Novel heterometallic platinum(II)-silver(I) alkynyl complex $[PtAg(dppm)_2(C{\equiv}CC_6H_4COOCH_3\text{-}4)_2Cl]$ with two crystal morphologies exhibiting morphology-dependent photoluminescence

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Additional IR Analysis

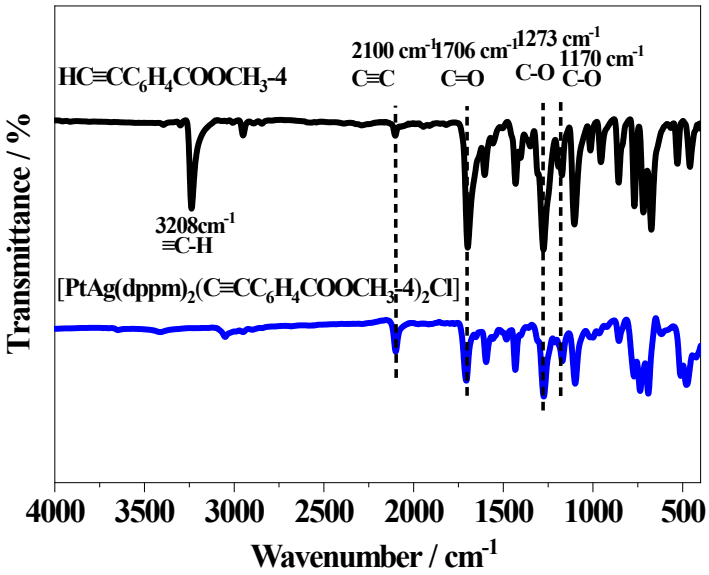

Fig. S1 FTIR spectra of complex **1**.

Characterizations

Additional ^{1}H and $^{31}P\{^{1}H\}$ NMR Analysis

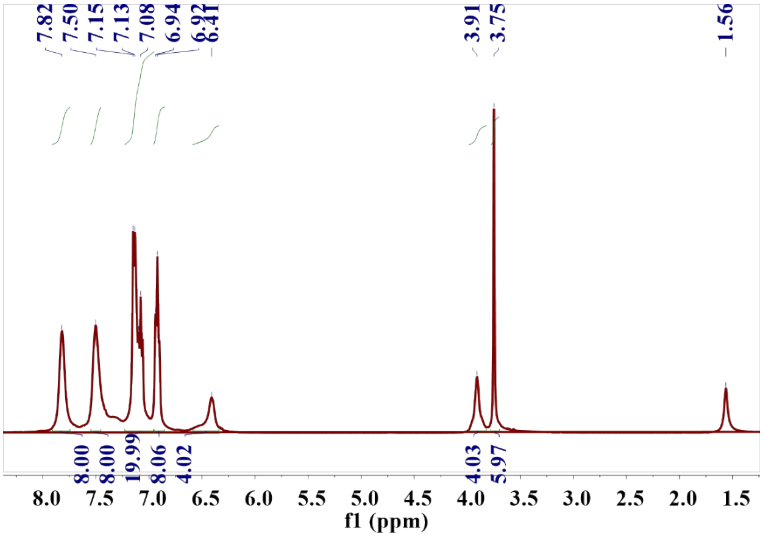

Fig. S2 ^{1}H NMR spectra of complex **1a**.

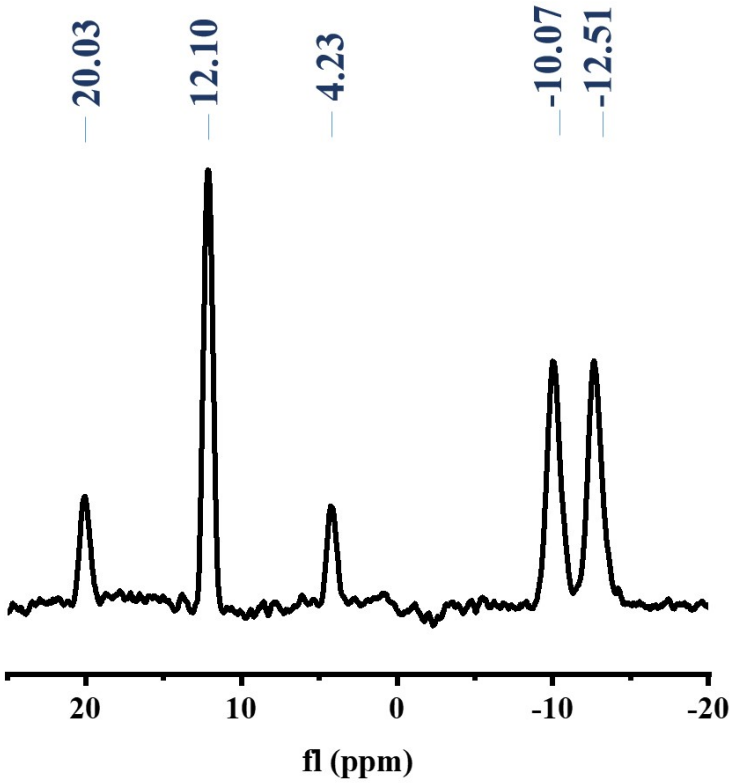

Fig. S3 $^{31}P\{^{1}H\}$ NMR spectra of complex **1**.

Characterizations

Additional ESI-MS Analysis

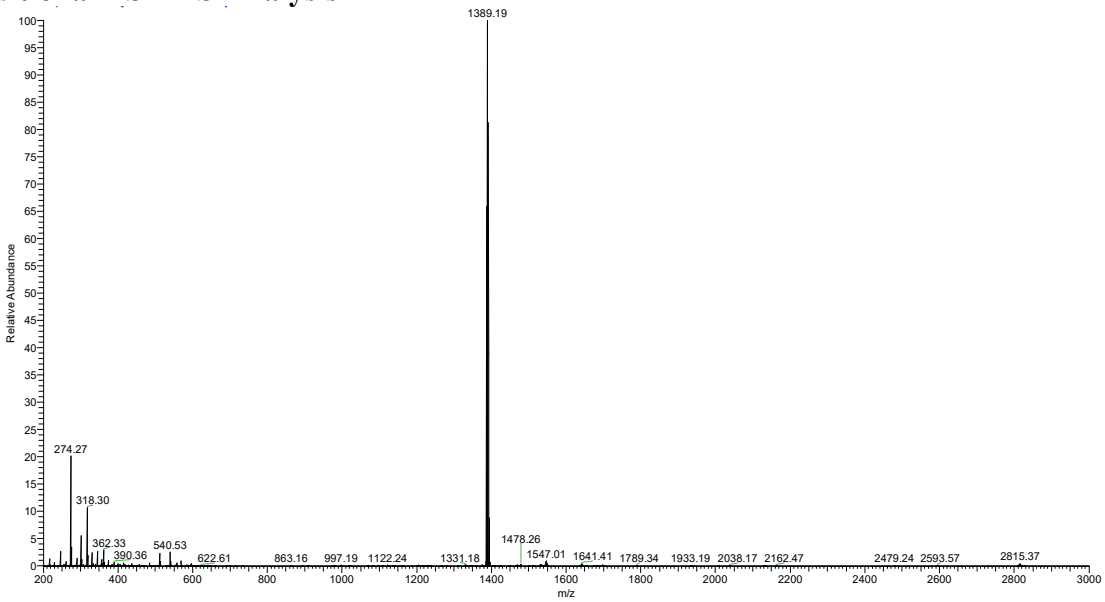

Fig. S4 ESI-MS spectra of complex **1**.

Crystal Structure

Table S1. Crystal data and structure refinement for **1**•CH_2Cl_2 (**1a**) and **1**•2CH_3OH **(1b)**.

Complex	**1**•CH_2Cl_2	**1•2**CH_3OH
Empirical formule	$C_{71}H_{60}AgCl_3O_4P_4Pt$	$C_{72}H_{66}AgClO_6P_4Pt$
Formula weight	1510.38	1489.53
Temperature (K)	99.97	100.02
radiation (λ, Å)	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic
Space group	*Pbca*	$P\bar{1}$
a (Å)	27.5216(5)	13.0729(11)
b (Å)	16.1867(2)	15.4714(13)
c (Å)	28.0818(5)	17.6099(14)
α (°)	90	101.452(3)
β (°)	90	91.844(3)
γ (°)	90	113.429(3)
V (Å^3)	12510.0(4)	3178.4(5)
Z	8	2
ρcalcd, g/cm^3	1.604	1.556
μ, mm^{-1}	2.828	2.702
R1 (F_o)	0.0214	0.0194
wR2(F_o^2)	0.0455	0.0431
GOF	1.053	1.054

Crystal Structure

Table S2. Bond lengths and bond angles for **1a** and **1b**.

	bond distance [Å]			
Crystal	**1a**		**1b**	
Pt-Ag	Pt(1)-Ag(2)	3.10066(19)	Pt(1)-Ag(2)	3.0418(3)
Pt-C	Pt(1)-C(1)	1.997(2)	Pt(1)-C(1)	1.998(3)
	Pt(1)-C(11)	2.010(2)	Pt(1)-C(11)	2.002(3)
Pt-P	Pt(1)-P(1)	2.2941(6)	Pt(1)-P(1)	2.3046(7)
	Pt(1)-P(4)	2.3080(6)	Pt(1)-P(4)	2.2960(7)
Ag-P	Ag(2)-P(2)	2.4599(6)	Ag(2)-P(3)	2.4676(7)
	Ag(2)-P(3)	2.4798(6)	Ag(2)-P(2)	2.4730(7)
Ag-Cl	Ag(2)-Cl(1)	2.5686(6)	Ag(2)-Cl(1)	2.5526(6)
C≡C	C(1)-C(2)	1.215(3)	C(1)-C(2)	1.213(4)
	C(11)-C(12)	1.209(3)	C(11)-C(12)	1.214(4)
	bond angle [º]			
C-Pt-C	C(1)-Pt(1)-C(11)	175.15(9)	C(1)-Pt(1)-C(11)	173.10(10)
C-Pt-P	C(1)-Pt(1)-P(1)	92.07(7)	C(1)-Pt(1)-P(1)	94.06(7)
	C(1)-Pt(1)-P(4)	92.00(7)	C(1)-Pt(1)-P(4)	90.98(7)
	C(11)-Pt(1)-P(1)	88.07(7)	C(11)-Pt(1)-P(1)	85.47(7)
	C(11)-Pt(1)-P(4)	87.83(7)	C(11)-Pt(1)-P(4)	89.89(7)
P-Pt-P	P(1)-Pt(1)-P(4)	175.90(2)	P(1)-Pt(1)-P(4)	174.16(2)
C-Pt-Ag	C(1)-Pt(1)-Ag(2)	109.43(7)	C(1)-Pt(1)-Ag(2)	104.16(7)
	C(11)-Pt(1)-Ag(2)	75.42(7)	C(11)-Pt(1)-Ag(2)	82.71(7)
P-Pt-Ag	P(1)-Pt(1)-Ag(2)	89.911(15)	P(1)-Pt(1)-Ag(2)	88.025(16)
	P(4)-Pt(1)-Ag(2)	89.186(15)	P(4)-Pt(1)-Ag(2)	87.872(16)
P-Ag-P	P(2)-Ag(2)-P(3)	145.14(2)	P(2)-Ag(2)-P(3)	133.78(2)
P-Ag-Cl	P(2)-Ag(2)-Cl(1)	104.50(2)	P(2)-Ag(2)-Cl(1)	107.97(2)
	P(3)-Ag(2)-Cl(1)	98.04(2)	P(3)-Ag(2)-Cl(1)	115.72(2)
P-Ag-Pt	P(2)-Ag(2)-Pt(1)	86.954(15)	P(2)-Ag(2)-Pt(1)	91.321(16)
	P(3)-Ag(2)-Pt(1)	85.921(15)	P(3)-Ag(2)-Pt(1)	87.814(16)
Cl-Ag-Pt	Cl(1)-Ag(2)-Pt(1)	150.996(16)	Cl(1)-Ag(2)-Pt(1)	109.726(19)

Photophysical Properties

Table S3 Photophysical data for **a powder sample of complex 1**, **1a**, and **1b**.

Complex	medium	λ_{abs} / nm ($\varepsilon \times 10^4$ /dm^3 mol^{-1} cm^{-1})	λ_{ex} / nm	λ_{em} / nm (τ_{em} / μs)
1a	crystal		398	476 (10.8)
1b	crystal		394	491 (3.3)
1	powder sample		396	490
	CH_2Cl_2	302 (0.38), 370 (0.26)	345	484 (2.0)
	CH_3CN	223 (0.90), 302 (0.40), 370 (0.31)	380	480 (2.0)
	EAC	305 (0.46), 368 (0.32)	360	481 (1.6)
	CH_3OH	302 (0.63), 370 (0.54)		

Photophysical Properties

Electronic absorption spectra

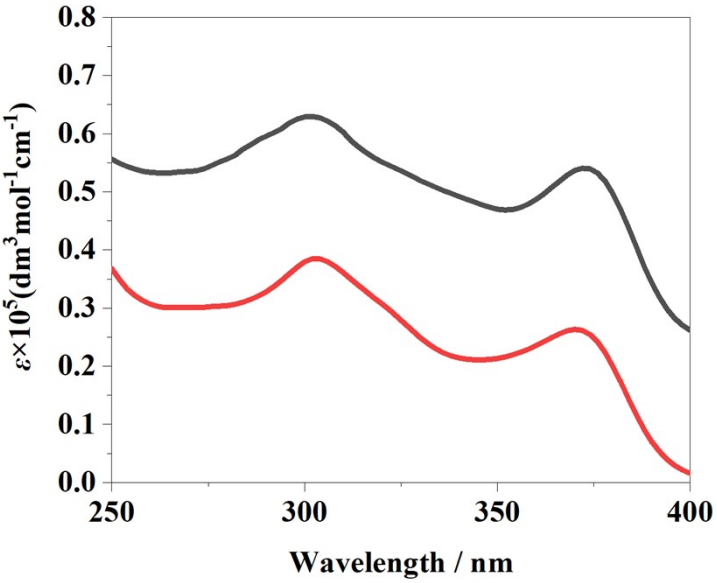

Fig. S5 The electronic absorption spectra of **1** in CH_3OH (black) and CH_2Cl_2 (red) solution.

Photophysical Properties

Calculation detail

All the calculations were performed at the PBE1PBE level[1] using the Gaussian 09 software package[2]. To analyze the emission properties of complex **1**, triplet excited states were calculated by the time-dependent DFT (TD-DFT) method at the gradient corrected correlation functional PBE1PBE level on the basis of the ground state geometry structure.The 6-31G(d) basis set[3] was used for the non-metal elements and the LanL2DZ basis set[4] for the metal. The initial structure of $[PtAg(dppm)_2(C{\equiv}CC_6H_4COOCH_3\text{-}4)_2Cl]$ was extracted from the crystallographically determined geometry. This initial structure was first optimized in the gas phase, and then calculated its electronic structures in the methanol and dichloromethane solvent environments using the widely-used Polarizable Continuum Model (PCM)[5]. The orbital compositions were analyzed with the Ros-Schuit method (SCPA) using the Multiwfn program[6].

Table S4. Partial molecular orbital compositions (%) in the triplet excited state for the simplified model of **1** in solid state by TD-DFT method at the PBE1PBE level.

complex	orbital	MO contribution (%)	
		PtAg	$C{\equiv}CC_6H_4COOCH_3$-4
1 without solvent	LUMO	6.713	87.337
	HOMO	13.488	83.881
1 with CH_2Cl_2	LUMO	6.768	88.150
	HOMO	15.683	81.689
1 with MeOH	LUMO	6.825	88.106
	HOMO	17.378	79.971

Photophysical Properties

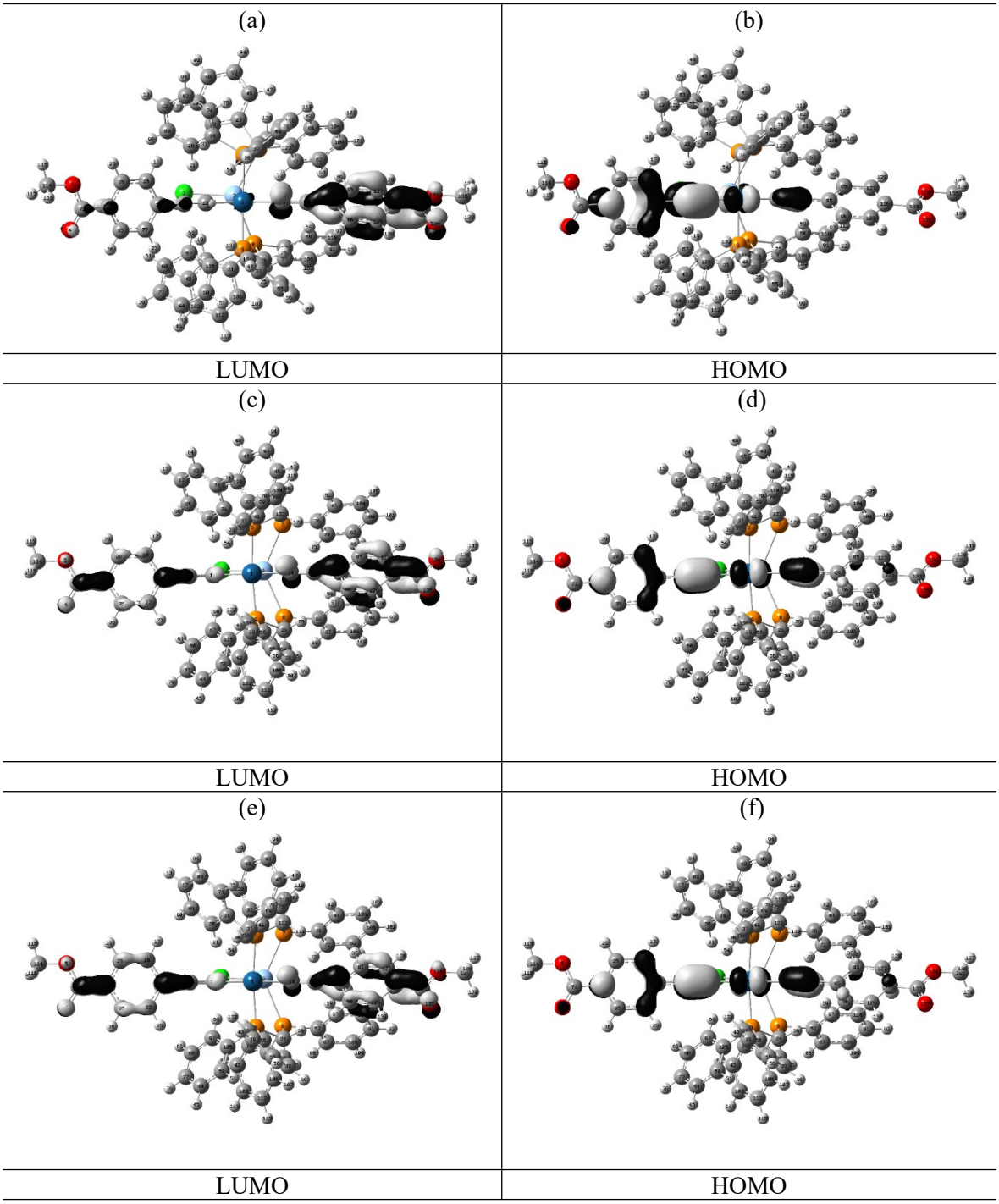

Fig. S6. Plots of the frontier molecular orbitals involved in the excitation transitions of the simplified model of **1** in the gas phase (a, b) in dichloromethane (c, d), and the methanol (e, f) solvent environments at the PBE1PBE level. The cyan, royalblue, green, orange, red, gray, and white spheres represent the silver, platinum, chlorine, phosphorus, oxygen, carbon, and hydrogen atoms, respectively.

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