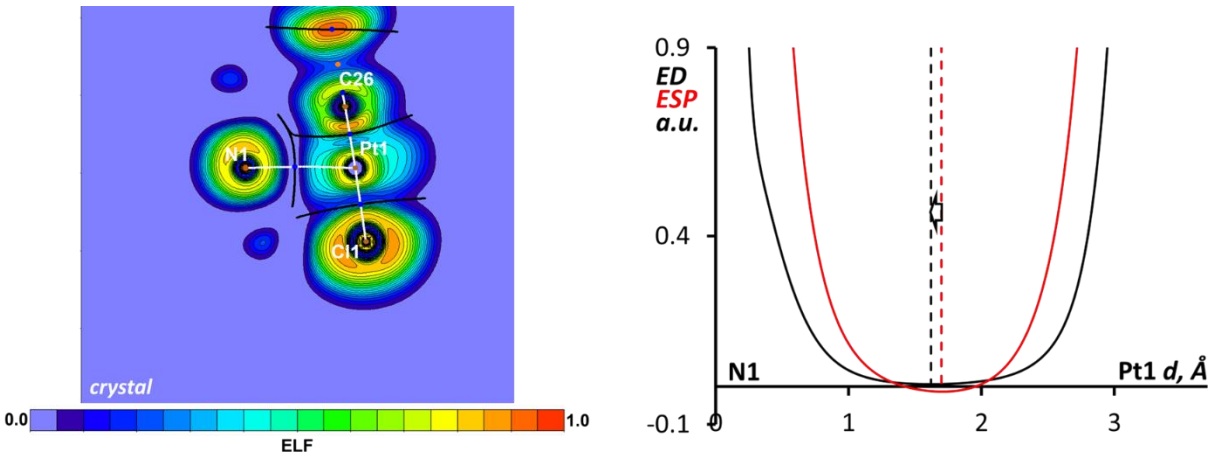


Figure 2.3. Left: ELF projections (contour lines with 0.05 step), bond paths (white lines), zero-flux surface projections (black lines), bond CPs (blue dots), nuclear CPs (brown dots), and ring CPs (orange dots). Right: The ED (black) vs. ESP (red) minima along the bond paths for the $N_{CN}\cdots$Pt contact in the crystal structure of **1**·½(1,4-DITFB).

Literature

1. Katkova, S.A., et al., *Intermolecular (Isocyano group)···PtII interactions involving coordinated isocyanides in cyclometalated PtII complexes.* J. Mol. Struct., 2022. **1253**: p. 132230.
2. Fornies, J., et al., *Luminescent benzoquinolate-isocyanide platinum(II) complexes: effect of PtPt and pipi interactions on their photophysical properties.* Chem Asian J, 2012. **7**(12): p. 2813-23.
3. Diez, A., et al., *Structural and luminescence studies on pi...pi and Pt...Pt interactions in mixed chloro-isocyanide cyclometalated platinum(II) complexes.* Inorg Chem, 2010. **49**(7): p. 3239-51.
4. Díez, Á., et al., *Synthesis and Luminescence of Cyclometalated Compounds with Nitrile and Isocyanide Ligands.* Organometallics, 2009. **28**(6): p. 1705-1718.
5. Martínez-Junquera, M., et al., *Isomerism, aggregation-induced emission and mechanochromism of isocyanide cycloplatinated(ii) complexes.* Journal of Materials Chemistry C, 2020. **8**(21): p. 7221-7233.
6. Kui, S.C., et al., *Luminescent organoplatinum(II) complexes with functionalized cyclometalated C^N^C ligands: structures, photophysical properties, and material applications.* Chemistry, 2012. **18**(1): p. 96-109.