Supporting Information

Solvent-induced lone pair activity tuning and vapoluminescence in a Pt_2Pb cluster

Jesús R. Berenguer,[a] Elena Lalinde,*[a] Antonio Martín,[b] M. Teresa Moreno,*[a] Santiago Ruiz,[a] Sergio Sánchez [a] and Hamid R. Shahsavari [a]

Experimental Section

Materials and Methods. All reactions were carried out under an argon atmosphere using standard Schlenk techniques and solvents from a solvent purification system (MBRAUN MB SPS-800). Elemental analyses were carried out with a Carlo Erba EA1110 CHNS/O microanalyzer. Mass spectra were recorded on a Microflex MALDI-TOF Bruker (MALDI) spectrometer operating in the linear and reflector modes using dithranol as the matrix. IR spectra were recorded on a Nicolet Nexus FT-IR spectrometer from Nujol mulls between polyethylene sheets. NMR spectra were recorded on Bruker ARX 300 or ARX 400 spectrometers at 298 K. Chemical shifts are reported in parts per million (ppm) relative to external standards ($SiMe_4$, $CFCl_3$, or Na_2PtCl_6 in D_2O for ^{195}Pt), and all coupling constants are given in hertz (Hz). The UV-vis absorption spectra were carried out in a Hewlett-Packard 8453 spectrophotometer. Diffuse reflectance UV-vis (DRUV) data of pressed powder were recorded on a Shimadzu (UV-3600 spectrophotometer with a Harrick Praying Mantis accessory) and recalculated following the Kubelka-Munk function. Excitation and emission spectra were obtained in a Jobin-Yvon Horiba Fluorolog 3-11 Tau-3 spectrofluorimeter. The lifetime measurements were performed in a Jobin Yvon Horiba Fluorolog operating in the phosphorimeter mode (with an F1-1029 lifetime emission PMT assembly, using a 450WXe lamp) or with a Datastation HUB-B with a nanoLED controller and software DAS6. The nanoLEDs employed for lifetime measurements were of 450 nm with pulse lengths of 0.8–1.4 ns. The lifetime data were fitted using the Jobin-Yvon software package. Thermogravimetric analyses (TGA) were recorded on a TA Instrument SDT

2960 using 2-10 mg samples at a 10 °C/min rate in 30-600°C range under nitrogen, and in the 600-750°C range in air. X-ray powder diffraction patterns were obtained at room temperature using a Rigaku D/max 2500 rotating anode generator by using graphite-monochromated CuK operating at 40 kV and 80 mA. Powder diffraction patterns were collected between 2θ of 3° and 50° with a 2θ stepping angle of 0.03° and an angle dwell of 1 s. Complexes [Pt(C_6F_5)(bzq)(acetone)][1] and [Pb(Spy)$_2$][2] were prepared as reported in the literature.

Preparation of [{Pt(C_6F_5)(bzq)}$_2$Pb(Spy)$_2$] (**1**). To a suspension of [Pb(Spy)$_2$] (0.0536 g, 0.125 mmol) in CH_2Cl_2 (15 ml) was added 2 equiv of [Pt(C_6F_5)(bzq)(acetone)] (0.150 g, 0.250 mmol), and the initial yellow suspension was partially dissolved, giving rise a red solution. The mixture was stirred for 1 hour and filtered through Celite. The red solution was evaporated to small volume (2 ml) and n-hexane was added (5 ml) to give an orange solid identified as **1** (0.157 g, 83% yield). Anal. Calcd for $C_{48}H_{24}F_{10}N_4PbPt_2S_2$: C, 38.23; H, 1.60; N, 3.71; S, 4.25. Found: C, 38.27; H, 1.57; N, 3.64; S, 4.11%. MALDI-TOF (+): *m/z* (%) 650 [Pt(bzq)(C_6F_5)(Spy)]$^+$ (22), 857 [Pt(bzq)(C_6F_5)Pb(Spy)]$^+$ (92), 1398 [{Pt(bzq)(C_6F_5)}Pb(Spy)]$^+$ (36), 1508 [M]$^+$ (3). IR (cm^{-1}): ν(C_6F_5 $_{Xsens}$) 800. ^{1}H NMR (δ, 400.17 MHz, CD_2Cl_2): 9.01 (s br, 1H, H^2_{bzq}), 8.12 (s br, 1H, H^4_{bzq}), 7.80 (d, $J_{H\text{-}H}$ = 8.5, 1H, $H^{5/6}_{bzq}$), 7.66 (d, $J_{H\text{-}H}$ = 7.7, 2H, $H^{5/6}_{bzq}$, H^7_{bzq}), 7.51 (s br, 1H, H^6_{Spy}), 7.39 (t, $J_{H\text{-}H}$ = 7.3, 1H, H^8_{bzq}), 7.30 (s br, 1H, H^3_{bzq}) 7.11 (s, 1H, H^4_{Spy}), 7.00 (s, 1H, H^3_{Spy}), 6.94 (s, 1H, H^9_{bzq}), 6.38 (s br, 1H, H^5_{Spy}).^{1}H NMR (δ, 400.17 MHz, CD_3COCD_3): 8.95 (d, $J_{H\text{-}H}$ = 3.5, $^3J_{Pt\text{-}H}$ = 21.6, H^2_{bzq}), 8.42 (d, $J_{H\text{-}H}$ = 6.8, H^4_{bzq}), 7.88 (d, $J_{H\text{-}H}$ = 8.8, 1H, $H^{5/6}_{bzq}$), 7.70 (m, 2H, $H^{5/6}_{bzq,}$ H^7_{bzq}), 7.52 (m, 1H, H^6_{Spy}), 7.48 (m, 1H, H^3_{bzq}), 7.43 (t, $J_{H\text{-}H}$ = 7.6, H^8_{bzq}), 7.31 (t, 1H, $J_{H\text{-}H}$ = 7.2, H^4_{Spy}), 7.09 (m, 2H, H^3_{Spy}, H^9_{bzq}), 6.63 (t, $J_{H\text{-}H}$ = 5.3, 1H, H^5_{Spy}). ^{19}F NMR (δ, 282.4 MHz, CD_2Cl_2): -116.5 (m, 2 *o*-F), -162.0 (t, 1 *p*-F), -162.9 (m, 2 *m*-F). ^{19}F NMR (δ, 282.4 MHz, CD_3COCD_3): -118.8 (dm, $^3J_{Pt\text{-}o\text{-}F}$ = 282, 2 *o*-F), -165.5 (t, 1 *p*-F), -166.0 (m, 2 *m*-F). ^{13}C{^{1}H} NMR (δ, 100.6 MHz, CD_3COCD_3): 156.8 (s, C^{10}_{bzq}), 148.7 (s, C^2_{bzq}), 146.3 (s, C^6_{Spy}), 139.6 (s, C^4_{bzq}), 137.6 (s, C^4_{Spy}), 135.0 (s, C^{6a}_{bzq}), 134.3 (s, C^9_{bzq}), 132.2 (s, C^3_{Spy}), 130.6 (s, C^8_{bzq}), 130.2 (s, C^6_{bzq}), 128.0 (s, C^{4a}_{bzq}), 124.5 (s, C^5_{bzq}), 123.7 (s, C^7_{bzq}), 123.3 (s, C^3_{bzq}), 120.5 (s, C^5_{Spy}) (see Chart S1 for labels).

Data for **[{Pt(C_6F_5)(bzq)}$_2$Pb(Spy)$_2$(acetone)]** (**2**). IR (cm^{-1}): *ν*(CO, Me_2CO) 1696. Characterization in solution is coincident with that described for **1** in CD_3COCD_3.

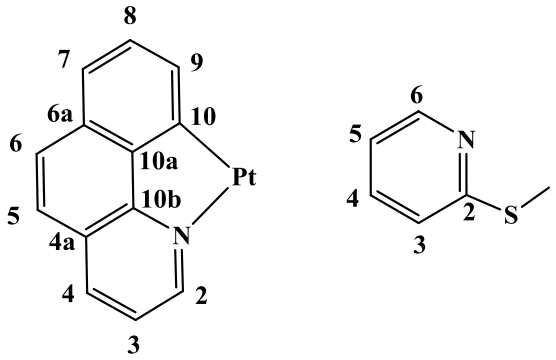


Chart S1. Numbering scheme for NMR spectra assignments

X-ray Crystallography. Details of the structural analyses for complex **1** and **2** are summarized in Table S1. Orange crystals were obtained by slow diffusion at -30ºC of *n*-hexane into solutions of the solid **1** in CH_2Cl_2 or acetone, respectively. In both cases, graphite-monochromatic Mo-K_α radiation was used, being the data collected with an Oxford Diffraction Xcalibur CCD diffractometer for **1** and with a NONIUS-*κ*CCD area-detector diffractometer for **2**. The diffraction frames were integrated and corrected for absorption using the Crysalis RED package[3] for **1** or the DENZO and SCALEPACK suite of programs[4] for **2**. The structures were solved by Direct and Patterson Methods using SHELXS-97,[5] and refined by full-matrix least squares on F^2 with SHELXL-97.[6] All non-hydrogen atoms were assigned anisotropic displacement parameters. All the hydrogen atoms were constrained to idealized geometries fixing isotropic displacement parameters 1.2 times the U_{iso} value of their attached carbon for the aromatic and methane carbons and 1.5 times for the methyl groups. Without taking into account the acetone molecule bonded to the lead atom in the structure of **2**, in both cases one molecule of crystallization solvent (CH_2Cl_2 or acetone) has been modelled. Nevertheless, examination with PLATON[7] showed the presence of one central void of 251 Å^3 (**1**) or 268 Å^3 (**2**) in the unit cell of each of the complexes. Inspection with SQUEEZE[8] revealed that these voids contain 49 e$^-$ (**1**) or 30 e$^-$ (**2**), which fits well with the presence of one extra molecule of CH_2Cl_2 or acetone. Therefore, we have included them in the empirical formula as crystallization solvent (**1**·1.5CH_2Cl_2, **2**·1.5acetone). Finally, both structures show some residual peaks greater than 1 eA^{-3} in the vicinity of the platinum atoms or the crystallization solvent, but with no chemical meaning.

Computational Details for Theoretical Calculations. DFT and TD-DFT calculations were performed on **1** and **2** using as starting point the X-ray geometries for the ground state optimization. The geometries of all stationary points were fully optimized, without symmetry constraints, employing the 1997 hybrid functional of Perdew, Burke and Ernzerhof[9] as implemented in the Gaussian09 program suite.[10] This functional uses 25% exchange and 75% correlation weighting and is denoted as PBE0. The basis set used for the metal centers (Pt and Pb) was the LanL2DZ effective core potential[11] and the 6-31+G(d,p) for the ligand atoms. No negative frequency was found in the vibrational frequency analysis. The calculated emission maxima were estimated from the differences between the ground state and triplet excited state energies at the optimized triplet state geometry.

(1) J. R. Berenguer, E. Lalinde, M. T. Moreno, S. Sánchez and J. Torroba, *Inorg. Chem.* 2012, **51**, 11665.

(2) N. Ghavale, S. Dey, A. Wadawale and V. K. Jain, *J. Organomet. Chem.*, 2011, **696,** 3491.

(3) *CrysAlis; RED. A program for Xcalibur CCD System X-Ray diffraction data reduction*; Oxford Diffraction Ltd.; Oxford, UK, 2005.

(4) Z. Otwinosky and W. Minor, *Methods Enzymol.*, 1997, **276**, 307.

(5) G. M. Sheldrick, SHELX-97, a program for Crystal Structure Determination; University of Göttingen: Göttingen, Germany, 1997.

(6) G. M. Sheldrick, SHELX-97, a program for the refinement of crystal structures; University of Göttingen: Göttingen, Germany, 1997.

(7) (a) A. L. Speck, *Acta Crystallogr., Sect. A.* 1990, **46,** c34. (b) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, Spek, A. L. 1998.

(8) A. L. Spek, *SQUEEZE, incorporated into PLATON: A Multipurpose Crystallographic Tool ed.*, Utrecht, University of Utrecht, The Netherlands 2005.

(9) J. P. Perdew, K. Burke and M. Ernzehof, *Phys. Rev. Lett.*, 1996, **77**, 3865

(10) Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa,

M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

(11) W. R Wadt and P. J. Hay, *J. Chem. Phys*. 1985, **82,** 284.

Table S1. Crystallographic data for **1**·1.5CH_2Cl_2 and **2**·1.5acetone

	1·1.5CH_2Cl_2	**2**·1.5acetone
empirical formula	$C_{49.5}Cl_3H_{27}F_{10}N_4PbPt_2S_2$	$C_{55.50}H_{39}F_{10}N_4O_{2.50}PbPt_2S_2$
F_w	1635.59	1653.40
T (K)	100(1)	193(1)
crystal system; space group	triclinic; *P*-1	triclinic; *P*-1
a(Å); α(deg)	12.3991(3); 100.356(3)	10.7618(3); 106.702(1)
b(Å); β(deg)	13.1073(4); 101.793(3)	13.8101(5); 95.471(2)
c(Å); γ(deg)	17.2525(6); 111.777(3)	19.2886(7); 98.767(2)
V (Å^3); Z	2445.98(13); 2	2684.20(16); 2
D_{calcd} (Mg/m^3)	2.221	2.046
absorption coefficient (mm^{-1})	9.467	8.487
F(000)	1526	1560
crystal size (mm)	0.38 x 0.23 x 0.12	0.30 x 0.15 x 0.15
θ range for data collection (deg)	4.19 to 25.68	1.62 to 26.37
index ranges	-15<=h<=14	-13<=h<=13
	-15<=k<=15	-17<=k<=16
	0<=l<=21	0<=l<=24
No of data/restraints/params	9235/0/620	10937/0/665
goodness of fit on F^2 [a]	1.026	1.033
final R indexes [$I > 2\sigma(I)$] [a]	R1 = 0.0258, wR2 = 0.0642	R1 = 0.0293, wR2 = 0.0735
R indices (all data) [a]	R1 = 0.0297, wR2 = 0.0658	R1 = 0.0358, wR2 = 0.0757
largest diff. peak and hole (e·Å^{-3})	1.822 and -1.831	1.520 and -1.039

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^2]^{1/2}$; goodness of fit = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{param})\}^{1/2}$; $w = [\sigma^2(F_o) + (g_1P)^2 + g_2P]^{-1}$; $P = [\max(F_o^2;0 + 2F_c^2]/3$.

Table S2. Selected distances [Å] and angles [deg] for **1**·1.5CH_2Cl_2 (X-ray) and for the computed structure (ground state S_0 and triplet state T_1)

	X-Ray	S_0	T_1
Distances (Å)			
Pt1-S1	2.383(1)	2.426	2.361
Pt1-N1	2.086(4)	2.123	2.109
Pt1-C10	2.021(5)	2.019	1.987
Pt1-C15	2.023(5)	2.015	2.031
Pt2-S2	2.412(1)	2.485	2.483
Pt2-N3	2.099(4)	2.128	2.127
Pt2-C34	2.011(5)	2.001	2.002
Pt2-C39	2.007(5)	2.008	2.009
Pt1-Pb1	2.7832(3)	2.817	2.988
Pt2-Pb1	3.1642(3)	3.222	3.132
Pb1-N2	2.565(5)	2.490	2.662
Pb1-N4	2.683(5)	2.709	2.528
S2-C49	1.773(6)	1.772	1.767
S1-C25	1.761(6)	1.746	1.759
Pb1-S2	2.797(1)	2.794	2.801
Pb1-S1	3.545(2)	3.596	3.707
Pb1⋯Cl1	3.640(6)		
Angles (º)			
Pt1-Pb1-Pt2	140.753(9)	146.89	143.26
N2-Pb1-N4	151.72(15)	148.69	149.30
Pt1-Pb1-S2	98.06(3)	103.31	98.82
Pt1-Pb1-N2	79.95(10)	82.08	77.18
Pt1-Pb1-N4	95.68(10)	94.98	93.17
N2-Pb1-Pt2	85.14(10)	82.82	86.35
S2-Pb1-N4	57.61(11)	57.45	59.03

N(4)-Pb1-Pt(2)	80.83(10)	83.07	84.46
S(2)-Pb1-N(2)	95.07(10)	92.71	93.29
Pt2-Pb1-S2	47.24(3)	48.14	49.08
C10-Pt1-N1	81.72(19)	80.96	81.60
S1-Pt1-C15	89.46(16)	90.48	90.59
N3-Pt2-C34	81.93(19)	81.16	81.09
S2-Pt2-C39	95.35(15)	94.82	94.65
Pt1-S1-C25	104.59(18)	106.82	107.59
Pt2-S2-C49	106.11(18)	106.59	107.53
S1-C25-N2	118.4(4)	120.42	118.37
S2-C49-N4	115.6(4)	118.89	115.23
S1-Pt1-Pb1	86.29(3)	86.26	86.93
S2-Pt2-Pb1	58.35(3)	56.90	58.48
Pb1-S2-Pt2	74.41(4)	74.94	72.43
Pb1-N2-C25	120.5(4)	121.83	123.07
Pb1-N4-C49	100.6(3)	99.64	102.97

Table S3. Selected bond lengths [Å] and angles [deg] for **2**·1.5acetone (X-ray) and for the computed structure (ground state S_0 and triplet state T_1)

	X-Ray	**S_0**	**T_1**
Distances (Å)			
Pt1-S1	2.4138(13)	2.445	2.459
Pt1-N1	2.102(4)	2.128	2.128
Pt1-C10	2.022(5)	2.006	2.004
Pt1-C15	2.011(4)	2.003	2.005
Pt2-S2	2.3679(12)	2.435	2.375
Pt2-N3	2.091(4)	2.125	2.105
Pt2-C34	2.020(4)	2.012	1.974
Pt2-C39	2.024(5)	2.016	2.035
Pb1-Pt1	2.9790(3)	3.020	3.013
Pb1-Pt2	2.8401(3)	2.867	2.923
Pb1-N2	2.497(4)	2.531	2.466
Pb1-N4	2.568(4)	2.581	2.653
Pb1-O1	2.775(5)	2.693	2.832
S1-C25	1.761(5)	17.50	1.755
S2-C49	1.745(5)	1.749	1.756
Pb1-S1	3.186(1)	3.304	3.109
Pb1-S2	3.678(3)	3.568	3.641
C50-O1	1.189(9)	1.222	1.221
Angles (º)			
Pt1-Pb-Pt2	133.291(8)	134.52	136.19
N2-Pb-N4	84.20(13)	86.29	84.58
O1-Pb-Pt1	87.5(1)	92.58	99.73
O1-Pb-Pt2	123.8(1)	113.29	104.43
Pb1-O1-C50	136.2(5)	145.48	140.66
N2-Pb1-Pt1	80.47(9)	81.87	83.77

N4-Pb1-Pt2	85.51(9)	84.04	81.42
N1-Pt1-C10	81.5(2)	81.08	81.14
Pt2-Pb1-N2	102.52(9)	98.44	98.63
Pt1-Pb1-N4	140.51(9)	140.84	141.93
S1-Pt1-C15	89.78(13)	91.84	93.01
N3-Pt2-C34	81.45(17)	80.92	81.27
S2-Pt2-C39	87.92(14)	88.06	87.04
Pt1-S1-C25	103.34(16)	107.54	106.83
S1-C25-N2	117.5(4)	119.90	118.23
S1-Pt1-Pb1	71.56(3)	75.55	68.38
Pt2-S2-C49	116.81(16)	112.83	114.04
S2-C49-N4	122.3(4)	122.90	121.56
S2-Pt2-Pb1	89.39(3)	84.18	86.20
Pb1-N4-C49	120.7(3)	112.79	109.72
Pb1-N2-C20 (Spy)	121.3(12)	116.04	118.42

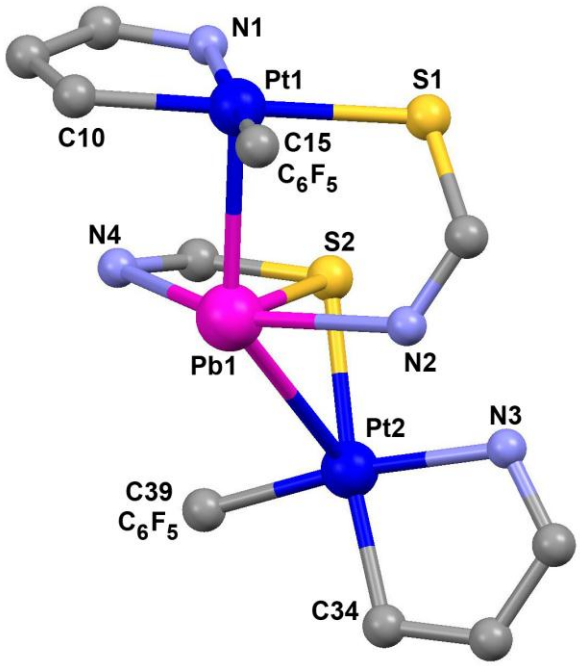


Fig. S1 Detail of the environment of Pb^{II} in the molecular structure of $[\{Pt(C_6F_5)(bzq)\}_2Pb(Spy)_2]\cdot 1.5CH_2Cl_2$ (**1**·$1.5CH_2Cl_2$)

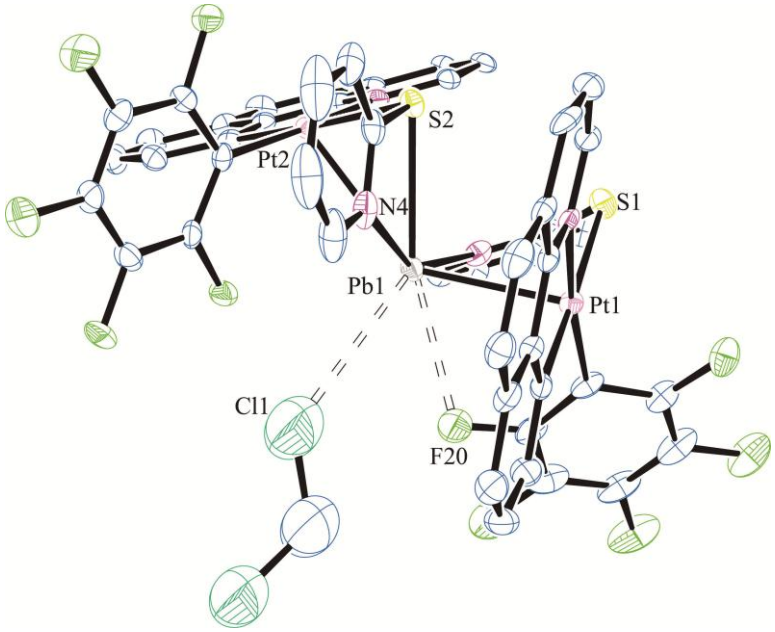


Fig. S2 Molecular structure of $[\{Pt(C_6F_5)(bzq)\}_2Pb(Spy)_2]\cdot 1.5CH_2Cl_2$ (**1**·$1.5CH_2Cl_2$) including the Pb···Cl(CH_2Cl_2) and Pb···F(C_6F_5) contacts. We note that the electronic deficiency could be somewhat reduced by the presence of secondary weak contacts with an *ortho*-fluorine atom [Pb(1)-F(20) 2.960(3) Å] of a C_6F_5 ligand and a chlorine atom of crystallization solvent [Pb···Cl 3.640(6) Å]. Although these distances [Pb···F(20) 2.9603(3) Å, Pb···Cl(1) 3.640(6) Å] are larger than the sum of the r_{cov} Pb and the r_{vWaals} of the corresponding halide, however they are below the van der Waals limit [Pb^{II}···F 3.46 Å, Pb···Cl 3.77 Å] [r_{cov} Pb (1.46) + r_{vWaals} F (1.47) = 2.93 Å; r_{cov} Pb (1.46) + r_{vWaals} Cl (1.75) = 3.21 Å].

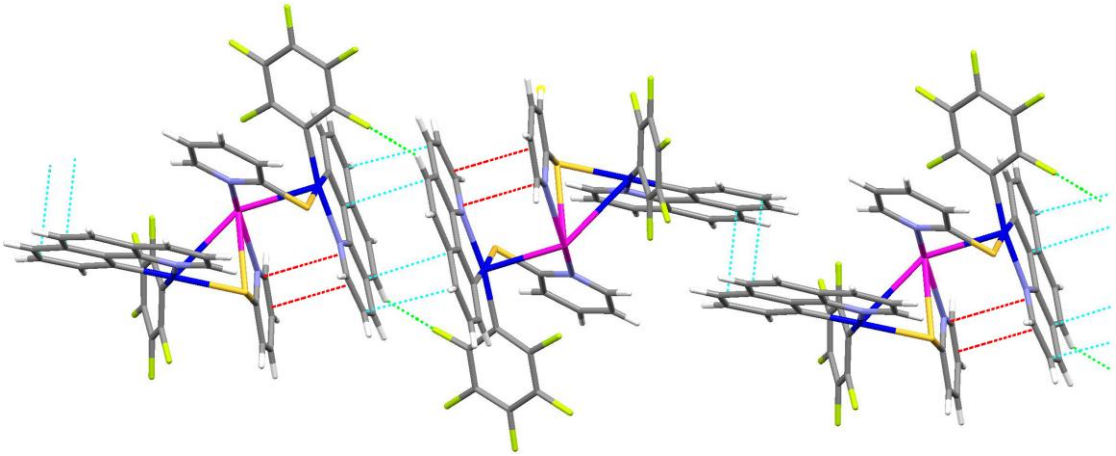


Fig. S3 Crystal packing of **1**·$1.5CH_2Cl_2$ showing the intra (red) and intermolecular (blue) π···π contacts. Intramolecular π···π interactions involve pyridine rings of the bzq and Spy ligands [distance between the centroids of the heterocyclic rings bzq(N1-C12)-Spy(N4-C49) 3.42 Å, minimum distances C-C 3.36 Å and N-N 3.24 Å; bzq(N3-C36)-Spy (N2-C25) 3.57 Å, minimum distances C-C 3.27 Å and N-N 3.29 Å]. The supramolecular packing shows the stacking along the [101] crystallographic direction,

supported by intermolecular π···π interactions (blue) involving two bzq(N1) or two bzq(N3) ligands (interplanar distances 3,31 Å, 3.32 Å, respectively, dihedral angles between planes 0º), assisted by secondary C-H···F interactions (green) (C···F 3.26 Å, H···F 2.43 Å, C-H···F 149.2º).

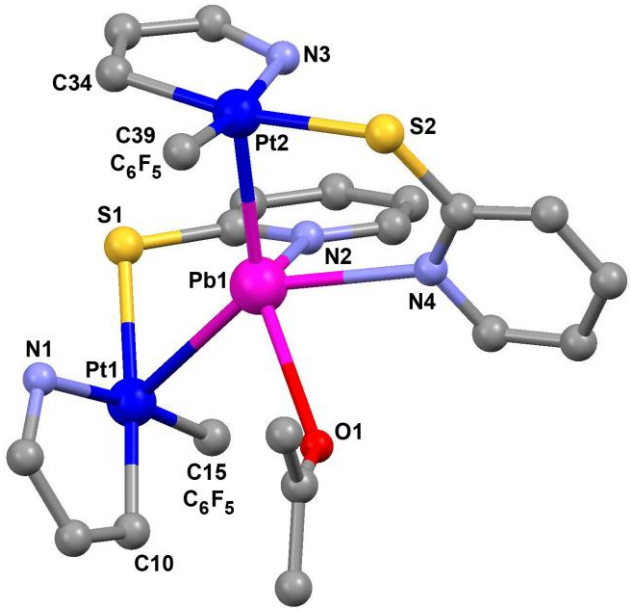


Fig. S4 Detail of the environment of Pb^{II} in the molecular structure of $[\{Pt(C_6F_5)(bzq)\}_2Pb(Spy)_2(Me_2CO)]\cdot 1.5Me_2CO$ (**2**·1.5Me_2CO).

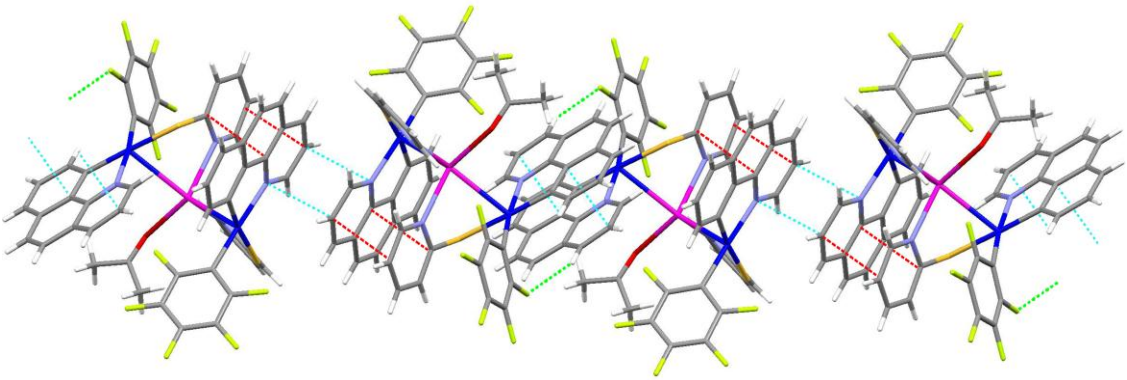


Fig. S5 Crystal packing of **2**·1.5Me_2CO showing the π···π intra (red) and intermolecular (blue) contacts. The molecule is stabilized by one intramolecular π···π interaction, which involve the pyridine rings of the bzq [N3-(C26-C36)] and the Spy [N2-(C1-C25)] ligands (distance between the centroids of the heterocyclic ligands 3.48 Å, minimum distances C-C 3.20 Å and N-N 3.19 Å). The supramolecular packing show the stacking along the *c*-axis supported by intermolecular π···π interactions involving two bzq(N3) and two bzq(N1) ligands (interplanar distances 3,23 Å, 3.30 Å, respectively, dihedral angles between planes 0º), assisted by secondary C-H···F interactions (green) (C···F 3.53 Å, H···F 2.654 Å, C-H···F 157.9º).

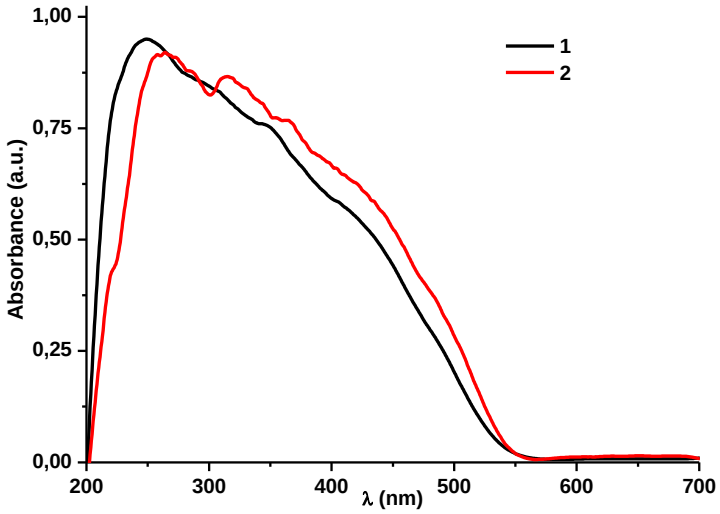
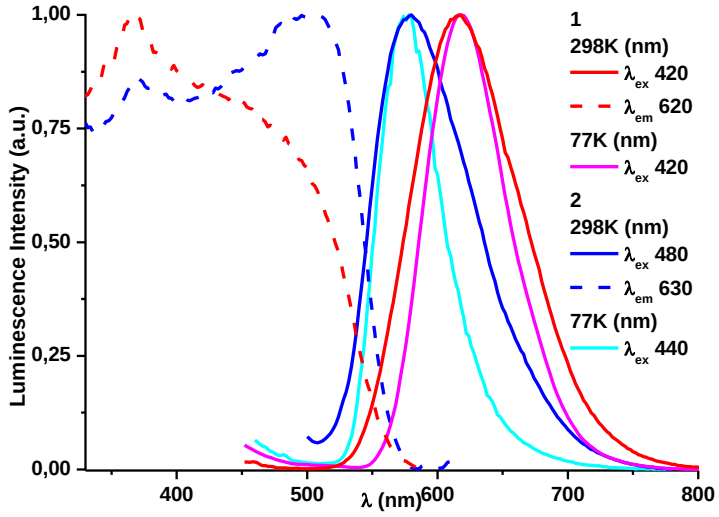
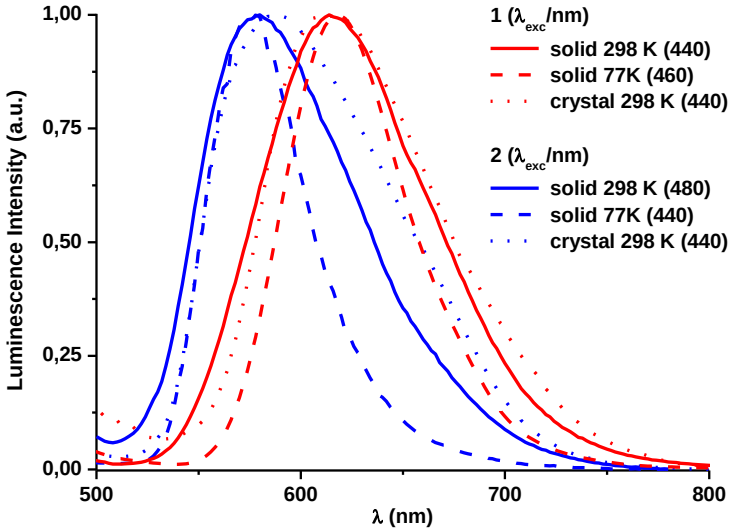


Fig. S6 Experimental absorption spectra in solid state of **1** and **2**. Absorption [nm]: **1** 249, 307, 350, 415, 437, 480, tail to 550; **2** 260, 315, 365, 440, 495, tail to 550.

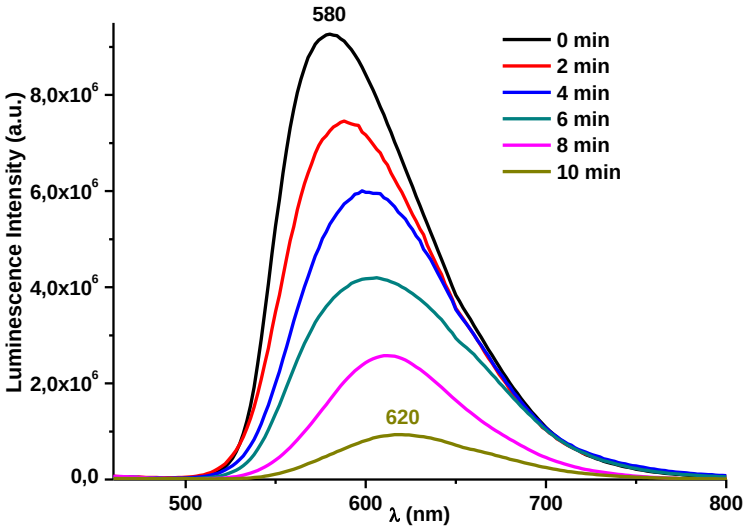


a)

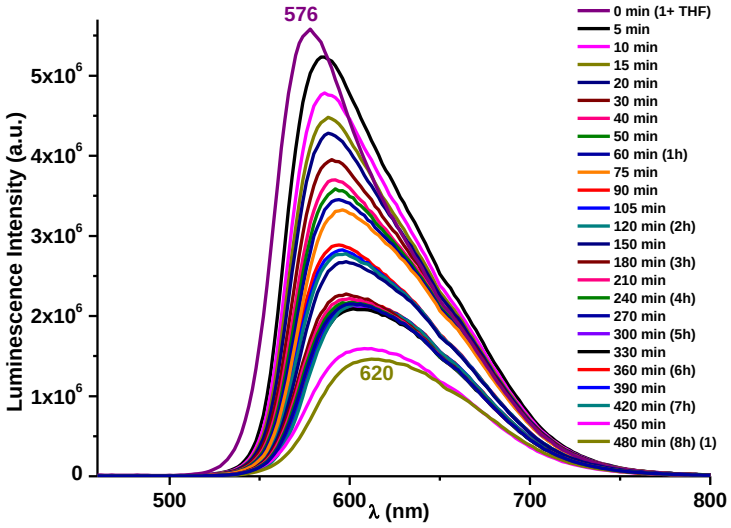


b)

Fig. S7 a) Normalized excitation an emission of **1** and **2** (powders) at 298 K an at 77 K. **b)** Normalized emission spectra of **1** (powder solid and crystals) and of **1** treated with a drop of acetone (**2)** in solid state (powder) and in crystalline form at 298 K and at 77 K. b



a)



b)

Fig. S8. Monitoring of the desolvatation by emission spectroscopy with the time, passing a stream of air, of a) **2**·x(acetone) b) **2**·x(THF).

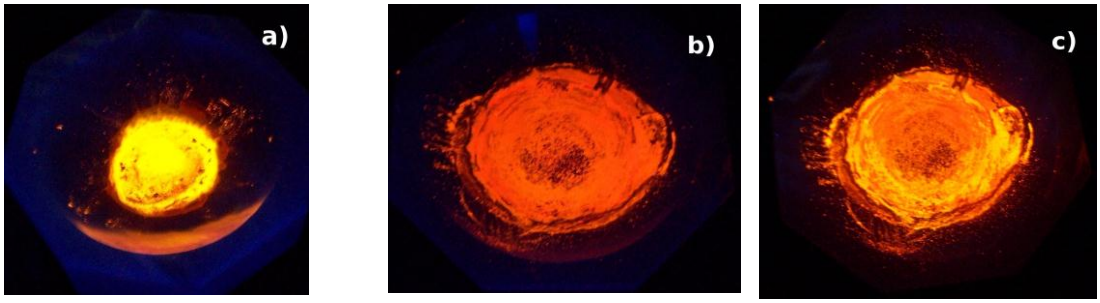


Fig. S9 Photos showing luminescence change of **2** under UV light irradiation (365 nm): **a)** solvated form of **2.**x(acetone), **b)** after grinding (to give **1**) **c)** after addition to **b** of a drop of acetone (showing the partial recovering of **2**).

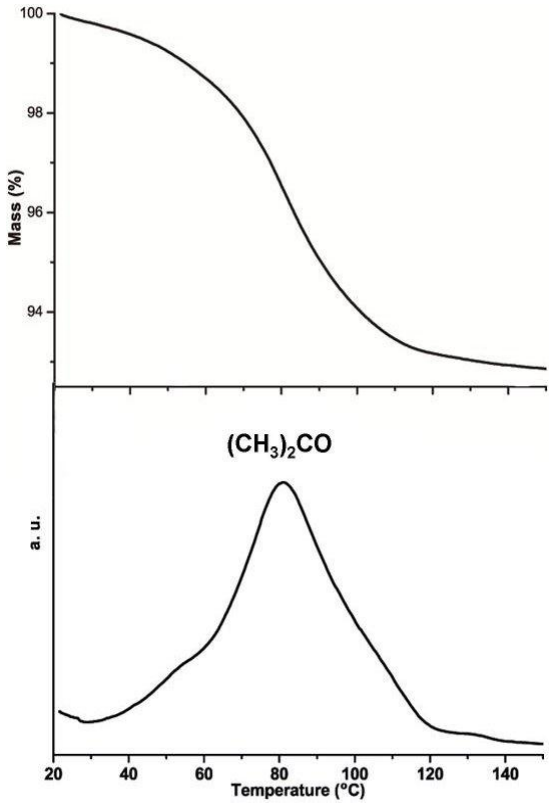


Fig. S10 Thermogravimetric analyses showing the weight lost in the sample **2.**x(acetone)).

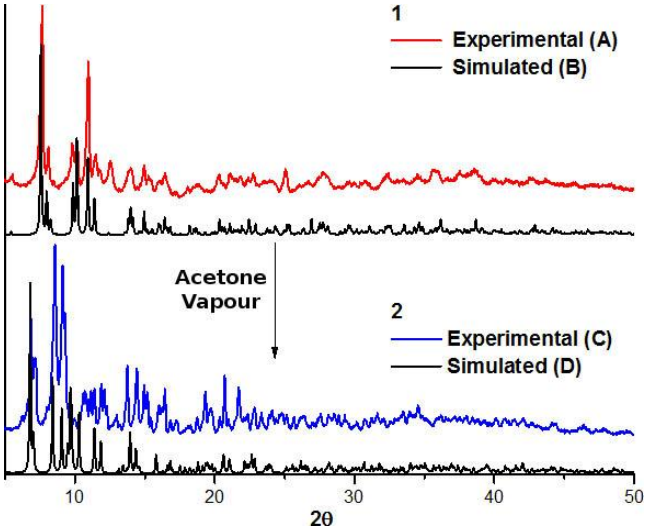


Fig. S11 Powder diffraction patterns for: (A) experimental data from the ground state **1**, (B) computed pattern from the single crystal data for **1**·1.5CH_2Cl_2. (C) experimental data from the sample **1** after exposure to acetone vapour (**2.**x(acetone)). (D) computed pattern from the single crystal data for **2**·1.5acetone.

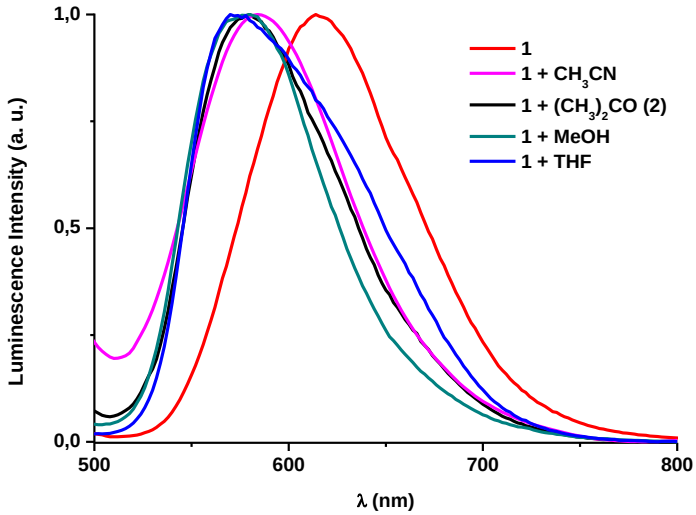


Fig. S12 Normalized emission spectra at 298 K after treating **1** with a drop of the respective solvent.

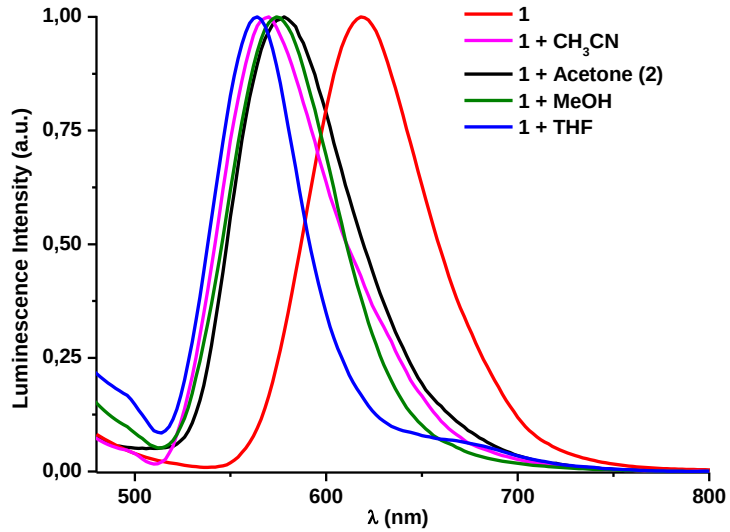


Fig. S13 Normalized emission spectra at 77 K after treating **1** with a drop of the respective solvents.

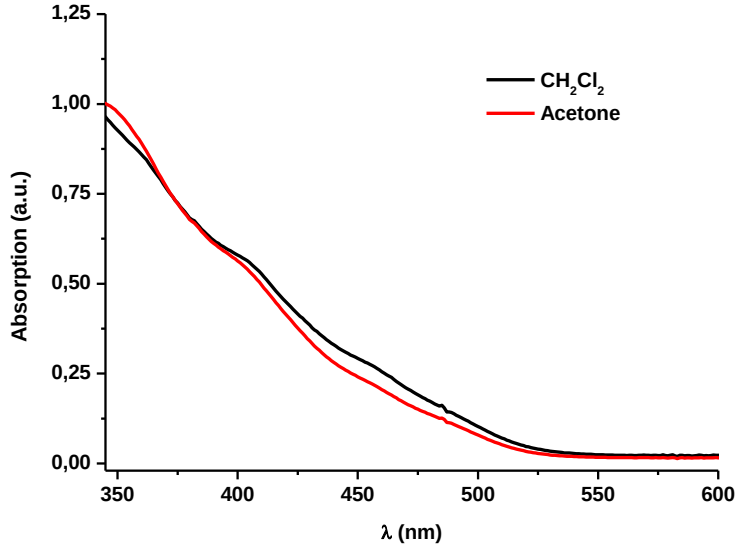


Fig. S14 Absorption spectra (low-energy region) of **1** in CH_2Cl_2 and acetone (5 x 10^{-4} M); Absorption in nm (10^3 $\varepsilon/M^{-1}cm^{-1}$): **$CH_2Cl_2$:** 215 (46.4), 240 (75.2), 310 (30.1), 357 (17.3), 405 (11.4), 455 (5.6), 485 (2.6). **Acetone:** 354 (20.1), 401 (11.7), 454 (4.9), 485 (2.5)

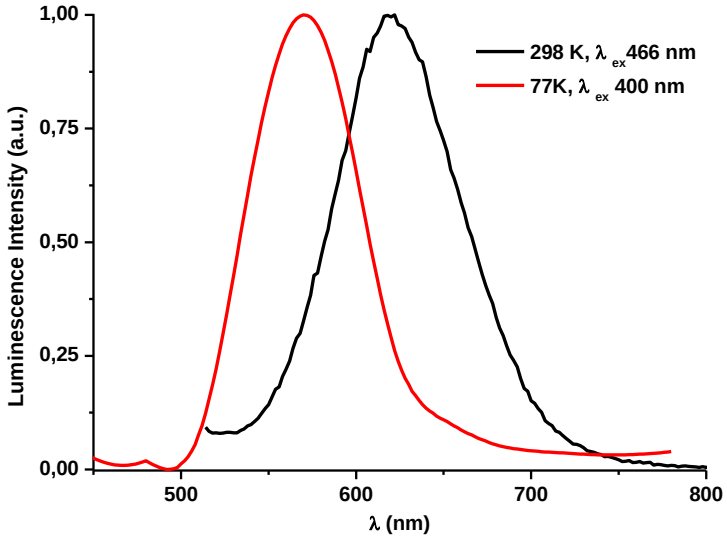


Fig. S15 Normalized emission spectra of **1** in CH_2C_2 10^{-3} M at 298 K and at 77 K.

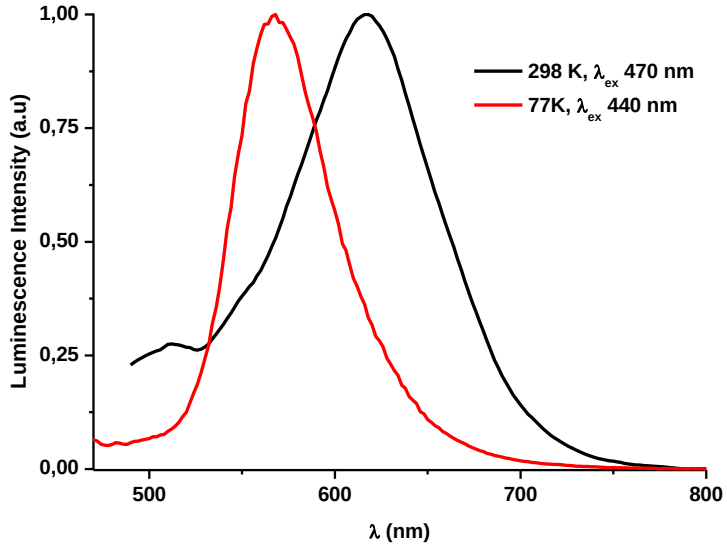


Fig. S16 Normalized emission spectra of **1** in acetone 10^{-3} M at 298 K and at 77 K.

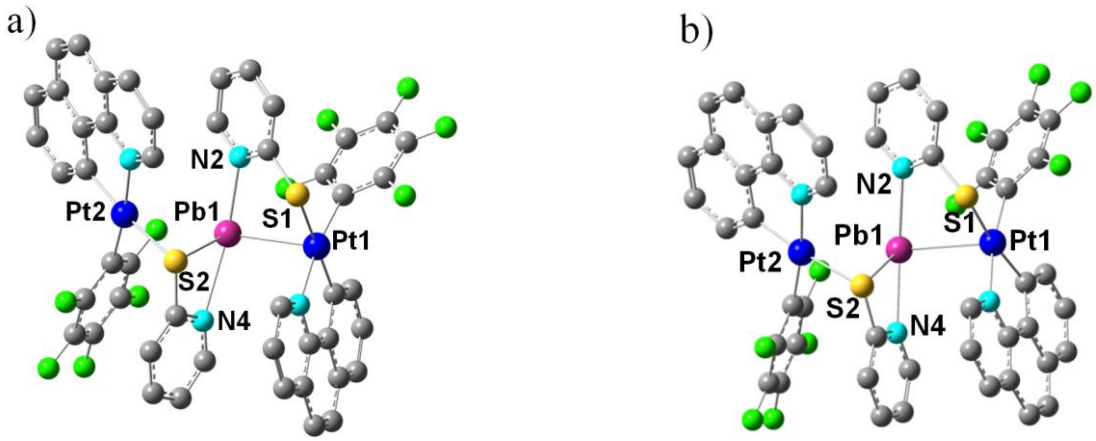


Fig. S17 DFT optimized geometries for ground state (a) and triplet state (b) of complex **1**. Hydrogen atoms are omitted for clarity.

Distances (Å)	**X-ray**	**S_0**	**T_1**
Pt1-Pb	2.7832(3)	2.817	2.988
Pt2-Pb	3.1642(3)	3.222	3.132
Pb-N2	2.565(5)	2.490	2.662
Pb-N4	2.683(5)	2.709	2.528
Pb-S2	2.797(1)	2.794	2,801

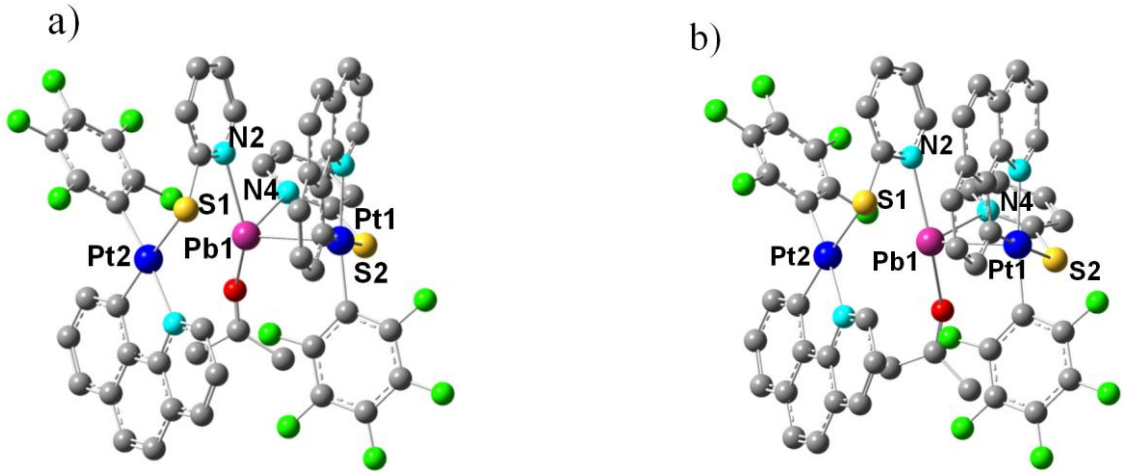


Fig. S18 DFT optimized geometries for ground state (a) and triplet state (b) of complex **2**. Hydrogen atoms are omitted for clarity.

Distances (Å)	**X-ray**	**S_0**	**T_1**
Pb-Pt1	2.9790(3)	3.020	3.013
Pb-Pt2	2.8401(3)	2.867	2.923
Pb-N2	2.497(4)	2.531	2.466
Pb-N4	2.568(4)	2.581	2.653
Pb-O1	2.775	2.693	2.832

Table S4. DFT optimized coordinates for ground state (S^o) and triplet state (T^1) of complex **1**.

Charge = 0 Multiplicity = 1

Pt	2.87934	-0.31595	-0.53908
Pt	-2.89121	0.13267	-0.40835
Pb	0.23593	0.0501	0.36233
S	1.94241	-1.85116	-2.16806
S	-1.09987	0.96472	-1.91553
F	2.35177	-3.56081	3.79092
F	5.78067	-4.5397	0.71508
F	4.43609	-5.13718	3.00623
F	-3.98678	5.24654	0.58696
F	1.62728	-1.45085	2.35124
F	-2.93876	5.22311	3.1008
F	-1.85954	2.92021	4.08633
F	5.06329	-2.42904	-0.76643
F	-1.82226	0.69903	2.61332
F	-3.97175	3.03304	-0.91036
N	2.7663	1.35894	-1.83863
N	0.03484	-2.33307	-0.33236
N	-3.12494	-1.62888	-1.57837
N	0.12083	2.67307	-0.30506
C	3.73343	1.07008	0.65504
C	3.44853	3.67649	-2.01887
C	2.91267	3.70745	-3.31853
C	4.55091	4.6803	-0.09983
C	4.07205	4.79078	-1.3699
C	4.80672	2.08426	2.59125
C	4.93461	3.30342	1.95503
C	-2.88963	1.75881	0.76938
C	-4.30233	-0.776	0.6821
C	3.35475	2.4629	-1.30719
C	3.29481	-1.85305	0.69598
C	3.86143	2.33178	0.01808
C	-2.78222	-3.17092	-3.3718
C	-0.69338	2.59936	-1.36421
C	-4.40272	-3.68998	-1.67064
C	-2.50505	-1.9743	-2.70102
C	4.45938	3.45324	0.638
C	-2.37797	1.80104	2.06299
C	4.35853	-2.68394	0.34473
C	-2.38101	2.9413	2.85857
C	2.26106	1.41103	-3.06486
C	-4.69165	-2.03192	0.14474
C	-4.06407	-2.46429	-1.05811
C	-4.95114	-0.37336	1.84233
C	2.32184	2.57481	-3.84104
C	-5.39906	-4.50476	-1.04281
C	-2.9293	4.11508	2.3605
C	-3.44095	2.95728	0.32066
C	-0.8525	-3.10319	0.31368
C	-5.67614	-2.8561	0.73903
C	-6.29274	-2.40441	1.92022
C	-3.73201	-4.02972	-2.85758

C	4.21525	0.97697	1.95295
C	-0.28958	-4.9874	-1.02281
C	-5.93041	-1.18147	2.4493
C	4.07267	-4.08881	2.26994
C	-1.18276	3.7393	-2.0065
C	0.02327	5.05897	-0.40131
C	4.75448	-3.78096	1.09923
C	-3.46304	4.1219	1.07837
C	-6.00254	-4.10277	0.10942
C	-1.05293	-4.43629	0.00959
C	0.63248	-4.2005	-1.68676
C	0.79233	-2.85187	-1.31627
C	-0.81556	4.98266	-1.51141
C	3.01342	-3.2861	2.66606
C	2.65706	-2.19484	1.88126
C	0.46551	3.87315	0.16885
H	2.96553	4.62436	-3.89988
H	5.01994	5.5359	0.3796
H	4.15394	5.72845	-1.91251
H	5.17398	1.97168	3.608
H	5.3991	4.14694	2.45843
H	-2.24253	-3.40333	-4.28282
H	-1.76114	-1.28213	-3.08211
H	1.78708	0.50256	-3.4244
H	-4.71565	0.58329	2.29534
H	1.89559	2.56856	-4.8378
H	-5.66543	-5.45018	-1.50729
H	-1.4323	-2.60924	1.09098
H	-7.0512	-3.0168	2.40009
H	-3.96642	-4.96504	-3.35936
H	4.14879	0.03789	2.49306
H	-0.40813	-6.03212	-1.29662
H	-6.41216	-0.82898	3.35772
H	-1.85047	3.63603	-2.85353
H	0.32798	6.01271	0.015
H	-6.75894	-4.73071	0.57367
H	-1.7829	-5.01968	0.55863
H	1.25601	-4.60259	-2.47728
H	-1.18885	5.88736	-1.98258
H	1.12932	3.87288	1.02999

Charge = 0 Multiplicity = 3

Pt	2.89693100	-0.09076600	-0.53718600
Pt	-2.91020800	-0.04322500	-0.43621700
Pb	0.08709400	0.07257000	0.46540200
S	2.09878000	-1.62108400	-2.14808600
S	-1.15685900	0.95288000	-1.88440300
F	2.70023200	-3.14180900	3.94039100
F	5.77921700	-4.42312000	0.61757500
F	4.63235600	-4.84826100	3.05033300
F	-4.56332300	4.98334500	0.14851500
F	1.93459600	-1.07185600	2.46753200
F	-3.84561600	5.16106100	2.77006000
F	-2.69100300	3.01849000	3.99723500
F	5.02054700	-2.36483500	-0.89730500

F	-2.26767800	0.75312900	2.65858200
F	-4.14536000	2.72799200	-1.22204400
N	2.67518000	1.58881800	-1.79400800
N	0.26421400	-2.44283100	-0.38852000
N	-2.86647100	-1.85147200	-1.55557000
N	-0.10569000	2.53767700	-0.05947500
C	3.88598100	1.23122700	0.56812200
C	3.18254400	3.97411700	-1.88739700
C	2.54720900	4.05244700	-3.13944700
C	4.38742100	4.93586100	0.00016700
C	3.78165100	5.08550600	-1.21265000
C	5.11284500	2.18079300	2.44956900
C	5.08040100	3.45128300	1.88755200
C	-3.19285800	1.62422500	0.64781200
C	-4.29080400	-1.07298600	0.58431100
C	3.23596300	2.71632100	-1.25009000
C	3.42149700	-1.62282200	0.68917800
C	3.87541200	2.54460000	-0.00463900
C	-2.24429100	-3.38850100	-3.27847700
C	-0.76658100	2.54611500	-1.22836000
C	-3.86374800	-4.06441400	-1.63163400
C	-2.15813600	-2.14685100	-2.64069200
C	4.45812100	3.65934000	0.64340300
C	-2.84904500	1.76844900	1.98951300
C	4.41257000	-2.51801600	0.28712900
C	-3.05457600	2.93657700	2.71500200
C	2.07842900	1.69326700	-2.98994600
C	-4.47599700	-2.39181100	0.08852600
C	-3.72133000	-2.78392800	-1.05247700
C	-5.07249100	-0.71196700	1.67553900
C	1.99936600	2.89730700	-3.68359800
C	-4.78296200	-4.97977100	-1.02468300
C	-3.64044500	4.03072200	2.09363700
C	-3.77950100	2.74832800	0.06941900
C	-0.49326500	-3.35696400	0.21963300
C	-5.38699800	-3.31379600	0.65784300
C	-6.14126200	-2.89888100	1.76932100
C	-3.09444800	-4.35186100	-2.77118200
C	4.53309400	1.08562100	1.80093800
C	0.55146000	-5.14332200	-0.97192900
C	-5.98067500	-1.61535200	2.25566000
C	4.24872100	-3.81820300	2.29939000
C	-1.09472100	3.73353200	-1.88086900
C	-0.01371600	4.92301700	-0.09201700
C	4.82847700	-3.59828300	1.05704000
C	-4.00478100	3.93492300	0.75747800
C	-5.50634100	-4.61649400	0.07005600
C	-0.38219700	-4.72085300	-0.03087200
C	1.32689400	-4.19708400	-1.62800300
C	1.16296900	-2.84512300	-1.30045700
C	-0.70565000	4.93560600	-1.30360700
C	3.26545900	-2.94860400	2.74845600
C	2.88218800	-1.87965400	1.94543800
C	0.26154400	3.69894300	0.49616900
H	2.49371500	5.00116200	-3.66478600
H	4.83377800	5.79355900	0.49692100

H	3.74421200	6.06046200	-1.69115400
H	5.60807200	2.03135900	3.40476600
H	5.54355500	4.29054300	2.39994200
H	-1.64133900	-3.57366100	-4.16037100
H	-1.49635100	-1.37242500	-3.01506100
H	1.64492100	0.78586000	-3.39443600
H	-4.99810000	0.28634200	2.09207200
H	1.50031500	2.91254800	-4.64622700
H	-4.89713800	-5.96805900	-1.46162800
H	-1.22569800	-2.97250200	0.92655300
H	-6.84772000	-3.58490600	2.22856500
H	-3.17955100	-5.32542900	-3.24714400
H	4.60636700	0.10577800	2.25984700
H	0.67264400	-6.19887000	-1.19665000
H	-6.57126800	-1.29031500	3.10845500
H	-1.64946900	3.69851700	-2.81110300
H	0.30416900	5.84134700	0.38871600
H	-6.20541200	-5.31967200	0.51612200
H	-1.01812100	-5.42319700	0.49629500
H	2.06015300	-4.48105100	-2.37463800
H	-0.94949200	5.87621100	-1.78839100
H	0.79415200	3.63010300	1.44111200

Table S5. DFT optimized coordinates for ground state (S^o) and triplet state (T^1) of complex **2**.

Charge = 0 Multiplicity = 1

Pt	-2.18321800	1.06554500	-1.07486500
Pb	-0.08156300	-0.23817700	0.65824700
Pt	2.64321000	-1.03380000	0.25807200
S	-1.26719700	-0.79136300	-2.37611300
S	2.80557900	-0.80551900	2.67690600
N	2.09325600	-3.08558700	0.21440700
F	-2.72510900	-0.36794400	1.76251000
F	-4.85050100	0.09036000	-2.44608200
C	-3.68519600	-0.06962200	-0.39105700
C	1.97369500	-3.55770800	-1.05576200
C	1.98418800	-3.92871200	1.23451400
C	-4.77589500	-0.38813400	-1.19864000
C	-3.72891300	-0.61659600	0.88212300
F	-6.84346800	-1.47665600	-1.58975900
C	-1.56723300	-2.26294900	-1.47841100
C	1.54376100	-5.77765900	-0.23095800
C	2.58911500	-1.30559200	-1.73444300
C	2.85814500	-0.42444900	-2.77272400
C	2.20825800	-2.62084900	-2.10163000
C	-5.82293200	-1.20068700	-0.77656000
C	1.71260700	-5.28893800	1.04947100
C	-2.84808200	2.72631700	-0.16625700
C	1.67524200	-4.91006700	-1.32808600
C	-2.05658800	3.86921500	-0.45755900
F	-4.68927200	-1.96433100	2.57688400
F	-6.79651500	-2.52955000	0.91938600
N	-1.21023000	-2.34325800	-0.18050700

N	0.17087600	-1.47178300	2.91083900
C	1.37537800	-1.37094800	3.50948700
C	-2.01279600	-4.59677200	-0.06673400
C	-1.43128400	-3.47658600	0.49919100
C	-5.80590800	-1.73998700	0.50450200
C	-4.74216900	-1.44488600	1.34437700
F	1.51445200	2.11597000	0.22835800
N	-0.73720500	2.44379400	-1.80743200
C	1.51573300	-1.69556300	4.87748000
C	-0.89244700	-1.86669400	3.63584100
C	3.48824400	0.78965900	0.09796400
C	-0.93943600	3.69923800	-1.32572500
C	0.27456200	2.22023000	-2.63736900
C	4.87658300	0.84464600	-0.02711700
C	2.85975500	2.02551700	0.11341100
F	5.58868300	-0.29106800	-0.05638200
F	2.85997600	4.39346300	0.07968500
F	5.57971700	4.39518500	-0.18258000
F	6.91971600	2.02157600	-0.24766900
C	0.97100100	4.51577900	-2.54227800
C	-2.14881800	-3.36903500	-2.12263000
C	1.74118200	-4.41245500	-3.70508100
C	-2.37349400	-4.53433700	-1.41387200
C	1.54924000	-5.30841300	-2.69798000
C	5.59262900	2.03171700	-0.12818000
C	-0.82325800	-2.20350600	4.97300600
C	4.91477900	3.24408800	-0.09658200
C	-0.09893400	4.77842900	-1.66987700
C	1.15090200	3.23809400	-3.03233100
C	3.53357600	3.23744500	0.02576000
O	-0.38043500	1.59323400	2.61008800
C	-0.04063700	2.69345600	3.01897400
C	2.09337200	-3.04684700	-3.44434700
C	2.73867900	-0.82549700	-4.11720900
C	0.42061900	-2.11155800	5.60441600
C	2.35793200	-2.10835400	-4.45899300
C	-3.94630700	2.93071400	0.66020300
C	-2.33579000	5.15737600	0.05624200
C	-0.39388100	6.06571900	-1.11592900
C	-3.46076700	5.30729700	0.88892000
C	-4.24654700	4.20658500	1.17431000
C	-1.46576100	6.24291000	-0.29536400
C	-1.06787600	3.73672600	3.35620100
C	1.40446500	3.06198000	3.19856700
H	2.12772600	-3.50407000	2.22163700
H	1.32300400	-6.82847000	-0.40008500
H	3.17158800	0.59195100	-2.55302300
H	1.63615400	-5.93642000	1.91590500
H	-2.17658800	-5.48768100	0.52890700
H	-1.11479800	-3.47555100	1.53784100
H	2.49740600	-1.61351200	5.33107700
H	-1.84296800	-1.89003300	3.11283900
H	0.40003700	1.19842900	-2.98397900
H	1.64472400	5.32015400	-2.82509000
H	-2.42926100	-3.27416500	-3.16525400
H	1.64567500	-4.73099100	-4.74003400

H	-2.83704500	-5.38752500	-1.90130100
H	1.30449200	-6.34394700	-2.91724900
H	-1.71485100	-2.51830600	5.50315600
H	1.96238100	3.00354100	-3.71226400
H	2.95767300	-0.10841000	-4.90471000
H	0.52853000	-2.36396500	6.65569100
H	2.27265600	-2.40361400	-5.50099400
H	-4.59874700	2.10041800	0.91159600
H	0.25224500	6.90092100	-1.37129200
H	-3.70533100	6.28610300	1.29279000
H	-5.12056400	4.32579000	1.81002500
H	-1.68309100	7.22906300	0.10782200
H	-2.05522800	3.41794500	3.02197000
H	-1.07581100	3.90171200	4.44019600
H	-0.80887400	4.69249100	2.88935600
H	2.03255800	2.16907700	3.17821500
H	1.55452600	3.61894700	4.12843300
H	1.69777300	3.72512500	2.37610800

Charge = 0 Multiplicity = 3

Pt	-2.20909900	1.13159600	-1.02217100
Pb	-0.09745700	-0.24193000	0.63110900
Pt	2.65306600	-1.13889100	0.21668000
S	-1.17985000	-0.74052900	-2.24056200
S	2.88859300	-0.99348100	2.57498100
N	1.95673900	-3.12123400	0.08612700
F	-2.79150400	-0.23828200	1.85807100
F	-4.83142800	0.07534900	-2.41164600
C	-3.70779000	-0.00550000	-0.32872900
C	1.77484200	-3.52455500	-1.22224800
C	1.70617300	-4.02807900	1.05423900
C	-4.77688800	-0.36444700	-1.14848600
C	-3.77025700	-0.51839200	0.95990600
F	-6.81899700	-1.49536800	-1.55422500
C	-1.60390100	-2.20618400	-1.37275400
C	1.07858800	-5.74198200	-0.53482900
C	2.57963700	-1.30171300	-1.74910700
C	2.93772200	-0.37117900	-2.74354100
C	2.08785800	-2.57340500	-2.20135700
C	-5.82088900	-1.18102100	-0.72692200
C	1.27941900	-5.31990400	0.78242300
C	-2.90497800	2.80181100	-0.16127300
C	1.32670500	-4.82004300	-1.57098000
C	-2.10709700	3.94310000	-0.44530500
F	-4.74654200	-1.83606800	2.66782100
F	-6.81063100	-2.47765000	0.98467000
N	-1.26634700	-2.29665300	-0.07021600
N	0.25078200	-1.52465300	2.92745800
C	1.48158300	-1.54419700	3.46957100
C	-2.22719000	-4.48406200	0.04755500
C	-1.57092600	-3.40742300	0.61699200
C	-5.82357500	-1.68412300	0.56857600
C	-4.78171000	-1.35004800	1.42094000
F	1.69975400	2.03593400	0.22225300
N	-0.75472000	2.50514400	-1.74819700

C	1.68121300	-1.93387100	4.80705100
C	-0.79822700	-1.84466800	3.69550200
C	3.63001300	0.64301300	0.11510000
C	-0.96909200	3.76584400	-1.28343600
C	0.27874900	2.27748000	-2.55137100
C	5.02012100	0.64789000	0.01707100
C	3.04123000	1.89977500	0.12726000
F	5.69580900	-0.50842900	-0.00394800
F	3.12454800	4.26743900	0.07375300
F	5.84513700	4.17262700	-0.13609800
F	7.10549700	1.75718200	-0.17011600
C	0.97431300	4.57304100	-2.45550800
C	-2.25109700	-3.26573200	-2.01941600
C	1.47979400	-4.18662100	-3.92656400
C	-2.56579000	-4.40965300	-1.30254600
C	1.17980700	-5.11036700	-2.96169900
C	5.77754400	1.81114300	-0.07295500
C	-0.68197500	-2.24340800	5.01958200
C	5.14043300	3.04541800	-0.05605800
C	-0.11880800	4.84213500	-1.61432700
C	1.16511600	3.29151300	-2.93142300
C	3.75729300	3.08749500	0.04168900
O	0.07163500	1.57490700	2.79657500
C	0.20561000	2.76729800	3.02018100
C	1.95329100	-2.88938200	-3.57500900
C	2.79958100	-0.66861800	-4.09932900
C	0.59234700	-2.29515400	5.58062500
C	2.31080500	-1.90881300	-4.51600100
C	-4.01774500	3.01179200	0.64480600
C	-2.39670300	5.23457100	0.05465400
C	-0.42839300	6.13418200	-1.07948800
C	-3.53459600	5.38909800	0.86855500
C	-4.32473200	4.29007900	1.14793100
C	-1.51966100	6.31784500	-0.28615700
C	-0.98097800	3.68061400	3.14814300
C	1.56920500	3.38526500	3.17191000
H	1.88879500	-3.70346500	2.07144300
H	0.75229300	-6.75114500	-0.76344700
H	3.32329600	0.60023000	-2.45048500
H	1.12973400	-6.00137900	1.61359800
H	-2.45367900	-5.36017900	0.64445900
H	-1.25995400	-3.42642400	1.65563600
H	2.68852100	-1.94062900	5.20887100
H	-1.77597500	-1.75945800	3.22926000
H	0.41451600	1.25551800	-2.89296600
H	1.65566800	5.37494000	-2.72670500
H	-2.50797800	-3.16027400	-3.06698900
H	1.36767900	-4.43853600	-4.97791800
H	-3.08061800	-5.23327100	-1.78880300
H	0.82691000	-6.09849800	-3.24499300
H	-1.56840400	-2.49683300	5.59025100
H	1.99322100	3.05070600	-3.58877800
H	3.08309000	0.06983600	-4.84384500
H	0.73318700	-2.60270600	6.61270700
H	2.21226900	-2.12738000	-5.57632800
H	-4.67432900	2.18291600	0.88979000

H	0.22278300	6.96783200	-1.32719500
H	-3.78472200	6.36992100	1.26393400
H	-5.20777000	4.41265600	1.77028900
H	-1.74686100	7.30721500	0.10343800
H	-1.88854000	3.18048700	2.80896400
H	-1.09421400	3.97442100	4.19892500
H	-0.82812700	4.60060000	2.57542600
H	2.31587200	2.61021000	3.35124000
H	1.58579900	4.13026400	3.97289900
H	1.82064000	3.90467700	2.23969900

Table S6. Composition (%) of frontier MOs in the ground state for **1** and **2** in gas phase.

		1							
MO	**Energy**	**Pt(1)**	**Bzq(1)**	**Spy(1)**	**Pb**	**Pt(2)**	**Bzq(2)**	**Spy(2)**	**C_6F_5**
LUMO+4	-1.20	1	22	19	6	2	15	34	2
LUMO+3	-1.25	1	43	15	1	3	30	7	0
LUMO+2	-1.57	6	55	2	14	2	15	4	1
LUMO+1	-1.86	0	29	1	1	3	65	0	1
LUMO	-2.14	10	54	2	14	4	9	5	2
HOMO	-5.75	11	14	64	0	3	5	1	1
HOMO-1	-5.90	2	19	5	1	24	39	9	0
HOMO-2	-6.21	10	21	5	10	25	3	8	19
HOMO-3	-6.28	4	4	3	1	20	3	2	63
HOMO-4	-6.31	9	18	5	0	4	1	0	62

		2								
MO	**Energy**	**Pt(1)**	**Bzq(1)**	**Spy(1)**	**Pb**	**Pt(2)**	**Bzq(2)**	**Spy(2)**	**C_6F_5**	**CH_3COCH_3**
LUMO+4	-1.11	2	3	40	2	1	50	1	1	0
LUMO+3	-1.14	4	66	10	4	0	1	13	1	0
LUMO+2	-1.48	2	14	14	10	7	48	2	1	1
LUMO+1	-1.69	3	77	0	2	1	16	0	1	0
LUMO	-2.03	3	7	3	8	8	69	1	1	0
HOMO	-5.50	21	23	51	1	1	1	1	1	0
HOMO-1	-5.67	0	0	0	0	13	16	69	0	0
HOMO-2	-5.84	33	16	5	13	18	3	7	4	2
HOMO-3	-6.14	17	16	6	0	1	6	2	53	0
HOMO-4	-6.17	4	22	26	0	4	21	8	14	0

Table S7. Selected vertical excitation energies computed by TD-DFT with the orbitals involved for complexes **1** and **2**.

1			
	λ (nm)	*f* [a]	Transition
S_1	445.44	0.019	HOMO→LUMO (93%)
S_2	411.18	0.0231	HOMO-1→LUMO (66%), HOMO-1→LUMO+1 (19%)
S_3	385.59	0.0117	HOMO→LUMO+1 (64%), HOMO-2→LUMO (15%)
S_4	377.16	0.0529	HOMO-2→LUMO (69%), HOMO→LUMO+1 (14%)
S_5	376.41	0.0187	HOMO-1→LUMO+1 (65%), HOMO→LUMO+1 (9%)
S_6	366.04	0.0168	HOMO-4→LUMO (62%), HOMO-3→LUMO (25%)
S_7	360.26	0.0223	HOMO→LUMO+2 (80%)
S_8	359.34	0.0107	HOMO-3→LUMO (46%), HOMO-4→LUMO (18%), HOMO-5→LUMO (17%)
S_9	355.18	0.0882	HOMO-5→LUMO (55%), HOMO-3→LUMO (15%)
S_{10}	337.90	0.0584	HOMO→LUMO+3 (28%), HOMO→LUMO+5 (27%), HOMO→LUMO+4 (24%)
2			
	λ (nm)	*f*	Transition
S_1	453.24	0.0044	HOMO→LUMO (89%)
S_2	439.94	0.0149	HOMO-1→LUMO (95%)
S_3	410.27	0.0234	HOMO→LUMO+1 (76%), HOMO-2→LUMO (16%)
S_4	397.45	0.0868	HOMO-2→LUMO (76%), HOMO→LUMO+1 (12%)
S_5	381.17	0.0128	HOMO→LUMO+2 (81%)
S_6	367.59	0.0213	HOMO-2→LUMO+1 (58%), HOMO-5→LUMO+2 (12%), HOMO-1→LUMO+1 (12%)
S_7	352.56	0.0109	HOMO-1→LUMO+2 (46%), HOMO-1→LUMO+1 (20%), HOMO-5→LUMO (11%)
S_8	350.12	0.0524	HOMO→LUMO+3 (53%), HOMO→LUMO+4 (26%)
S_9	344.12	0.0156	HOMO-6→LUMO (80%)
S_{10}	341.01	0.0432	HOMO→LUMO+4 (35%), HOMO→LUMO+3 (24%), HOMO-2→LUMO+2 (22%),

[a] Oscillator strenght

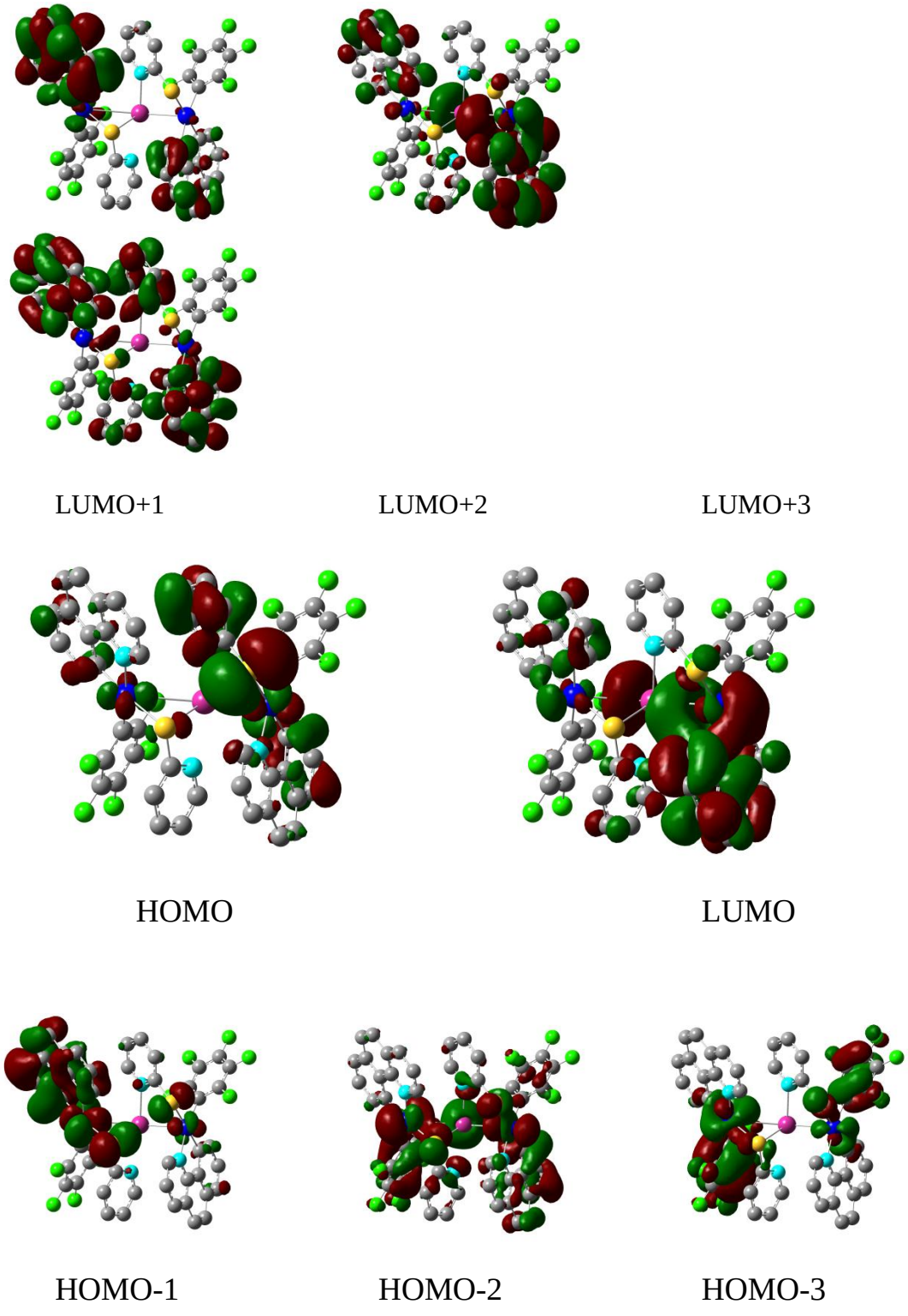
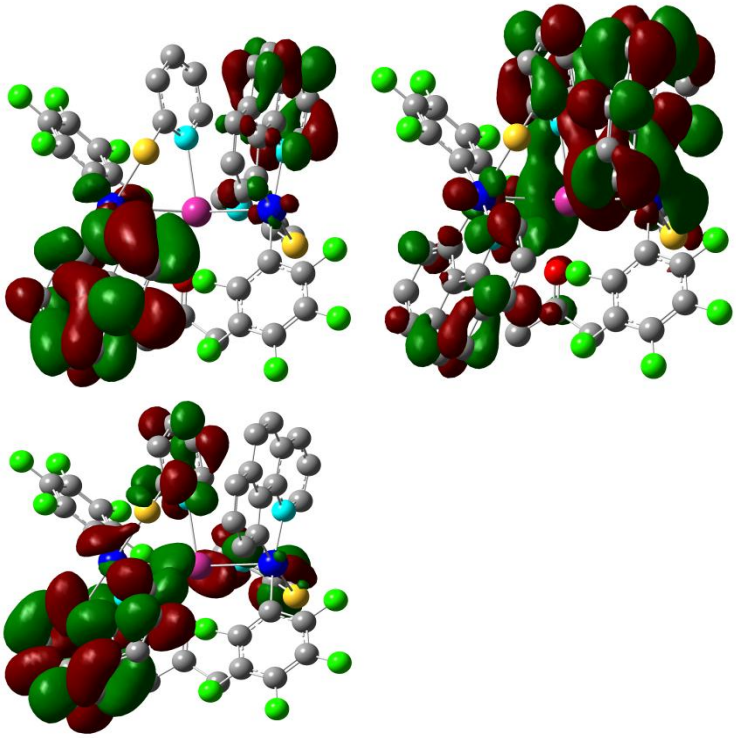
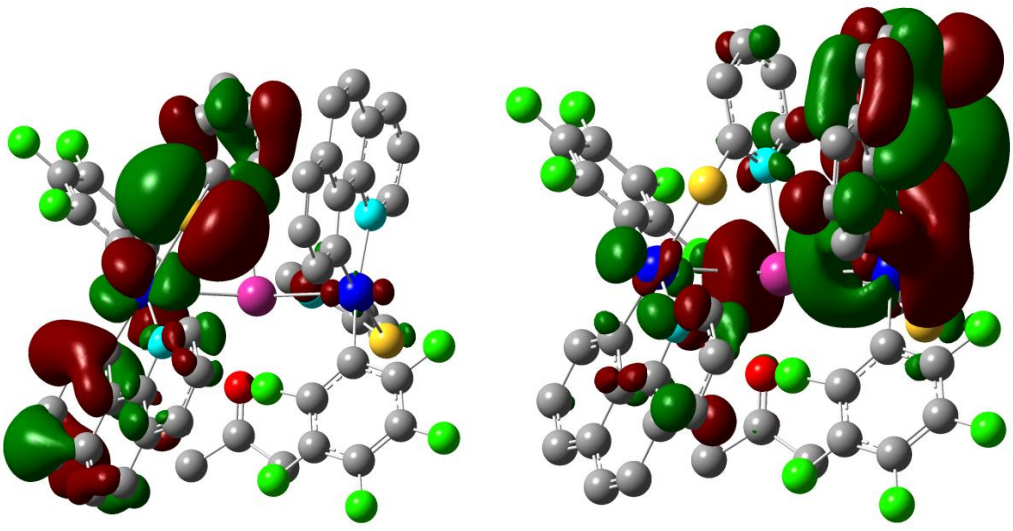


Fig. S19 Frontier MOs of **1** optimized in the ground state.



LUMO+1 LUMO+2 LUMO+3



HOMO LUMO

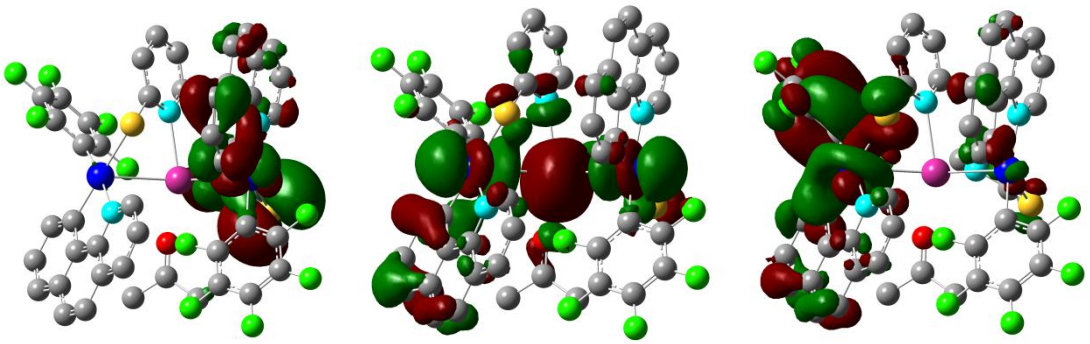


Fig. S20 Frontier MOs of **2** optimized in the ground state.

Table S8. NBO analysis of Pb(II) for **1** and **2**

	Natural electron configuration	Lone pair NBO on Pb	Lone pair occupancy
1 (S_0)	6s(1.83) 6p(0.78) 7p(0.03)	s(97.58%) p 0.02(2.42%)	1.86803
1 (T_1)	6s(1.84) 6p(0.96) 7p(0.02)	s(97.97%) p 0.02(2.03%)	0.93504
		s(97.90%) p 0.02(2.10%)	0.93663
2 (S_0)	6s(1.81) 6p(0.68) 7p(0.02)	s(99.66%) p 0.00(0.34%)	1.81125
2 (T_1)	6s(1.81) 6p(0.77) 7p(0.03)	s(99.17%) p 0.01(0.83%)	0.91419
		s(99.39%) p 0.01(0.61%)	0.91223

1 (S_0) → $sp^{0.025}$

1 (T_1) → $sp^{0.021}$

2 (S_0) → $sp^{0.003}$

2 (T_1) → $sp^{0.008}$, $sp^{0.006}$

Table S9 Composition (%) of molecular orbitals for the computed T_1 states of **1** and **2**

1

eV	Symmetry		Pt(1)	bzq(1)	Spy(1)	Pb	Pt(2)	bzq(2)	Spy(2)	C_6F_5
252	HSOMO-3.35	A	15	37	3	25	6	4	8	2
251	LSOMO-4.59	A	25	25	48	0	0	1	0	1

2

eV	Symmetry	Pt(1)	bzq(1)	Spy(1)	Pb	Pt(2)	bzq(2)	Spy(2)	C_6F_5	Acetone
268	HSOMO-3.17	3	2	6	11	11	64	1	2	0
267	LSOMO-4.53	0	0	1	0	20	44	35	0	0