Electronic Supplementary Information

Half-lantern cyclometalated Pt(II) and Pt(III) complexes with bridging heterocyclic thiolate ligands: Synthesis, structural characterization, electrochemical and photophysical properties

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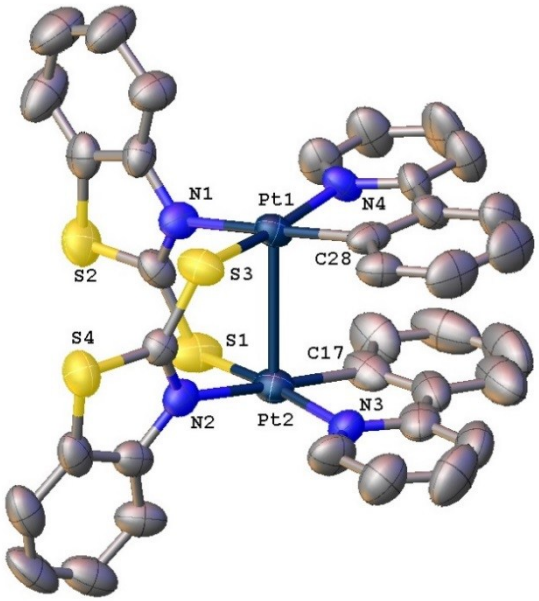
Table S1. Crystal data and structure refinements of complexes **1d** and **2c**·$CHCl_3$.

	1d	**2c**·$CHCl_3$
Formula	$C_{36}H_{24}N_4Pt_2S_4$	$C_{30}H_{22}Cl_2N_6Pt_2S_2$·$CHCl_3$
Formula weight	1030.80	1110.90
T, K	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	12.280(3)	10.492(2)
b (Å)	12.690(3)	24.782(5)
c (Å)	21.636(4)	13.530(3)
α (deg)	90	90
β (deg)	99.26(3)	99.24(3)
γ (deg)	90	90
Z	4	4
Density, Mg/m^3	2.058	2.125
Reflections collected	22128	10780
Independent reflections	5767 [R(int) = 0.1165]	4961 [R(int) = 0.1610]
Data / restraints / parameters	5767 / 0 / 416	4961 / 0 / 367
Goodness-of-fit on F^2	0.939	1.013
Final R indices [I>2sigma(I)]	R1 = 0.0278, wR2 = 0.0465	R1 = 0.0636, wR2 = 0.1529
R indices (all data)	R1 = 0.0676, wR2 = 0.0500	R1 = 0.0802, wR2 = 0.1588
CCDC No.	1820794	1820795

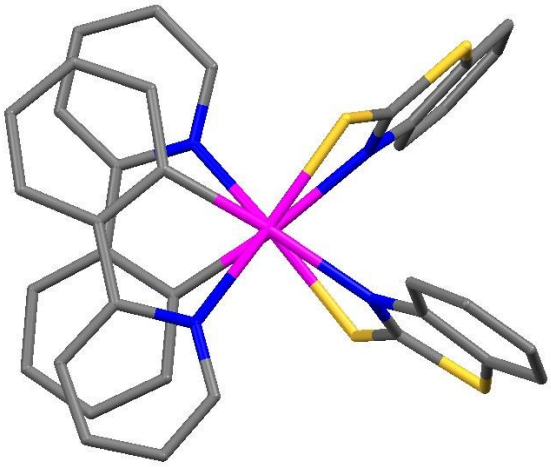
Crystal Structure of 1d

The ORTEP view of the molecular structure of **1d** is depicted in the Figure S1a and the crystal data and structural refinement parameters from the X-ray single-crystal analysis is summarized in the Table S1. As expected, complex **1d** contains two Pt(ppy) units doubly bridged by two 2-mercaptobenzothiozolate ligands arranging in head-to-tail manner, with short Pt···Pt distance of 2.9423(7) Å, slightly shorter than that found for **1d**·CH_2Cl_2 [2.9694(3) Å].[1] Each Pt(II) center is located in a slightly distorted planar environment, surrounded by two ppy chelating moieties, while two thiolate ligands link two Pt(II) centers as bridging groups producing structures with *anti*-configuration. However, the strong Pt–C bonds certainly influence their *trans* positions preferring the N-coordination to the S-coordination of the N^S ligands and Pt–N distances at the *trans* positions definitely lengthen as expected.[2, 3] Moreover, the crystal packing of complex **1d** displayed no π···π ppy intermolecular interactions.

Figure S1b exposes a top ORTEP view of **1d** structure along with the Pt···Pt axis, clearly illustrating an offset arrangement of the upper and lower ppy cyclometalating ligands. This configuration would has certainly effect on the torsion angels of bridging ligands toward the Pt···Pt axis.



(a)



(b)

Figure S1. (a) ORTEP plot of the structure of **1d** with the atom labeling scheme. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Pt1-Pt2 2.9423(7), Pt1-N4(ppy) 2.051(6), Pt1-S3 2.289(2), Pt1-N1(Spy) 2.141(6), Pt1-C28 1.983(8), N1(Spy)-Pt1-N4(ppy) 93.6(2), N1(Spy)-Pt1-S3 90.71(17), N4(ppy)-Pt1-C28 80.9(3), N1(Spy)-Pt1-Pt2-N2(Spy) 73.4(3), N4(ppy)-Pt1-Pt2-N3(ppy) 100.8(3). **(b)** Top ORTEP view of **1d** structure along with the Pt···Pt axis.

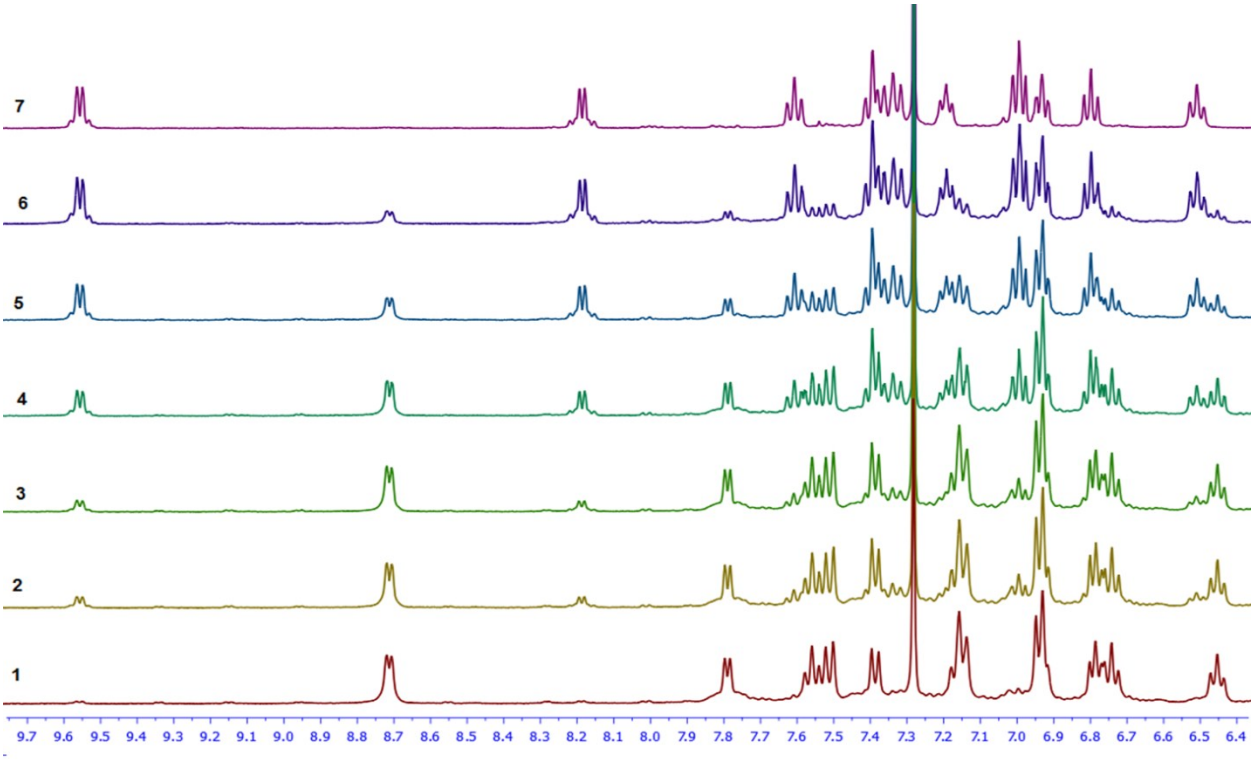


Figure S2. ^{1}H NMR following experiment for conversion of **1a** to **2a** in $CDCl_3$ at 298 K. 1) Complex **1a**, 2) 15 min, 3) 30 min, 4) 1 h, 5) 2 h, 6) 4 h and 7) 6 h after dissolving of **1a** in $CDCl_3$.

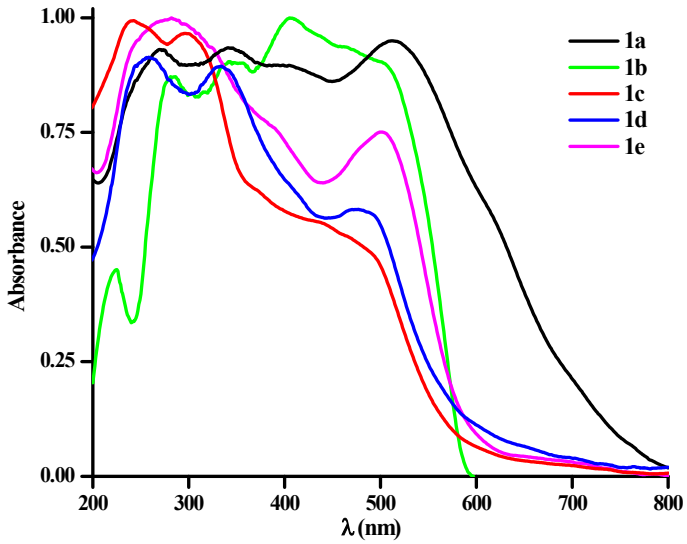


Figure S3. Normalized absorption spectra of **1a-e** in the solid state at 298 K.

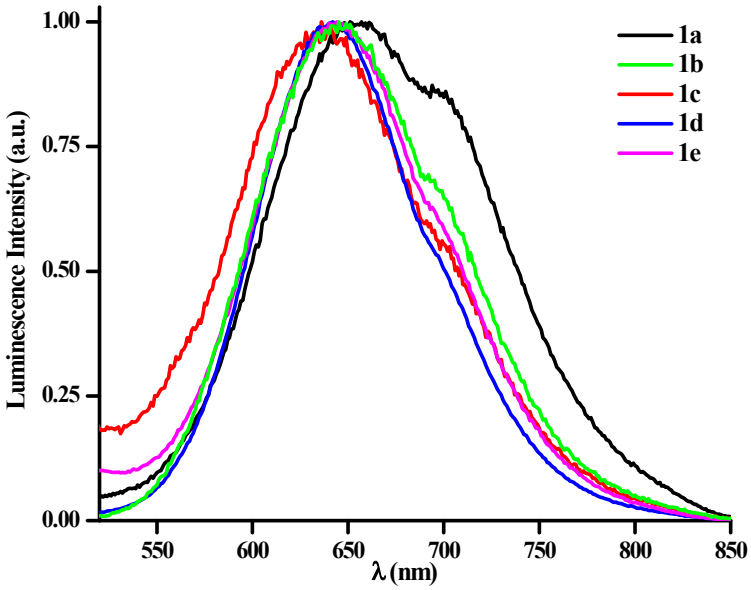


Figure S4. Normalized emission spectra of **1a-e** in CH_2Cl_2 (5×10^{-5} M) at 298 K (λ_{ex} 480 nm).

References:

1. Y. Zhu, K. Luo, L. Zhao, H. Ni and Q. Li, *Dyes Pigm.*, 2017, **145**, 144-151.
2. E. V. Puttock, M. T. Walden and J. A. G. Williams, *Coord. Chem. Rev.*, 2018, **367**, 127-162.
3. M. Yoshida and M. Kato, *Coord. Chem. Rev.*, 2018, **355**, 101-115.