Supporting Information

Multi-Stimuli Responsive Properties of Aggregated Isocyanide Cycloplatinated(II) Complexes

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1.- Experimental section

**General comments.** All reactions were carried out under an atmosphere of dry N₂, using standard Schlenk techniques. Solvents were obtained from a solvent purification system (M-BRAUN MB SPS-800). Elemental analyses were carried out with a Carlo Erba EA1110 CHNS-O or a Perkin-Elmer CHNS/O 2400 Series II microanalyzer. Mass spectra were recorded on a Microflex MALDI-TOF Bruker (MALDI) spectrometer operating in the linear and reflector modes using dithranol as matrix or on a HP-5989B mass spectrometer (ESI). IR spectra of powders (3) were obtained on a Perkin Elmer Spectrum UATR Two FT-IR Spectrometer with the diamond crystal ATR accessory covering the region between 4000 and 450 cm⁻¹. IR spectra of 1 and 2 (Nujol emulsions) were obtained on a Nicolet Nexus FT-IR Spectrometer covering the region between 4000 and 200 cm⁻¹. NMR spectra were recorded on a Bruker Avance 400 spectrometer at 293 K. Chemical shifts are reported in parts per million (ppm) relative to external standards (SiMe₄), and all coupling constants are given in hertz (Hz). NMR labelling is given in Scheme 1. The UV-vis absorption spectra were measured with a Hewlett-Packard 8453 spectrophotometer. Diffuse Reflectance UV-vis (DRUV) spectra were carried out in SiO₂ pellets, using a Shimadzu UV-3600 spectrophotometer with a Harrick Praying Mantis accessory, and recalculate following the Kubelka Munk function. Excitation and emission spectra were obtained in a Shimadzu RF-60000. The measurements in solid state and PS films were carried out on air and in solutions under N₂ atmosphere. The lifetime measurements up to 10 µs at 298 K at all samples at 77 K were performed with a Jobin Yvon Horiba Fluorolog operating in the phosphorimeter mode (with an F1-1029 lifetime emission PMT assembly, using a 450 W Xe lamp) and the Jobin Yvon software packing, that works with Origin 6.0. The decay data were analysed by tail fitting to the functions “One-phase exponential decay function with time constant parameter” (ExpDec1) and “Two-phase exponential decay function with time constant parameters (ExpDec2)” The lifetimes below 10 µs at 298 K were measured with a Datastation HUB-B with a nanoLED controller, using the technique “Time Correlated Single Photon Counting” (TCSPC). The nanoLEDs employed for lifetime measurements were of 450, 390 and 370 nm with pulse lengths of 0.8–1.4 ns. The decay data were treated with the software DAS6 (Jobin Yvon-Horiba). In our hands, the estimated uncertainty in the phosphorimeter mode is ±10% or better and with the nanoLEDs is below ±5% of the quoted value. Quantum yields of solids, solutions and PS films were measured using a Hamamatsu Absolute PL
Quantum Yield Measurement System C11347-11. For all measurements ($\tau$ and $\phi$), the emission and/or excitation used are those indicated in each case in the Tables 2 and S10. The estimated uncertainty in the quantum yield in this way on the instrumentation employed is in our hands of $\pm1\%$ for very emissive samples and below $\pm5\%$ for weak emissive samples. The powder X-ray diffraction (XRD) patterns were obtained at room temperature by using a Rigaku Miniflex II with graphite-monochromated CuK$_\alpha$ operating at 30 kV and 15 mA. PXRD patterns were collected between 20 of $3^\circ$ and $60^\circ$ with a 20 stepping angle of 0.03 and an angle dwell of 1s. Thermogravimetric analysis (TGA) was performed under the N$_2$ atmosphere using a SDT2960 Simultaneous DTA-TGA instrument at atmospheric pressure with a $5^\circ$C/min heating rate. All digital images of pictures of the vapochromic changes and crystals were acquired by using a Nikon Eclipse Ti2 microscope and a Photometrics prime 95B 25 mm camera with objectives at 10x magnification (numerical aperture 0.45) and 40x (numerical aperture 0.95). The images were automatically stitched by the Nikon NIS-Elements AR image analysis software. The microscope was attached to an Edinburgh FLS 1000 fluorescence spectrometer where their luminescent spectra were obtained. Complexes $[\text{Pt(dfppy)(Hdfppy)}\text{Cl}]_1$, $[\text{Pt(dfppy)(\mu-Cl)}]_2$ and $[\text{Pt(ppy-CHO)(\mu-Cl)}]_2$ was prepared as reported in the literature. Other commercially available reagents were used as received.

Preparation of $[\text{Pt(ppy-CHO)(Hppy-CHO)}\text{Cl}]$ (1b). It was prepared using the same procedure as complex $[\text{Pt(dfppy)(Hdfppy)}\text{Cl}]_1$ by reaction of $\text{K}_2\text{PtCl}_4$ (1.804 g, 4.347 mmol) with 2 equiv. of 4-(2-pyridyl)benzaldehyde (1.593 g, 8.694 mmol) in a mixture of 2-ethoxyethanol and water (3:1, v/v; 50 mL) at 80 °C for 12 h. After cooling, the resulting orange precipitate was filtered off and washed consecutively with water (15 mL), ethanol (10 mL) and diethyl ether (10 mL) to give an orange solid (2.214 g, 85 %). IR (cm$^{-1}$): $\nu$(C=O) 1635 (vs). ESI(+): $m/z$ (%): 560 [M-Cl]$^+$ (100). Anal. Caled for C$_{24}$H$_{17}$ClN$_2$O$_2$Pt (595.95): C, 48.37; H, 2.88; N, 4.70. Found: C, 48.98; H, 2.96; N, 5.00. $^1$H NMR (400 MHz, CDCl$_3$, $\delta$) (tentatively assigned): 9.92 (s, CHO$_{\text{ppy-CHO}}$), 9.75 (s, CHO$_{\text{Hppy-CHO}}$), 9.68 (d, $J_{\text{H-H}} = 6.3$, $^3J_{\text{Pt-H}} = 47$, H$_{11}$ppy-CHO), 8.21 (d, $J_{\text{H-H}} = 7.7, 2$H, H$_{7/11}$Hppy-CHO), 8.07 (d, $J_{\text{H-H}} = 7.3, 3$H$_{\text{Hppy-CHO}}$), 7.84 (d, $J_{\text{H-H}} = 7.5, 4$H$_{\text{ppy-CHO}}$), 7.78 (d, $J_{\text{H-H}} = 7.7, 2$H, H$_{7/11}$Hppy-CHO), 7.72 (d, $J_{\text{H-H}} = 7.7, 3$H$_{\text{Hppy-CHO}}$), 7.63 (d, $J_{\text{H-H}} = 8.2, 3$H$_{\text{ppy-CHO}}$), 7.50 (t, $J_{\text{H-H}} = 7.3, 3$H$_{\text{Hppy-CHO}}$), 7.47-7.44 (m, H$_9$, H$_8$), 7.21 (d, $J_{\text{H-H}} = 6.4, 3$H$_{\text{ppy-CHO}}$), 6.69 (s, $^3J_{\text{Pt-H}} = 47, 4$H$_{11}$ppy-CHO).
Preparation of [Pt(dfppy)Cl(CNBu)] (1a). To a yellow suspension of [Pt(dfppy)(Hdfppy)Cl] (0.665 g, 1.087 mmol) in CH₂Cl₂ (15 mL), CNBu (0.122 mL, 1.087 mmol) was added to give an orange-yellow solution. After 90 min of stirring, the solution was concentrated to 5 mL. After 1 h of stirring, the suspension was filtered through celite, [Pt(dfppy)(CNBu)] (0.065 g, 0.233 mmol) was filtered, which was proposed as the double salt [Pt(dfppy)(CNBu)][Pt(dfppy)Cl₂] (2a). The filtrate was evaporated to dryness and the yellow residue was treated with hexane (15 mL) to give 1a as a yellow-orange solid (0.481 g, 88 %). Compound 1a: IR (cm⁻¹, Nujol): ν(C≡N) 2207 (vs); ν(Pt-Cl) 289 (w). ESI (+): m/z (%): 468 [M-Cl]⁺ (100), 971 [2M-Cl]⁺ (37). Anal. Calcd for C₁₆H₁₅ClF₂N₂Pt (503.84): C, 38.14; H, 3.00; N, 5.56. Found: C, 38.49; H, 3.40; N, 6.07. Not enough soluble to be characterized by NMR spectroscopy.

Preparation of [Pt(dfppy)Cl(CNBu)] (1a). To a yellow suspension of [Pt(dfppy)(Hdfppy)Cl] (0.665 g, 1.087 mmol) in CH₂Cl₂ (10 mL), CNBu (0.122 mL, 1.087 mmol) was added to give an orange-yellow solution. After 90 min of stirring, the solvent was evaporated to dryness. The residue was treated with 30 mL of toluene and an insoluble red solid (0.050 g, 4.5 %) was filtered, which was proposed as the double salt [Pt(dfppy)(CNBu)] [Pt(dfppy)Cl₂] (2a). The filtrate was evaporated to dryness and the yellow residue was treated with hexane (15 mL) to give 1a as a yellow-orange solid (0.481 g, 88 %). Compound 1a: IR (cm⁻¹, Nujol): ν(C≡N) 2207 (vs); ν(Pt-Cl) 289 (w). ESI (+): m/z (%): 468 [M-Cl]⁺ (100), 971 [2M-Cl]⁺ (37). Anal. Calcd for C₁₆H₁₅ClF₂N₂Pt (503.84): C, 38.14; H, 3.00; N, 5.56. Found: C, 38.49; H, 3.40; N, 6.07. Not enough soluble to be characterized by NMR spectroscopy.
solvent was evaporated to dryness and treated with 30 mL of toluene, precipitating a yellow solid (0.04 g, 2.2 %), which was filtered and proposed as the double salt [Pt(ppy-CHO)(CNBu')$_2$][Pt(ppy-CHO)Cl$_2$] (2b). The filtrate was evaporated to dryness and treated with 15 mL of n-hexane, to give a red solid (0.321 g, 85 %) corresponding to 1b·0.5 Toluene (confirmed by TGA, elemental analysis and X-ray). When 1b·0.5 Toluene was dissolved in CH$_2$Cl$_2$ (10 mL), evaporated to dryness and treated with n-hexane (10 mL), a yellow-orange solid (0.304 g, 83 %) was obtained corresponding to 1b. IR (cm$^{-1}$, Nujol): 1b $\nu$(C≡N) 2205 (vs); $\nu$(Pt-Cl) 289 (w). Anal. Calcd for 1b C$_{17}$H$_{17}$ClN$_2$O$_2$Pt (495.87): C, 41.18; H, 3.46; N, 5.65. Found: C, 41.60; H, 3.81; N, 5.95.

IR (cm$^{-1}$) 1b·0.5 Toluene, $\nu$(C≡N) 2202 (vs). Anal. Calcd for 1b·0.5 Toluene C$_{20.5}$H$_{21}$ClN$_2$O$_2$Pt (541.94): C, 45.43; H, 3.91; N, 5.17. Found: C, 45.39; H, 3.59; N, 5.22.

ESI (+): m/z (%): 460 [M-Cl]$^+$ (47), 956 [2M-Cl]$^+$ (100). 1H NMR (400 MHz, CDCl$_3$, $\delta$): 9.91 (s, CHO), 9.50 (d, $J_{H-H} = 5.8$, $J_{Pt-H} = 34$, H$_2$, 3J$_{Pt-H} = 68$, H$_{11}$), 7.92-7.86 (m, H$_4$, 3J$_{Pt-H} = 67$, H$_{10}$), 7.75 (d, $J_{H-H} = 7.7$, H$_5$), 7.61-7.52 (m, H$_9$, H$_8$), 7.31 (t, $J_{H-H} = 6.4$, H$_3$), 1.70 (s, 9H, CH$_3$, Bu$^t$).

13C{$^1$H} NMR (100.6 MHz, CDCl$_3$, $\delta$): 192.2 (s, CHO$_{ppy-CHO}$), 164.6 (s, 2J$_{Pt-C} = 94$, C$_6$$_{ppy-CHO}$), 149.8 (s, 2J$_{Pt-C} = 37$, C$_7$$_{ppy-CHO}$), 149.2 (s, 2J$_{Pt-C} = 21$, C$_2$$_{ppy-CHO}$), 141.1 (s, 1J$_{C-Pt} = 1029$, C$_{ppy-CHO}$), 140.4 (s, C$_4$$_{ppy-CHO}$), 137.3 (s, 3J$_{Pt-C} = 67$, C$_{10}$$_{ppy-CHO}$), 136.2 (s, 2J$_{Pt-C} = 110$, C$_{11}$$_{ppy-CHO}$), 126.7 (s, C$_9$$_{ppy-CHO}$), 124.2 (s, 3J$_{Pt-C} = 40$, C$_8$$_{ppy-CHO}$), 123.5 (s, 3J$_{Pt-C} = 27$, C$_3$$_{ppy-CHO}$), 119.8 (s, 3J$_{Pt-C} = 34$, C$_5$$_{ppy-CHO}$), 118.4 (s, 1J$_{Pt-C} = 1823$, C≡N), 59.0 (m, C(CH$_3$)$_3$, Bu$^t$), 30.3 (s, CH$_3$ Bu$^t$).

Compound 2b: MALDI-TOF (+): m/z (%): 543 (100) [Pt(ppy-CHO)(CNBu$^t$)$_2$]$^+$; MALDI-TOF (-): m/z (%): 447 (100) [Pt(ppy-CHO)Cl$_2$]$^-$. IR (cm$^{-1}$, Nujol): $\nu$(C≡N) 2242 (s), 2218 (s). Anal. Calcd for C$_{34}$H$_{34}$Cl$_2$N$_4$O$_2$Pt$_2$ (991.7): C, 41.18; H, 3.46; N, 5.65. Found: C, 40.98; H, 3.12; N, 5.39. Not enough soluble to be characterized by NMR spectroscopy.

Alternative reaction between (NBu$_4$)[Pt(ppy-CHO)Cl$_2$] [prepared with [Pt(ppy-CHO)(µ-Cl)]$_2$ and 2 equiv. of NBu$_4$Cl in MeOH at reflux (12h)] and [Pt(ppy-CHO)(CNBu$^t$)$_2$]ClO$_4$ dissolved in acetone, gave a deep yellow solid, which is a mixture of 2b and 1b.

**Preparation of [Pt(dfppy)(CNBu$^t$)$_2$]ClO$_4$ (3a).** To a yellow suspension of [Pt(dfppy)(Hdfppy)Cl] (0.303 g, 0.495 mmol) in CH$_2$Cl$_2$ (10 mL)/acetone (10 mL) was added excess of KClO$_4$ (0.686 g, 4.95 mmol). After 30 min of stirring, tert-butylisocyanide (0.123 mL, 1.088 mmol) (1:2.2) was added to give a red suspension, which gradually became yellow after 2 h. Then, the mixture was evaporated to dryness.
and extracted with CH$_2$Cl$_2$/H$_2$O (1/1) (3 x 40 mL). The organic phase was dried over Mg$_2$SO$_4$ and filtered through celite. The solvent was removed under reduced pressure and the residue was treated with hexane (20 mL) to afford a pale-yellow solid (0.284 g, 88%). IR (cm$^{-1}$): ν(C≡N) 2236 (vs), ν(C≡N) 2215 (vs); ν(ClO$_4$) 1085 (vs), 622 (s). ESI(+): m/z (%): 551 (100) [M-ClO$_4$]$^+$. Anal. Calcd for C$_{21}$H$_{24}$ClF$_2$N$_3$O$_3$Pt (650.97): C, 38.75; H, 3.72; N, 5.45. Found: C, 38.50; H, 3.45; N, 5.92. $^1$H NMR (400 MHz, CDCl$_3$, δ): 8.90 (d, $J_{H-H}$ = 5.8, $^3J_{Pt-H}$ = 39, H$^2$), 8.14 – 8.02 (m, 2H, H$^5$, H$^4$), 7.73 (t, $J_{H-H}$ = 6.0, H$^3$), 6.91 (dd, $J_{H-H}$ = 2.4, $^3J_{Pt-H}$ = 7.9, $^3J_{Pt-H}$ = 68, H$^{11}$), 6.66 (ddd, $J_{H-H}$ = 2.4, $^3J_{Pt-H}$ = 8.7, $^3J_{Pt-H}$ = 11.6, H$^9$), 1.76 (s, 9H, CH$_3$, Bu$^3$), 1.75 (s, 9H, CH$_3$, Bu$^3$). $^{13}$C($^1$H) NMR (100.6 MHz, CDCl$_3$, δ): 163.6 (dd, $^1J_{C-F}$ = 258, $^3J_{Pt-C}$ = 12, C$^{10}_{ddppy}$), 163.0 (d, $^2J_{Pt-C}$ = 76, $^3J_{C-F}$ = 7.3, C$^6_{ddppy}$), 160.3 (dd, $^1J_{C-F}$ = 262, $^3J_{Pt-C}$ = 13, C$^8_{ddppy}$), 154.7 (s, $^2J_{Pt-C}$ = 33, C$^2_{ddppy}$), 152.0 (d, $^3J_{C-F}$ = 6.9, $^1J_{C-Pt}$ = 884, C$^{12}_{ddppy}$), 142.1 (s, C$^4_{ddppy}$), 131.9 (m, C≡N$_{trans-C}$), 130.3 (m, $^2J_{Pt-C}$ = 98, C$^7_{ddppy}$), 126.1 (s, $^3J_{Pt-C}$ = 33, C$^3_{ddppy}$), 123.3 (d, $^4J_{C-F}$ = 22, $^3J_{Pt-C}$ = 51, C$^5_{ddppy}$), 119.6 (dd, $^2J_{C-F}$ = 20, $^4J_{C-F}$ = 2.7, C$^{11}_{ddppy}$), 112.0 (d, C≡N$_{trans-N}$), 103.0 (t, $^1J_{C-F}$ = 26, C$^9_{ddppy}$), 60.7 (s, C(CH$_3$)$_3$, Bu$^3$), 60.6 (m, C(CH$_3$)$_3$, Bu$^3$), 30.1 (s, CH$_3$ Bu$^3$), 29.9 (s, CH$_3$ Bu$^3$). $^{19}$F NMR (376.5 MHz, CDCl$_3$, δ): -105.4 (m, $^4J_{F-Pt}$ = 50, F$^{10}$), -107.2 (m, $^4J_{F-Pt}$ = 40, F$^8$).

**Preparation of [Pt(ppy-CHO)(CNBu$^3$)$_2$]ClO$_4$ (3b).** This compound was prepared as a pale yellow solid (0.330 g, 83%) following the procedure described for 3a using a yellow suspension of [Pt(ppy-CHO)(Hppy-CHO)Cl] (0.367 g, 0.616 mmol) in CH$_2$Cl$_2$ (10 mL)/acetone (10 mL) with an excess of KClO$_4$ (0.853 g, 6.16 mmol). IR (cm$^{-1}$): ν(C≡N) 2223 (vs), ν(C≡N) 2248 (vs); ν(ClO$_4$) 1085 (vs), 624 (s). ESI(+): m/z (%): 543 [M-ClO$_4$]$^+$ (63). Anal. Calcd for C$_{22}$H$_{26}$ClF$_2$N$_3$O$_3$Pt (643.00): C, 41.10; H, 4.08; N, 5.51. Found: C, 41.05; H, 3.95; N, 5.06. $^1$H NMR (400 MHz, CD$_2$Cl$_2$, δ): 10.01 (s, CHO), 8.78 (d, $J_{H-H}$ = 5.3, $^3J_{Pt-H}$ = 41, H$^2$), 8.19 (t, $J_{H-H}$ = 7.6, H$^4$), 8.06 (s, $^3J_{Pt-H}$ = 53, H$^{11}$), 8.03 (d, $J_{H-H}$ = 8.4, H$^9$), 7.87 (d, $J_{H-H}$ = 8.0, H$^8$), 7.77 (dd, $J_{H-H}$ = 7.9, H$^3$), 7.63 (t, $J_{H-H}$ = 6.1, H$^1$), 1.77 (s, 9H, CH$_3$, Bu$^3$), 1.73 (s, 9H, CH$_3$, Bu$^3$). $^{13}$C($^1$H) NMR (100.6 MHz, CD$_2$Cl$_2$, δ): 191.7 (s, CHO$_{ppy-CHO}$), 165.3 (s, C$^6_{ppy-CHO}$), 153.5 (s, C$^2_{ppy-CHO}$), 152.2 (s, C$^7_{ppy-CHO}$), 149.2 (s, C$^{12}_{ppy-CHO}$), 142.2 (s, C$^4_{ppy-CHO}$), 137.5 (s, C$^{10}_{ppy-CHO}$), 136.2 (s, C$^{11}_{ppy-CHO}$), 129.4 (s, C$^9_{ppy-CHO}$), 126.5 (s, C$^3_{ppy-CHO}$), 124.9 (s, C$^8_{ppy-CHO}$), 121.5 (s, C$^5_{ppy-CHO}$), 60.8 (s, C(CH$_3$)$_3$, Bu$^3$), 60.5 (s, C(CH$_3$)$_3$, Bu$^3$), 29.8 (s, CH$_3$ Bu$^3$), 29.7 (s, CH$_3$ Bu$^3$).

**X-ray Crystallography.** Details of the X-ray analyses are summarized in Tables S1-S5.

Yellow (1a and 1b), red (1b·0.5Toluene and 1b·0.5Fluorobenzene (PhF)) and pale
yellow (3a·0.25CH₂Cl₂) crystals were obtained by slow diffusion of n-hexane into solutions of the complexes in CH₂Cl₂ (1a, 3a·0.25CH₂Cl₂), THF (1b), toluene (1b·0.5Toluene) and fluorobenzene (1b·0.5PhF) at room temperature. Slow evaporation of a CHCl₃ solution of 1a·CHCl₃ (298 K) gave pale-yellow crystals. The diffraction data were collected using graphite-monochromatic Mo-Kα radiation with a Bruker APEX-II diffractometer at 298 K (1a, 1a·CHCl₃ and 3a·0.25CH₂Cl₂) and 100 K (1b, 1b·0.5Toluene and 1b·0.5PhF) using the APEX-II software. The structures were solved with the WINGX program suite⁵ by intrinsic phasing using SHELXT program⁶ and refined by full-matrix least squares on F² with SHELXL.⁷ All non-hydrogen atoms were assigned anisotropic displacement parameters. All the hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters equal to 1.2 times the Uiso value of their respective attached carbon for the aromatic and CH₂ hydrogen atoms, except those of methyl groups, which were fixed to 1.5 times the Uiso value of their attached carbons. For 1a·CHCl₃, 1b·0.5Toluene, 1b·0.5PhF and 3a·0.25CH₂Cl₂, one CHCl₃ molecule, a half toluene and fluorobenzene molecule and a 0.25 dichloromethane molecule, respectively, were properly resolved from the difference density map. During the refinement, several restraints and constraints had to be applied. DFIX, FLAT, EADP, RIGU and TWIN/BASF instructions were employed to model the molecules' geometry and temperature parameters. For 1a, the planarity of the disordered phenyl ring fragment was reached with FLAT and EADP. For 1a·CHCl₃, the tertbutyl group was modelled as a rotational disorder over two positions in 50:50 ratios. The 3a·0.25CH₂Cl₂ data included instructions DFIX restraining two C-C bonds of two tertbutyl and three Cl-O bonds in perchlorate anions to have equal lengths. Moreover, four tertbutyl moieties EADP constrains were applied to chemically equivalent atoms. One of the perchlorate anion (ClO₄⁻) was obtained as a distorted fragment and RIGU restraints was applied to the Uif coefficients of this anion. In 1a, 1b·0.5Toluene and 1b·0.5PhF, the twinning was treated with the appropriate TWIN law and BASF parameter to refine the twin components due to a small but non-zero Flack parameter.

**Computational details.** Calculations were carried out with the Gaussian 16 package⁸ for compounds 1a, 1b and 3a, using Becke’s three-parameter functional combined with Lee-Yang-Parr’s correlation functional (B3LYP).⁹ Optimizations on the singlet state (S₀) were performed using as a starting point the molecular geometry obtained through X-ray diffraction analysis. No negative frequency was found in the vibrational frequency
analysis of the final equilibrium geometries. The basis set used was the LanL2DZ effective core potential for Pt and 6-31G(d,p) for the ligand atoms. DFT and TD-DFT calculations were carried out using the polarized continuum model approach (PCM) implemented in the Gaussian 16 software, in the presence of dichloromethane. To study the packing interaction, the dimeric, trimeric and tetrameric \( 1\text{a} \) and \( 1\text{b} \) geometries in the ground (\( S_0 \)) and the first triplet excited (\( T_1 \)) were optimized in gas phase based on \( 1\text{a} \) and \( 1\text{b·0.5Toluene} \) crystals structures by using a pair of symmetry-related platinum(II) moieties (dimers), trimers and tetramers with the shortest intermolecular Pt···Pt distance. In \( 1\text{b·0.5Toluene} \), as the solvated molecules of toluene were found to exert insignificant influence on the calculated results, the calculations were performed without considering the toluene molecules. The calculations were carried out through the Grimme approach using atom pair-wise additive schemes using dispersion-corrected B3LYP-D3 method to elucidate the dispersion effects for non-bonding interaction. The emission energy was calculated as the difference of the optimized \( T_1 \) and \( S_0 \) state in the optimized \( T_1 \) geometry (adiabatic electronic transition). The results were visualized with GaussView 6. Overlap populations between molecular fragments were calculated using the GaussSum 3.0 software.
2.- Characterization of complexes

Figure S1. NMR spectra of 1a in CDCl₃ at 298 K, (a) $^1$H, (b) $^{13}$C {$^1$H}. 

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Figure S2. NMR spectra of 1b in CDCl₃ (0.4 M) at 298 K, (a) ¹H, (b) ¹³C{¹H}.
Figure S3.- MALDI-TOF spectra of 2a a) in the positive mode and b) in the negative mode
Figure S4.- MALDI-TOF spectra of 2b a) in the positive mode and b) in the negative mode.
Figure S5. NMR spectra of 3a in CDCl₃ at 298 K, (a) $^1$H, (b) $^{13}$C{$^1$H}. 
Figure S6. NMR spectra of 3b in CD$_2$Cl$_2$ at 298 K, (a) $^1$H, (b) $^{13}$C{$^1$H}. 
### 3.- Crystal Structures

#### Table S1. X-ray Crystallographic Data for 1a and 1a·CHCl₃.

|                  | 1a                     | 1a·CHCl₃                |
|------------------|------------------------|-------------------------|
| **Empirical formula** | C₁₆H₁₅ClF₂N₂Pt        | C₁₇H₁₆C₄F₂N₂Pt         |
| **F<sub>W</sub>** | 503.84                 | 623.21                  |
| **T (K)**        | 298(2)                 | 293(2)                  |
| **Wavelength (Å)** | 0.71076                | 0.71076                 |
| **Crystal system** | Monoclinic             | Monoclinic              |
| **Space group**  | P 2₁/c                 | P 2₁/n                  |
| **Crystal size (mm<sup>3</sup>)** | 0.31 x 0.10 x 0.04 | 0.35 x 0.09 x 0.09 |
| **a (Å)**        | 7.1648(6)              | 7.1424(2)               |
| **b (Å)**        | 17.3048(12)            | 17.0802(5)              |
| **c (Å)**        | 26.219(2)              | 17.3858(6)              |
| **α (°)**        | 90                     | 90                      |
| **β (°)**        | 90.408(3)              | 95.8610(10)             |
| **γ (°)**        | 90                     | 90                      |
| **V (Å<sup>3</sup>)** | 3250.7(4)            | 2109.87(11)             |
| **Z**            | 8                      | 4                       |
| **D<sub>calc</sub> (Mg/m<sup>3</sup>)** | 2.059                 | 1.962                   |
| **Absorption coefficient (mm<sup>-1</sup>)** | 8.814                 | 7.178                   |
| **F(000)**       | 1904                   | 1184                    |
| **θ range for data collection (deg)** | 2.821 to 27.878 | 2.986 to 27.929 |
| **Index ranges** | h: -9<=h<=9, -          | k: -9<=k<=9, -          |
|                 | 22<=k<=22, -           | l: 22<=l<=22            |
| **Reflections collected** | 207979                | 111603                  |
| **Independent reflections** | 7771 [R(int) = 0.0554] | 5038 [R(int) = 0.0424] |
| **Data / restraints/parameters** | 7771 / 3 / 356 | 5038 / 0 / 262 |
| **Goodness-of-fit on F<sup>2</sup>** | 1.157                  | 1.052                   |
| **Final R indices** | R<sub>1</sub> = 0.0332 | R<sub>1</sub> = 0.0235 |
| **[I > 2σ(I)]<sup>a</sup>** | wR<sub>2</sub> = 0.0666 | wR<sub>2</sub> = 0.0598 |
| **R indices (all data)<sup>a</sup>** | R<sub>1</sub> = 0.0377, wR<sub>2</sub> = 0.0694 | R<sub>1</sub> = 0.0320, wR<sub>2</sub> = 0.0681 |
| **Largest diff. peak and hole (e. Å<sup>-3</sup>)** | 1.481 and -1.509 | 0.690 and -0.981 |

<sup>a</sup> R₁ = \( \frac{\sum|F_o| - |F_c|}{\sum|F_o|} \); wR<sub>2</sub> = \( \frac{\sum w(F_o^2 - F_c^2)^2/\sum wF_o^2}{1/2} \); goodness of fit = \( \frac{\sum[w(F_o^2 - F_c^2)]/(N_{obs} - N_{param})}{1/2} \); \( w = \sigma^2(F_o) + (g_1P)^2 + g_2P \); P = \[max(F_o^2 ; 0 + 2F_c^2)/3 \).
|                     | 1b                  | 1b·0.5 Toluene       | 1b·0.5 PhF            |
|---------------------|---------------------|----------------------|-----------------------|
| **Empirical formula** | C₁₇H₁₇ClN₂O²Pt      | C₂₀.₅₅H₂₁ClN₂O²Pt    | C₂₁₀H₁₉.₅₀ClF₀.₅₀N₂O²Pt |
| F<sub>W</sub>       | 495.86              | 541.93               | 543.91                |
| T (K)               | 100(2)              | 100(2) K             | 100(2) K              |
| Wavelength (Å)      | 0.71075             | 0.71076              | 0.71076               |
| Crystal system      | Orthorhombic        | Monoclinic           | Monoclinic            |
| Space group         | P n m a             | P 21                 | P 21                  |
| Crystal size (mm<sup>3</sup>) | 0.28 x 0.08 x 0.05 | 0.17 x 0.13 x 0.05   | 0.24 x 0.06 x 0.04    |
| a (Å)               | 16.347(2)           | 6.956(8)             | 6.9231(5)             |
| b (Å)               | 6.8397(9)           | 17.430(2)            | 17.1451(13)           |
| c (Å)               | 14.4809(19)         | 15.5724(19)          | 15.6681(11)           |
| α (°)               | 90                  | 90                   | 90                    |
| β (°)               | 90                  | 92.380(4)            | 92.561(3)             |
| γ (°)               | 90                  | 90                   | 90                    |
| V (Å<sup>3</sup>)   | 1619.1(4)           | 1886.4(4)            | 1857.9(2)             |
| Z                   | 4                   | 4                    | 4                     |
| D<sub>calc</sub> (Mg/m<sup>3</sup>) | 2.034              | 1.908               | 1.945                 |
| Absorption coefficient (mm<sup>-1</sup>) | 8.834              | 7.591               | 7.711                 |
| F(000)              | 944                 | 1044                 | 1044                  |
| θ range for data collection (deg) | 3.294 to 28.076    | 2.931 to 25.683      | 3.167 to 27.925       |
| Index ranges        | -21<=h<=21, -9<=k<=9, -19<=l<=19 | -8<=h<=8, -21<=k<=21, -18<=l<=18 | -9<=h<=9, -22<=k<=22, -20<=l<=20 |
| Reflections collected | 82601              | 56454               | 104182                |
| Independent reflections | 2107 [R(int) = 0.0314] | 7095 [R(int) = 0.0255] | 8827 [R(int) = 0.0250] |
| Data / restraints/ parameters | 2107 / 0 / 130    | 7095 / 1 / 461      | 8827 / 1 / 465        |
| Goodness-of-fit on F<sup>2</sup> a | 1.121              | 1.071               | 1.079                 |
| Final R indices     | R<sub>1</sub> = 0.0146 | R<sub>1</sub> = 0.0101 | R<sub>1</sub> = 0.0110 |
| [I > 2σ(I)]<sup>a</sup> | wR<sub>2</sub> = 0.0366 | wR<sub>2</sub> = 0.0246 | wR<sub>2</sub> = 0.0294 |
| R indices (all data)<sup>a</sup> | R<sub>1</sub> = 0.0189, wR<sub>2</sub> = 0.0372 | R<sub>1</sub> = 0.0102, wR<sub>2</sub> = 0.0247 | R<sub>1</sub> = 0.0111, wR<sub>2</sub> = 0.0295 |
| Largest diff. peak and hole (e. Å<sup>-3</sup>) | 0.979 and -1.737    | 0.528 and -0.559     | 1.910 and -0.606      |

<sup>a</sup> R<sub>1</sub> = Σ|F<sub,o</sub>|−|F<sub,c</sub>|/Σ|F<sub,o</sub>|; wR<sub>2</sub> = [Σw(F<sub,o</sub><sup>2</sup>−F<sub>c</sub><sup>2</sup>)<sup>2</sup>/ΣwF<sub,o</sub><sup>2</sup>]<sup>1/2</sup>; goodness of fit = {Σ[|F<sub,o</sub>|−F<sub>c</sub>|<sup>2</sup>]/N<sub>obs</sub> − N<sub>param</sub>})<sup>1/2</sup>; w = [σ²(F<sub,o</sub>)+g<sub>1</sub>P<sup>2</sup>+g<sub>2</sub>P]<sup>-1</sup>; P = [max(F<sub,o</sub><sup>2</sup>;0+2F<sub>c</sub><sup>2</sup>)<sup>3</sup>].
Table S3. Selected distances (Å) and angles (°) for complexes 1a, 1a·CHCl₃, 1b, 1b·0.5 Toluene and 1b·0.5 PhF

**1a (Molecule A)**

| Distances (Å) | Angles (°) |
|---------------|------------|
| Cl(1)-Pt(1)  | 2.385(2)   |
| N(1)-Pt(1)   | 2.054(3)   |
| N(1)-Pt(1)   | 1.986(3)   |
| C(12)-Pt(1)  | 1.921(7)   |
| C(12)-N(2)   | 1.134(8)   |
| C(5)-C(6)    | 1.459(9)  |

| Distances (Å) | Angles (°) |
|---------------|------------|
| Cl(2)-Pt(2)  | 2.39011(7) |
| N(3)-Pt(2)   | 2.048(5)   |
| C(27)-Pt(2)  | 1.993(6)   |
| C(28)-Pt(2)  | 1.911(6)   |
| C(28)-N(4)   | 1.144(8)   |
| C(22)-C(23)  | 1.397(10)  |

| Distances (Å) | Angles (°) |
|---------------|------------|
| Pt(1)-Cl(1)  | 2.3988(12) |
| Pt(1)-N(1)   | 2.054(3)   |
| Pt(1)-C(11)  | 1.986(4)   |
| Pt(1)-C(12)  | 1.898(4)   |
| C(12)-N(2)   | 1.140(5)   |
| C(5)-C(6)    | 1.467(6)   |

| Distances (Å) | Angles (°) |
|---------------|------------|
| Pt(1)-Cl(1)  | 2.39528(8) |
| Pt(1)-N(1)   | 2.057(3)   |
| Pt(1)-C(12)  | 1.992(3)   |
| C(13)-Pt(1)  | 1.894(3)   |
| N(2)-C(13)   | 1.150(4)   |
| C(5)-C(6)    | 1.460(5)   |

| Distances (Å) | Angles (°) |
|---------------|------------|
| Pt(1)-Cl(1)  | 2.4054(9)  |
| Pt(1)-N(1)   | 2.057(3)   |
| Pt(1)-C(12)  | 1.992(3)   |
| C(13)-Pt(1)  | 1.913(4)   |
| N(2)-C(13)   | 1.148(5)   |
| C(5)-C(6)    | 1.470(5)   |

**1a·CHCl₃**

| Distances (Å) | Angles (°) |
|---------------|------------|
| Pt(1)-Cl(1)  | 2.39528(8) |
| Pt(1)-N(1)   | 2.057(3)   |
| Pt(1)-C(12)  | 1.992(3)   |
| C(13)-Pt(1)  | 1.913(4)   |
| N(2)-C(13)   | 1.148(5)   |
| C(5)-C(6)    | 1.470(5)   |

**1b (Molecule B)**

| Distances (Å) | Angles (°) |
|---------------|------------|
| Pt(1)-Cl(1)  | 2.385(2)   |
| N(1)-Pt(1)   | 2.054(3)   |
| C(12)-Pt(1)  | 1.921(7)   |
| C(12)-N(2)   | 1.134(8)   |
| C(5)-C(6)    | 1.459(9)   |

| Distances (Å) | Angles (°) |
|---------------|------------|
| Cl(2)-Pt(2)  | 2.39011(7) |
| N(3)-Pt(2)   | 2.048(5)   |
| C(27)-Pt(2)  | 1.993(6)   |
| C(28)-Pt(2)  | 1.911(6)   |
| C(28)-N(4)   | 1.144(8)   |
| C(22)-C(23)  | 1.397(10)  |

| Distances (Å) | Angles (°) |
|---------------|------------|
| Pt(2)-Cl(2)  | 2.3968(9)  |
| Pt(2)-N(3)   | 2.062(3)   |
| Pt(2)-C(29)  | 1.990(4)   |
| Pt(2)-C(30)  | 1.909(4)   |
| N(4)-C(30)   | 1.151(5)   |
| C(22)-C(23)  | 1.468(5)   |

**1b·0.5 Toluene (Molecule A)**

| Distances (Å) | Angles (°) |
|---------------|------------|
| Pt(1)-Cl(1)  | 2.39528(8) |
| Pt(1)-N(1)   | 2.057(3)   |
| Pt(1)-C(12)  | 1.992(3)   |
| C(13)-Pt(1)  | 1.894(3)   |
| N(2)-C(13)   | 1.150(4)   |
| C(5)-C(6)    | 1.460(5)   |

| Distances (Å) | Angles (°) |
|---------------|------------|
| Pt(1)-Cl(1)  | 2.39528(8) |
| Pt(1)-N(1)   | 2.057(3)   |
| Pt(1)-C(12)  | 1.992(3)   |
| C(13)-Pt(1)  | 1.913(4)   |
| N(2)-C(13)   | 1.148(5)   |
| C(5)-C(6)    | 1.470(5)   |

**1b·0.5 Toluene (Molecule B)**

| Distances (Å) | Angles (°) |
|---------------|------------|
| Pt(2)-Cl(2)  | 2.3968(9)  |
| Pt(2)-N(3)   | 2.062(3)   |
| Pt(2)-C(29)  | 1.990(4)   |
| Pt(2)-C(30)  | 1.909(4)   |
| N(4)-C(30)   | 1.151(5)   |
| C(22)-C(23)  | 1.468(5)   |

**1b·0.5 PhF (Molecule A)**
### Distances (Å)

|                  |        |                  |        |
|------------------|--------|------------------|--------|
| \( \text{Cl}(1)-\text{Pt}(1) \) | 2.4001(9) | \( \text{N}(1)-\text{Pt}(1)-\text{Cl}(1) \) | 94.23(9) |
| \( \text{N}(1)-\text{Pt}(1) \) | 2.061(3) | \( \text{C}(12)-\text{Pt}(1)-\text{N}(1) \) | 80.88(14) |
| \( \text{C}(12)-\text{Pt}(1) \) | 1.988(4) | \( \text{C}(13)-\text{Pt}(1)-\text{C}(12) \) | 92.87(15) |
| \( \text{C}(13)-\text{Pt}(1) \) | 1.908(4) | \( \text{C}(13)-\text{Pt}(1)-\text{Cl}(1) \) | 92.02(11) |
| \( \text{C}(13)-\text{N}(2) \) | 1.152(5) | \( \text{N}(2)-\text{C}(13)-\text{Pt}(1) \) | 177.6(3) |
| \( \text{C}(5)-\text{C}(6) \) | 1.461(5) |                  |        |

### Angles (°)

|                  |        |                  |        |
|------------------|--------|------------------|--------|
| \( \text{Cl}(1)-\text{Pt}(1) \) | 2.4001(9) | \( \text{N}(1)-\text{Pt}(1)-\text{Cl}(1) \) | 94.23(9) |
| \( \text{N}(1)-\text{Pt}(1) \) | 2.061(3) | \( \text{C}(12)-\text{Pt}(1)-\text{N}(1) \) | 80.88(14) |
| \( \text{C}(12)-\text{Pt}(1) \) | 1.988(4) | \( \text{C}(13)-\text{Pt}(1)-\text{C}(12) \) | 92.87(15) |
| \( \text{C}(13)-\text{Pt}(1) \) | 1.908(4) | \( \text{C}(13)-\text{Pt}(1)-\text{Cl}(1) \) | 92.02(11) |
| \( \text{C}(13)-\text{N}(2) \) | 1.152(5) | \( \text{N}(2)-\text{C}(13)-\text{Pt}(1) \) | 177.6(3) |
| \( \text{C}(5)-\text{C}(6) \) | 1.461(5) |                  |        |

### 1b·0.5 PhF (Molecule B)

#### Distances (Å)

|                  |        |                  |        |
|------------------|--------|------------------|--------|
| \( \text{Cl}(2)-\text{Pt}(2) \) | 2.3935(9) | \( \text{N}(3)-\text{Pt}(2)-\text{Cl}(2) \) | 94.17(9) |
| \( \text{N}(3)-\text{Pt}(2) \) | 2.062(3) | \( \text{C}(29)-\text{Pt}(2)-\text{N}(3) \) | 80.78(14) |
| \( \text{C}(29)-\text{Pt}(2) \) | 1.988(4) | \( \text{C}(30)-\text{Pt}(2)-\text{C}(29) \) | 92.42(15) |
| \( \text{C}(30)-\text{Pt}(2) \) | 1.905(4) | \( \text{C}(30)-\text{Pt}(2)-\text{Cl}(2) \) | 92.66(11) |
| \( \text{C}(30)-\text{N}(4) \) | 1.153(5) | \( \text{N}(4)-\text{C}(30)-\text{Pt}(2) \) | 177.1(3) |
| \( \text{C}(22)-\text{C}(23) \) | 1.465(6) |                  |        |

#### Angles (°)

|                  |        |                  |        |
|------------------|--------|------------------|--------|
| \( \text{Cl}(2)-\text{Pt}(2) \) | 2.3935(9) | \( \text{N}(3)-\text{Pt}(2)-\text{Cl}(2) \) | 94.17(9) |
| \( \text{N}(3)-\text{Pt}(2) \) | 2.062(3) | \( \text{C}(29)-\text{Pt}(2)-\text{N}(3) \) | 80.78(14) |
| \( \text{C}(29)-\text{Pt}(2) \) | 1.988(4) | \( \text{C}(30)-\text{Pt}(2)-\text{C}(29) \) | 92.42(15) |
| \( \text{C}(30)-\text{Pt}(2) \) | 1.905(4) | \( \text{C}(30)-\text{Pt}(2)-\text{Cl}(2) \) | 92.66(11) |
| \( \text{C}(30)-\text{N}(4) \) | 1.153(5) | \( \text{N}(4)-\text{C}(30)-\text{Pt}(2) \) | 177.1(3) |
| \( \text{C}(22)-\text{C}(23) \) | 1.465(6) |                  |        |
### Table S4. X-ray Crystallographic Data for 3a·0.25CH₂Cl₂.

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| **Empirical formula**                        | C21.25H24.50C11.50F2 N3 O4 Pt              |
| Fₘ                                         | 672.20                                     |
| T (K)                                        | 298(2) K                                   |
| Wavelength (Å)                              | 0.71073 Å                                  |
| Crystal system                              | Triclinic                                  |
| Space group                                 | P -1                                       |
| Crystal size (mm³)                           | 0.170 x 0.160 x 0.140 mm³                  |
| a (Å)                                       | 14.3923(13)                                |
| b (Å)                                       | 14.4072(11)                                |
| c (Å)                                       | 26.822(2)                                  |
| α (°)                                       | 103.518(3)°                                |
| β (°)                                       | 104.516(3)°                                |
| γ (°)                                       | 95.340(3)°                                 |
| V (Å³)                                      | 5166.4(8)                                  |
| Z                                            | 8                                          |
| Dcalcd (Mg/m³)                              | 1.728                                      |
| Absorption coefficient (mm⁻¹)               | 5.631                                      |
| F(000)                                      | 2612                                       |
| θ range for data collection (deg)           | 2.962 to 25.682°                           |
| Index ranges                                | -17<=h<=17, -17<=k<=17, -32<=l<=32         |
| Reflections collected                       | 238281                                     |
| Independent reflections                     | 19517 [R(int) = 0.0396]                    |
| Data / restraints / parameters              | 19517 / 3 / 1112                           |
| Goodness-of-fit on F² a                     | 1.102                                      |
| Final R indices                             | R₁ = 0.0391                                 |
| [I > 2σ(I)]a                                 | wR₂ = 0.1045                               |
| R indices (all data)a                       | R₁ = 0.0527, wR₂ = 0.1171                  |
| Largest diff. peak and hole (e. Å⁻³)        | 1.604 and -1.109 e.Å⁻³                     |

* R₁ = 〈(F₀ - |Fc|)²〉/〈F₀²〉; wR₂ = (Σw(F₀² - F_c²)²/ΣwF₀²)¹/²; goodness of fit = (Σ{(w(F₀² - F_c²)²)/Nobs})¹/² / (Nobs - Nparam); w = {(σ²(F₀)² + (g₁P)² + g₂P)⁻¹}; P = [max(F₀² ; 0 + 2F_c²)] / 3.
Table S5. Selected distances (Å) and angles (°) for 3a·0.25CH₂Cl₂

|                      | Distances (Å) | Angles (°)          |
|----------------------|---------------|---------------------|
| Pt(1)-C(12)         | 1.940(9)      | C(12)-Pt(1)-C(17)   | 88.9(4) |
| Pt(1)-C(17)         | 2.011(10)     | C(12)-Pt(1)-C(11)   | 94.6(3) |
| Pt(1)-C(11)         | 2.019(7)      | C(17)-Pt(1)-N(1)    | 95.5(3) |
| Pt(1)-N(1)          | 2.042(6)      | C(11)-Pt(1)-N(1)    | 81.2(3) |
| C(12)-N(2)          | 1.139(10)     | N(2)-C(12)-Pt(1)    | 178.7(8) |
| C(17)-N(3)          | 1.133(12)     | N(3)-C(17)-Pt(1)    | 175.5(10)|
| C(6)-C(5)           | 1.451(10)     |                     |         |
| Pt···Pt             | 4.56 / 5.16 / 4.71 |                     |         |
| d_{interplanar}^a   | 3.391 / 3.538 |                     |         |

^a The shortest interplanar distance

The shortest interplanar distance
Figure S7. Different views of the crystal packing of 1a·CHCl₃ with the solvent channels marked in green. These channels have an aperture size of 11.1 Å x 10.3 Å (estimated from the diagonal atom pairs $F_2(1/2-x, -1/2+y, 1.5-z)$···$F_2(1/2+x, ½-y, -1/2+z)$ and $Cl_1(x,y,z)$···$Cl_1(1-x,-y,1-z)$) and the total void volume occupies 26.3% of the unit cell (calculated by the PLATON program).
Figure S8. Crystal packing of 1b·0.5 PhF, a) columnar stacking along the a axis showing the π⋯π interplanar and Pt–Pt distances. b) Pictures of crystals under daylight or UV irradiation. c) Top view from the a axis of five stackings showing the toluene solvent localization and secondary contacts. d) View of packing structure with the solvent channels marked in red along the a, b and c axis, respectively.
Figure S9. Different views of the crystal packing of 1b·0.5 Toluene with the solvent channels marked in red. The total solvent-accessible volume occupies 22.7 % of the total volume of the unit cell (or 213.7 Å³ per toluene molecule) for the 1b·0.5Toluene structure and 18.1 % for 1b·0.5PhF.

Figure S10. Top view of columns from the a axis in the single infinite crystal packing of 3a·0.25CH₂Cl₂.
**Figure S11.** Connectivity and crystal packing of 3b showing a head-to-head stacking of the cations in a columnar way along the a axis.

4.- Photophysical Properties and Theoretical Calculations

| Compound | Media | $\lambda_{\text{abs}}$/nm ($\varepsilon \times 10^{-3}$ M$^{-1}$ cm$^{-1}$) |
|----------|-------|---------------------------------------------------------------------|
| 1a       | CH$_2$Cl$_2$ | 243 (45.9), 267 (22.8), 312 (12.8), 322 (13.9), 362 (4.2), 379 (3.4) |
|          | THF    | 243 (43.7), 255$_{\text{sh}}$ (21.4), 271 (15.8), 311 (9.4), 321 (11.3), 362 (2.9), 382 (2.7) |
| 1b       | CH$_2$Cl$_2$ | 252 (53.0), 297 (49.1), 322$_{\text{sh}}$ (24.1), 335 (20.3), 389 (6.9), 408 (6.3) |
|          | THF    | 251 (26.6), 301 (22.0), 322$_{\text{sh}}$ (11.4), 335 (8.6), 392 (3.1), 412 (3.3) |
| 3a       | CH$_2$Cl$_2$ | 237 (29.1), 263 (35.8), 309$_{\text{sh}}$ (9.4), 325 (8.8), 351 (4.4), 368 (2.7) |
| 3b       | CH$_2$Cl$_2$ | 239 (25.1), 278 (40.0), 287$_{\text{sh}}$ (32.8), 323 (10.8), 337 (12.9), 360 (6.3), 375 (4.7) |
Figure S12. Normalized absorption spectra of complexes 1a and 1b in CH$_2$Cl$_2$ and THF (5 × 10$^{-5}$ M).
**Table S7.** DFT optimized geometries for ground state and triplet state of 1a, 1b and 3a in CH$_2$Cl$_2$.

|  |  |  |  |
|---|---|---|---|
| **1a** |  |  |  |
| Cl(1)-Pt(1) | 2.3988(12) | 2.508 | 2.508 |
| N(1)-Pt(1) | 2.054(3) | 2.093 | 2.060 |
| C(11)-Pt(1) | 1.986(4) | 2.009 | 1.981 |
| C(12)-Pt(1) | 1.898(4) | 1.923 | 1.934 |
| C(12)-N(2) | 1.141(5) | 1.166 | 1.166 |
| C(5)-C(6) | 1.466(6) | 1.466 | 1.394 |
| N(1)-Pt(1)-Cl(1) | 95.21(10) | 95.13 | 94.62 |
| C(11)-Pt(1)-N(1) | 80.85(16) | 80.45 | 81.49 |
| C(12)-Pt(1)-C(11) | 94.18(17) | 96.12 | 96.16 |
| C(12)-Pt(1)-Cl(1) | 89.75(13) | 88.31 | 87.72 |
| N(2)-C(12)-Pt(1) | 179.8(5) | 179.1 | 178.7 |

|  |  |  |  |
|---|---|---|---|
| **1b** |  |  |  |
| Pt(1)-Cl(1) | 2.3952(8) | 2.507 | 2.494 |
| Pt(1)-N(1) | 2.057(3) | 2.100 | 2.079 |
| Pt(1)-C(12) | 1.992(3) | 2.011 | 1.970 |
| Pt(1)-C(13) | 1.894(3) | 1.920 | 1.937 |
| N(2)-C(13) | 1.150(4) | 1.166 | 1.164 |
| C(5)-C(6) | 1.460(5) | 1.468 | 1.407 |
| N(1)-Pt(1)-Cl(1) | 96.59(8) | 94.72 | 94.25 |
| C(12)-Pt(1)-N(1) | 80.60(13) | 80.29 | 81.78 |
| C(12)-Pt(1)-C(11) | 91.81(13) | 96.19 | 95.96 |
| C(12)-Pt(1)-Cl(1) | 91.00(9) | 88.79 | 88.01 |
| N(2)-C(13)-Pt(1) | 175.7(3) | 179.0 | 178.3 |

|  |  |  |  |
|---|---|---|---|
| **3a** |  |  |  |
| N(1)-Pt(1) | 2.042(6) | 2.099 | 2.066 |
| C(11)-Pt(1) | 2.019(7) | 2.038 | 2.015 |
| C(12)-Pt(1) | 1.940(9) | 1.940 | 1.944 |
| C(17)-Pt(1) | 2.011(10) | 2.056 | 2.050 |
| C(12)-N(2) | 1.139(10) | 1.163 | 1.164 |
| C(17)-N(3) | 1.133(12) | 1.163 | 1.164 |
| C(5)-C(6) | 1.451(10) | 1.466 | 1.393 |
| N(1)-Pt(1)-C(17) | 95.5(3) | 96.25 | 96.02 |
| C(11)-Pt(1)-N(1) | 81.2(3) | 80.18 | 80.77 |
| C(12)-Pt(1)-C(11) | 94.6(3) | 93.74 | 93.66 |
| C(12)-Pt(1)-C(17) | 88.9(4) | 89.84 | 89.56 |
| N(2)-C(12)-Pt(1) | 178.7(8) | 179.54 | 179.48 |
| N(3)-C(17)-Pt(1) | 175.5(10) | 178.58 | 178.63 |
Figure S13. Selected frontier Molecular Orbitals for 1a in the ground state.
Figure S14. Selected frontier Molecular Orbitals for 1b in the ground state.
Figure S15. Selected frontier Molecular Orbitals for 3a in the ground state.
Table S8. Composition (%) of Frontier MOs in terms of ligands and metals in the ground state for 1a, 1b and 3a in CH₂Cl₂.

### 1a

| MO     | eV  | Pt | dfppy | CNBu¹ | Cl |
|--------|-----|----|-------|-------|----|
| LUMO+5 | 0.2 | 17 | 8     | 75    | 0  |
| LUMO+4 | 0.06| 15 | 52    | 33    | 0  |
| LUMO+3 | -0.53| 24 | 57    | 18    | 1  |
| LUMO+2 | -0.65| 45 | 31    | 15    | 8  |
| LUMO+1 | -1.1 | 1  | 98    | 1     | 0  |
| LUMO   | -1.98| 8  | 86    | 6     | 0  |
| HOMO   | -6.16| 30 | 55    | 0     | 15 |
| HOMO-1 | -6.57| 7  | 85    | 0     | 7  |
| HOMO-2 | -6.78| 92 | 5     | 1     | 2  |
| HOMO-3 | -6.95| 19 | 4     | 1     | 76 |
| HOMO-4 | -7.26| 25 | 36    | 3     | 35 |
| HOMO-5 | -7.37| 41 | 28    | 12    | 19 |

### 1b

| MO     | eV  | Pt | ppy-CHO | CNBu¹ | Cl |
|--------|-----|----|---------|-------|----|
| LUMO+5 | 0.05| 13 | 61      | 26    | 0  |
| LUMO+4 | -0.51| 26 | 53      | 20    | 1  |
| LUMO+3 | -0.58| 46 | 28      | 18    | 8  |
| LUMO+2 | -0.73| 2  | 97      | 1     | 0  |
| LUMO   | -1.45| 4  | 91      | 5     | 0  |
| LUMO   | -2.43| 4  | 94      | 2     | 0  |
| HOMO   | -6.14| 34 | 49      | 0     | 17 |
| HOMO-1 | -6.75| 89 | 8       | 1     | 1  |
| HOMO-2 | -6.84| 6  | 85      | 0     | 9  |
| HOMO-3 | -6.93| 18 | 10      | 1     | 71 |
| HOMO-4 | -7.12| 5  | 85      | 0     | 9  |
| HOMO-5 | -7.29| 27 | 39      | 4     | 30 |

### 3a

| MO     | eV  | Pt | dfppy | CNBu¹ |
|--------|-----|----|-------|-------|
| LUMO+5 | -0.38| 7  | 68    | 25    |
| LUMO+4 | -0.45| 16 | 9     | 76    |
| LUMO+3 | -1.11| 38 | 24    | 38    |
| LUMO+2 | -1.38| 23 | 44    | 33    |
| LUMO+1 | -1.51| 1  | 99    | 1     |
| LUMO   | -2.54| 13 | 73    | 14    |
| HOMO   | -6.77| 5  | 94    | 1     |
| HOMO-1 | -7.13| 14 | 83    | 2     |
| HOMO-2 | -7.59| 92 | 8     | 1     |
| HOMO-3 | -8.05| 56 | 30    | 14    |
| HOMO-4 | -8.57| 9  | 90    | 1     |
| HOMO-5 | -8.67| 48 | 39    | 13    |
Table S9. Selected vertical excitation energies singlets ($S_0$) and the first triplet computed by TDDFT/SCRF (CH$_2$Cl$_2$) with the orbitals involved for 1a, 1b and 3a.

| State | λ/nm  | f     | Transition (% Contribution)                                      |
|-------|-------|-------|-----------------------------------------------------------------|
| **1a** |       |       |                                                                  |
| T    | 436.99|       | H-1->LUMO (19%). HOMO->LUMO (66%)                                |
| T    | 363.04|       | H-1->LUMO (57%). HOMO->LUMO (27%)                                |
| T    | 334.42|       | H-1->LUMO (17%). H-1->L+1 (17%). HOMO->L+1 (37%). H-7->L+1 (9%) |
| S    | 359.98| 0.0533| HOMO->LUMO (97%)                                                 |
| S    | 316.84| 0.0125| H-2->LUMO (99%)                                                  |
| S    | 309.22| 0.1516| H-1->LUMO (90%)                                                  |
| S    | 284.02| 0.0256| H-4->LUMO (19%). HOMO->L+1 (72%)                                 |
| S    | 271.91| 0.0633| H-4->LUMO (11%). H-2->L+2 (69%)                                  |
| S    | 269.88| 0.1623| H-5->LUMO (17%). H-4->LUMO (40%). H-2->L+2 (23%)                 |
| S    | 265.02| 0.0267| H-5->LUMO (60%). H-4->LUMO (23%)                                 |
| S    | 254.28| 0.1231| H-5->LUMO (12%). H-1->L+1 (19%). HOMO->L+3 (58%)                 |
| **1b** |       |       |                                                                  |
| T    | 506.99|       | H-2->LUMO (16%). HOMO->LUMO (77%)                                |
| T    | 407.71|       | H-4->LUMO (60%). H-4->L+2 (11%). H-4->L+1 (8%)                   |
| T    | 404.86|       | H-2->LUMO (70%). HOMO->LUMO (17%)                                |
| S    | 401.18| 0.0772| HOMO->LUMO (97%)                                                 |
| S    | 357.88| 0.0022| H-4->LUMO (27%). H-1->LUMO (58%)                                 |
| S    | 346.86| 0.0038| H-4->LUMO (44%). H-1->LUMO (41%)                                 |
| S    | 318.01| 0.1864| H-2->LUMO (67%). HOMO->L+1 (28%)                                 |
| S    | 308.89| 0.1504| H-5->LUMO (13%). H-2->LUMO (22%). HOMO->L+1 (60%)                |
| S    | 293.41| 0.2144| H-5->LUMO (13%). H-5->LUMO (67%)                                 |
| S    | 286.14| 0.0529| H-6->LUMO (79%). H-5->LUMO (15%)                                 |
| **3a** |       |       |                                                                  |
| T    | 441.22|       | HOMO->LUMO (83%)                                                 |
| T    | 351.75|       | H-1->LUMO (92%)                                                  |
| T    | 338.38|       | H-4->L+1 (10%), HOMO->L+1 (62%)                                  |
| S    | 346.61| 0.0797| HOMO->LUMO (92%)                                                 |
| S    | 315.45| 0.1348| H-1->LUMO (89%)                                                  |
| S    | 296.76| 0.0226| H-2->LUMO (99%)                                                  |
| S    | 269.10| 0.0062| H-3->LUMO (40%), HOMO->L+1 (49%)                                 |
| S    | 261.01| 0.0027| H-1->L+3 (12%), HOMO->L+3 (80%)                                  |
| S    | 259.57| 0.2571| HOMO->L+2 (71%)                                                  |
| S    | 255.50| 0.4544| H-3->LUMO (47%), H-1->L+1 (10%), HOMO->L+1 (35%)                 |
| S    | 248.65| 0.0339| H-2->L+3 (63%), H-1->L+1 (23%)                                  |
| S    | 246.58| 0.1663| H-2->L+3 (24%), H-1->L+1 (50%), HOMO->L+2 (12%)                  |
| S    | 241.10| 0.0502| H-1->L+2 (82%)                                                  |
Figure S16. Calculated stick absorption spectra for 1a, 1b and 3a in the ground state in CH$_2$Cl$_2$ compared with the experimental data.
Figure S17. Low-energy region of the UV–vis absorption spectra of 1a in CH$_2$Cl$_2$ at different concentrations. c) Representation of the absorbance at the 390 nm band vs concentration.

Figure S18. $^1$H NMR spectra of 1b·0.5Toluene in CD$_2$Cl$_2$ at different concentrations.
**Table S10.** Photophysical data for compounds 1a, 1b, 3a and 3b in solution and in polystyrene film (PS).

| Compound | Media   | [M]    | T°/K | λ<sub>em</sub>/nm (λ<sub>ex</sub>/nm) | τ/µs | Φ     |
|----------|---------|--------|------|-----------------------------------|------|-------|
| 1a       | CH₂Cl₂  | 5x10⁻⁵ | 77   | 465<sup>a</sup>, 552<sub>max</sub>, 645 (365) 558, 645<sub>max</sub> (440) | 14.9 (465) 9.7 (552) 6.4 (645) |       |
|          | THF     | 5x10⁻⁵ | 77   | 460<sup>a</sup>, 558 (365) 460<sup>a</sup>, 564<sub>max</sub> (420) | 26.9 (460) 6.5 (564) |       |
|          | PS (10% wt) | 298 |       | 467<sup>a</sup>, 580<sub>max</sub> (385) 585 (410) 635 (480) | 0.2 (76%), 2.6 (24%) (467) 0.2 (59%), 1.3 (41%) (580) 0.2 (54%), 1.6 (46%) (635) | 0.06 (385) 0.19 (480) |
|          | PS (1% wt) | 298 |       | 467<sup>a</sup>, 570 (385) 575 (420) | 0.2 (65%), 2.1 (35%) (467) 0.2 (69%), 1.8 (31%) (575) | 0.05 |
| 1b       | CH₂Cl₂  | 5x10⁻⁴ | 298 | 529<sup>a</sup> (410) | 1.6<sup>b</sup> | 0.03 |
|          |         | 5x10⁻⁵ | 77   | 540<sup>a</sup>, 640 (440) | 14.8 (540) 10.1 (640) |       |
|          | THF     | 5x10⁻⁴ | 298 | 529<sup>a</sup> (415) | <1%<sup>b</sup> | 0.02 |
|          |         | 5x10⁻⁵ | 77   | 517<sup>a</sup> (415) | 26.0<sup>b</sup> |       |
|          | PS (10% wt) | 298 |       | 536<sup>a</sup> | 0.4 (24%), 6.6 (76%)<sup>b</sup> | 0.25 |
|          | PS (1% wt) | 298 |       | 524<sup>a</sup> | 1.0<sup>b</sup> | 0.27 |
| 3a       | CH₂Cl₂  | 5x10⁻⁴ | 298 | 471<sup>a</sup> (365) | 0.1 (24%), 0.7 (76%)<sup>b</sup> | 0.01 |
|          |         | 5x10⁻⁵ | 77   | 475<sup>a</sup>, 577 (365) 594 (420) | 39.1 (475) 6.6 (580) |       |
|          | PS (1% wt) | 298 |       | 474<sub>sh</sub>, 600<sub>max</sub> (365) | <1% (474) 1.8 (61%), 3.0 (39%) (600) | 0.27 |
| 3b       | CH₂Cl₂  | 5x10⁻⁴ | 298 | 511<sup>a</sup> (375) | 0.3 (12%), 3.1 (88%)<sup>b</sup> | 0.02 |
|          |         | 5x10⁻⁵ | 77   | 524<sup>a</sup> (385) 524<sup>a</sup>, 618 (420) | 24.5 (524) 14.5 (618) |       |
|          | PS (1% wt) | 298 |       | 524<sup>a</sup> | 3.2<sup>b</sup> | 0.09 |

<sup>a</sup>) the v₀→₀ transition of the structured emission,  <sup>b</sup>) Measured in the highest energy peak.
Figure S19. Normalized excitation (dashed line) and emission (solid line) spectra in PS at 1-10% wt at 298 K of 1b ($\lambda_{ex}$ 420 nm).

Figure S20. Normalized excitation (dashed line) and emission (solid line) spectra of 1b in CH$_2$Cl$_2$ (a) and THF (b) at 5×10$^{-4}$ M at 298 K (left) and at 5×10$^{-5}$ M at 77 K (right).
Figure S21. Emission spectra of 1b in CH$_2$Cl$_2$ at different concentrations at a) 298 K (5 x 10$^{-5}$ to 0.01 M, $\lambda_{ex}$ 420 nm; 0.01-0.4 M, $\lambda_{ex}$ 480 nm) and b) 77 K (5 x 10$^{-5}$ to 10$^{-3}$ M, $\lambda_{ex}$ 420 nm; 0.01-0.4 M, $\lambda_{ex}$ 520 nm). Images under UV light (365 nm).

Figure S22. Normalized excitation and emission spectra of 1a in CH$_2$Cl$_2$ 5 x 10$^{-4}$ M at 77 K.

Figure S23. Normalized excitation and emission spectra of 1a in THF 5 x 10$^{-4}$ M (a), 5 x 10$^{-5}$ M (b) at 77 K. Photographs taken under lamps of the $\sim\lambda_{exc}$ indicated.
Figure S24. Normalized emission spectra of 3a in CH₂Cl₂ at 5×10⁻⁴ M at 298 K (a) and 77 K (b).

Figure S25. Normalized emission spectra of 3b in CH₂Cl₂ at 5×10⁻⁴ M at 298 K (a) and 77 K (b).
Table S11. Composition (%) of Frontier MOs in terms of ligands and metals in the first triplet state for 1a, 1b and 3a in CH$_2$Cl$_2$.

### 1a

| MO     | eV  | Pt | dfppy | CNBu$^t$ | Cl |
|--------|-----|----|-------|----------|----|
| SOMO   | -3.61 | 6  | 91    | 2        | 1  |
| SOMO-1 | -4.64 | 9  | 90    | 0        | 1  |

### 1b

| MO     | eV  | Pt | ppy-CHO | CNBu$^t$ | Cl |
|--------|-----|----|---------|----------|----|
| SOMO   | -4  | 4  | 95      | 1        | 0  |
| SOMO-1 | -4.7 | 16 | 81      | 0        | 3  |

### 3a

| MO     | eV  | Pt | dfppy | CNBu$^t$ |
|--------|-----|----|-------|----------|
| SOMO   | -4.15 | 7  | 88    | 5        |
| SOMO-1 | -5.13 | 3  | 96    | 1        |

### Comparison

|        | 1a        | 1b        | 3a        |
|--------|-----------|-----------|-----------|
| Spin density on Pt | 0.137727 | 0.191229 | 0.084966 |
| E of emission ($T_1$-$S_0$ opt) | 521 nm   | 619 nm   | 531 nm   |
Figure S26. Frontier orbitals plots obtained by DFT for the first triplet state of 1a, 1b and 3a.
| Compound | \(\lambda_{abs}/\text{nm}\) |
|----------|------------------|
| 1a       | 238, 258, 320, 388, 425, 472, tail to 550 |
| 1a-CHCl\(_3\)-R | 288, 317, 370, 508, 545, tail to 600 |
| 1a-CHCl\(_3\)-G | 320, 370, 390, 435, 465, tail to 500 |
| 1a-CHCl\(_3\)-R with vapors of acetone | 288, 300, 318, 375, 410, 450, tail to 520 |
| 1a-CHCl\(_3\)-G-ground | 296, 318, 372, 393, 445, tail to 550 |
| 1a-CHCl\(_3\)-G-\(\Delta\) | 298, 320, 372, 393, 470, tail to 550 |
| 1a(THF) | 280, 315, 376, 449, tail to 520 |
| 1a(MeOH) | 280, 315, 375, 493, tail to 610 |
| 1a(EtOH) | 282, 319, 371, 505, tail to 610 |
| 1a(CHCl\(_3\)) | 320, 385, 461, 487, 510, 530, 550, tail to 630 |
| 1a(CH\(_2\)Cl\(_2\)) | 235, 270, 318, 368, 519, 560, tail to 650 |
| 1b       | 297, 335, 356, 398, 420, 493\(_{sh}\), 530\(_{sh}\), tail to 550 |
| 1b-ground | 297, 322, 342, 401, 427, 500\(_{sh}\), 530\(_{sh}\), tail to 550 |
| 1b-0.5Toluene | 297, 334, 373, 425, 509, 550, tail to 610 |
| 1b-0.5Toluene after 1 month | 297, 334, 395, 425, 550, tail to 610 |
| 1b-0.5Toluene with vapors of acetone | 297, 332, 357, 401, 422, 494\(_{sh}\), 532\(_{sh}\), tail to 550 |
| 2a       | 293, 321, 381, 425, 516, tail to 620 |
| 2b       | 293, 311, 333, 398, 420, tail to 500 |
| 3a       | 317, 353, 370, 404\(_{sh}\), 462\(_{sh}\), tail to 480 |
| 3a-0.25CH\(_2\)Cl\(_2\)) | 236, 328, 351, 373, 436\(_{sh}\), 476\(_{sh}\), tail to 485 |
| 3a-Acetone | 302, 319, 355, 370, 432\(_{sh}\), 525, tail to 600 |
| 3a-CHCl\(_3\)) | 279, 317, 334, 352, 370, 465\(_{sh}\), 530, tail to 610 |
| 3a-THF | 277, 317, 349, 370, 432\(_{sh}\), 462\(_{sh}\), 525, tail to 600 |
| 3b       | 283, 299, 315, 340, 358, 380, 440\(_{sh}\), tail to 480 |
Figure S27. Normalized excitation and emission spectra of 1a in solid state at 298 K (a) and 77 K (b).

Figure S28. Normalized excitation and emission spectra of 1a-CHCl₃-G (identical to the emission of crystals of 1a·CHCl₃) in solid state at 298 K (a) and 77 K (b).

Figure S29. Normalized excitation and emission spectra of 1a-CHCl₃-R in solid state at 298 K (a) and 77 K (b).
Figure S30. Thermogravimetric analysis (scan rate of 5 °C min$^{-1}$) of a) (1a-CHCl$_3$-R form), and b) (1a-CHCl$_3$-G form), revealing their composition as 1a·CHCl$_3$.

Figure S31. Photographs showing the color and the luminescence change of 1a-CHCl$_3$-G after grinding.
Figure S32. Plot of emission wavelength changes of 1a during 5-cycles of being exposed to CHCl₃ and acetone vapors. The procedure is accomplished by depositing a drop of 1a in acetone on a glass and letting it to dry, once the solid is dried (orange emission) its emission is measured from the glass holder. Then, the solid is exposed to the CHCl₃ vapor, producing a red-shift in the color of the solid and its emission. After measuring the new emission spectrum, the solid reverts to the initial color with acetone vapors. This procedure is carried out for five cycles without noticing an apparent change in the sample.

Figure S33. Normalized emission spectra of 1a solid and those solids obtained by evaporation of the appropriate solutions of 1a in different solvents at 77 K. (1a Solid and THF λⁿ 420 nm; MeOH and EtOH λⁿ 530 nm; CHCl₃ and CH₂Cl₂ λⁿ 570 nm).
Figure S34. Normalized excitation and emission spectra of 1b in solid state at 298 K (a) and 77 K (b).

Figure S35. Normalized excitation and emission spectra of 1b·0.5Toluene in solid state at 298 K (a) and 77 K (b).

Figure S36. Normalized excitation and emission spectra of 1b-ground in solid state at 298 K (a) and 77 K (b).
Figure S37. Thermogravimetric analysis (scan rate of 5 °C min⁻¹) of the pristine solid 1b after exposure to saturated vapors of toluene, revealing its composition as 1b·0.5Toluene.

Figure S38. Normalized emission and excitation spectra of 1b·0.5Toluene after one month exposed to air at 298 K.

Figure S39. Images of the red crystals in the PS film (10%) of 1b, obtained by exposition to toluene, after two months on standing at air. The left image has a magnification of 40x, while right image has a magnification of 10x.
Figure S40. Normalized emission spectra of 2a ($\lambda_{ex}$ 550 nm 298 K, $\lambda_{ex}$ 580 nm 77 K) (a) and 2b ($\lambda_{ex}$ 515 nm 77 K) (b) in solid state.

Figure S41. Emission spectra in solid state at 298 K and 77 K of 3a-pristine and 3a·0.25CH$_2$Cl$_2$ (a) and 3b-pristine (b).

Figure S42. a) Normalized excitation and emission spectra of vapochromic response of 3a-pristine in solid state at 298 K ($\lambda_{ex}$ 420-430 nm). b) Normalized absorption spectra calculated from their reflectance spectra in the solid state.
Figure S43. a) Normalized emission and excitation spectra of 3a-acetone (a) and 3a-CHCl₃ (b) in solid state at 77 K.

Table S13. Composition (%) of Frontier MOs in terms of ligands and metals in the ground state for 1a, [1a]₂, [1a]₃ and 1b, [1b]₄ in gas phase.

|       | MO       | eV   | Pt | dfppy | CNBu¹ | Cl |
|-------|----------|------|----|-------|-------|----|
| 1a    | LUMO+3   | -0.28| 44 | 30    | 15    | 10 |
|       | LUMO+2   | -0.37| 23 | 54    | 22    | 1  |
|       | LUMO+1   | -1.04| 1  | 98    | 1     | 0  |
|       | LUMO     | -1.88| 7  | 87    | 5     | 1  |
|       | HOMO     | -5.82| 30 | 32    | 0     | 37 |
|       | HOMO-1   | -6.34| 13 | 3     | 1     | 83 |
|       | HOMO-2   | -6.39| 2  | 88    | 0     | 10 |
|       | HOMO-3   | -6.63| 91 | 7     | 1     | 1  |

|       | MO       | eV   | Pt | dfppy | CNBu¹ | Cl |
|-------|----------|------|----|-------|-------|----|
| [1a]₂ | LUMO+3   | -0.91| 1  | 98    | 1     | 0  |
|       | LUMO+2   | -1.15| 1  | 97    | 1     | 0  |
|       | LUMO+1   | -1.57| 3  | 94    | 2     | 0  |
|       | LUMO     | -2.02| 9  | 84    | 6     | 1  |
|       | HOMO     | -5.7 | 84 | 6     | 2     | 7  |
|       | HOMO-1   | -5.74| 30 | 47    | 1     | 22 |
|       | HOMO-2   | -5.97| 37 | 37    | 1     | 26 |
|       | HOMO-3   | -6.27| 5  | 77    | 0     | 18 |
### [1a]₃

| MO          | eV  | Pt | dfppy | CNBuᵢ | Cl |
|-------------|-----|----|-------|-------|----|
| LUMO+3      | -1.15 | 2  | 97    | 2     | 0  |
| LUMO+2      | -1.39 | 3  | 96    | 2     | 0  |
| LUMO+1      | -1.72 | 5  | 91    | 3     | 0  |
| LUMO        | -2.04 | 11 | 82    | 7     | 1  |
| HOMO        | -5.22 | 86 | 8     | 3     | 3  |
| HOMO-1      | -5.6  | 28 | 53    | 1     | 19 |
| HOMO-2      | -5.78 | 33 | 38    | 1     | 28 |
| HOMO-3      | -5.94 | 37 | 33    | 1     | 30 |

### 1b

| MO          | eV  | Pt | ppy-CHO | CNBuᵢ | Cl |
|-------------|-----|----|---------|-------|----|
| LUMO+3      | -0.40 | 25 | 47      | 27    | 1  |
| LUMO+2      | -0.66 | 1  | 98      | 1     | 0  |
| LUMO+1      | -1.46 | 3  | 94      | 4     | 0  |
| LUMO        | -2.35 | 4  | 93      | 2     | 0  |
| HOMO        | -5.83 | 31 | 32      | 0     | 37 |
| HOMO-1      | -6.38 | 14 | 4       | 1     | 82 |
| HOMO-2      | -6.64 | 77 | 19      | 1     | 3  |
| HOMO-3      | -6.66 | 3  | 71      | 0     | 26 |

### [1b]₄

| MO          | eV  | Pt | ppy-CHO | CNBuᵢ | Cl |
|-------------|-----|----|---------|-------|----|
| LUMO+3      | -2.09 | 1  | 98      | 0     | 0  |
| LUMO+2      | -2.15 | 2  | 97      | 1     | 0  |
| LUMO+1      | -2.29 | 5  | 92      | 2     | 0  |
| LUMO        | -2.46 | 8  | 88      | 4     | 1  |
| HOMO        | -5.43 | 81 | 14      | 3     | 2  |
| HOMO-1      | -5.77 | 33 | 54      | 1     | 12 |
| HOMO-2      | -5.83 | 37 | 39      | 1     | 24 |
| HOMO-3      | -5.83 | 34 | 38      | 1     | 27 |
Figure S44. Optimized geometries of [1b]₄ model at the S₀ and T₁ states. Contour plots of HOMO and LUMO at the S₀ and spin density at the T₁ optimized geometries [B3LYP/6-31G(d,p)].
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