Electronic Supplementary Information (ESI)

4-Pyridylisocyanide Gold(I) and Gold(I)-plus-Silver(I) Luminescent and Mechanochromic Materials: The Silver Role

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Contents

EXPERIMENTAL GENERAL SECTION

All reactions were carried out under dry N_2. The solvents were purified according to standard procedures.[1] [Au($C_6F_3Cl_2$-3,5)(tht)] (tht = tetrahydrothiophene) was prepared according to literature procedures.[2] 4-Pyridylisocyanide (CNPy-4) was prepared from 4-Pyridylamine, as described by Ugi *et al*. for other isocyanides,[3] in 20% yield. The synthesis of [Au(C_6F_5)(CNPy-4)] was reported by our group.[4] The rest of the reactants were purchased from commercial suppliers and used as received.

The technical measurements were carried out with equipment of the LTI services or the IU CINQUIMA (both of the University of Valladolid) unless otherwise stated.

Infrared spectra were recorded with Perkin–Elmer Frontier (4000–200 cm^{-1}) equipped with an ATR accessory (Attenuated total reflection) for the direct recording of solid samples. The NMR spectra were recorded with Varian 500/54 Premium Shielded instrument. The ^{1}H and ^{13}C NMR spectra are referenced to tetramethylsilane (TMS), while ^{19}F NMR spectra are referenced to $CFCl_3$. UV-Vis absorption spectra of solutions were recorded in a Shimadzu UV-2550 spectrophotometer.

Luminescence spectra were recorded with a Perkin-Elmer LS-55 spectrometer, a fluorescence spectrometer FS5-NIR equipped with an integrating sphere module (SC-30) and a single photon PMT detector (Hamamatsu, R2658P). The emission lifetime and quantum yield measurements of the solid samples were carried out on Hamamatsu-Quantaurus-Tau spectrometer with an integrating sphere. Absolute Quantum Photoluminescence Yields and Emission Lifetimes of luminescent compounds were carried out at the LTI services of the University of Burgos. The elemental analyses were performed with a Carlo Erba 1108 microanalyzer (Vigo University).

Experimental procedure for X-ray Crystallography

A crystal was attached to a glass fiber and transferred to an Agilent Supernova diffractometer with an Atlas CCD area detector. Data collection was performed with Mo-Kα radiation (λ = 0.71073 Å) at room temperature. Data integration, scaling and empirical absorption correction was carried out using the CrysAlisPro program package.[5] Using Olex2,[6] the structure was solved with the olex2.solve[7] and refined with Shelx program.[8] The non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at idealized positions and refined using the riding model. Refinement proceeded smoothly to give the residuals shown in Tables ESI1 and ESI2. CCDC 1908107, 1908108, 1916476 and 1934756 contain the supporting crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

SYNTHESIS AND CHARACTERIZATION OF THE COMPOUNDS

[Au(C$_6$F$_5$)(CNPy-4)] (1)

The synthesis and characterization of **1** in $CDCl_3$ was reported by our group.[4] The following ^{1}H and ^{19}F NMR data in acetone allow us to compare them with the corresponding Ag silver derivative [Ag[Au(C$_6$F$_5$)(CNPy-4)]$_2$](BF$_4$) (**3**).

^{1}H NMR (499.72 MHz, acetone-*d*$_6$, 298 K, Figure ESI1): δ 8.92 (m, 2H, C*H*–N, Py), 7.92 (m, 2H, C*H*–C, Py).

^{19}F NMR (470.15 MHz, acetone-*d*$_6$, 298 K, Figure ESI2): δ –116.67 (m, 2F$_o$), –159.38 (t, $^3J_{Fm\text{-}Fp}$ = 20.0 Hz, 1F$_p$), –164.08 (m, 2F$_m$).

IR (ATR, neat): 2220 cm^{-1} ($\nu_{C\equiv N}$). *Anal*. calcd for $C_{12}H_4AuF_5N_2$: C 30.79, H 0.86, N 5.98; found C 30.56, H 0.91, N 6.08.

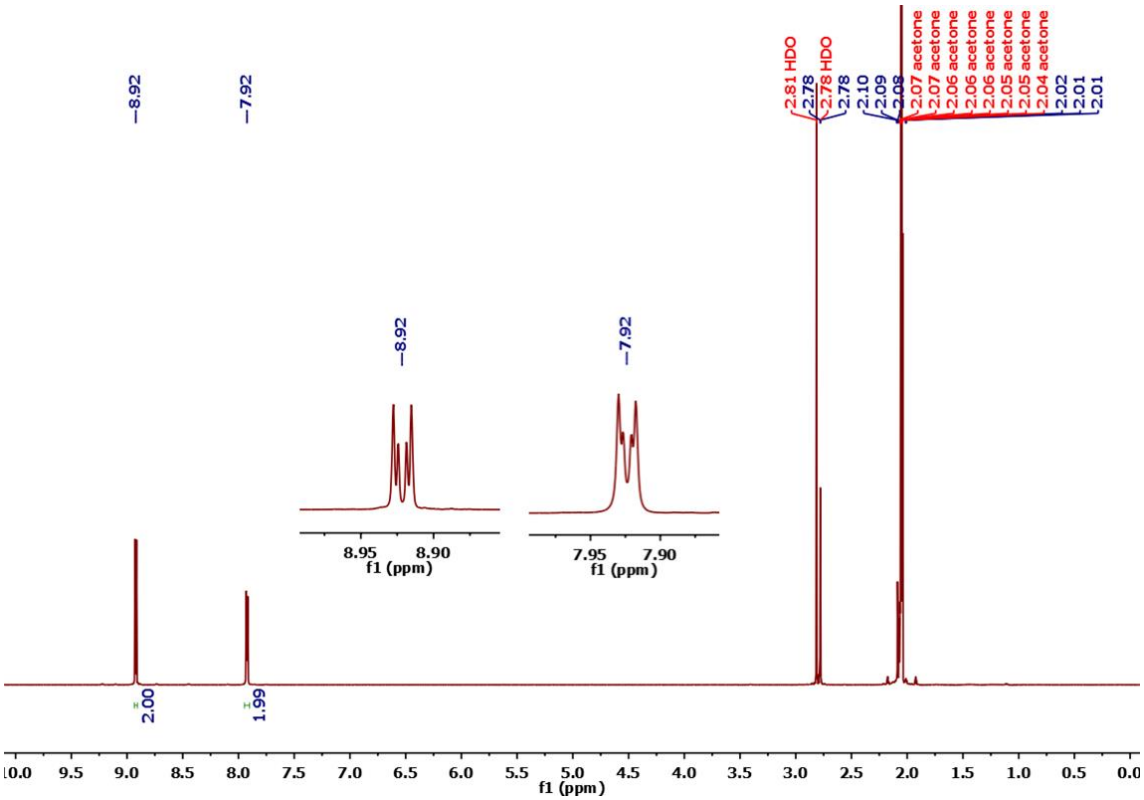


Figure ESI1. ^{1}H NMR spectra of **1** at 298 K in acetone-*d*$_6$

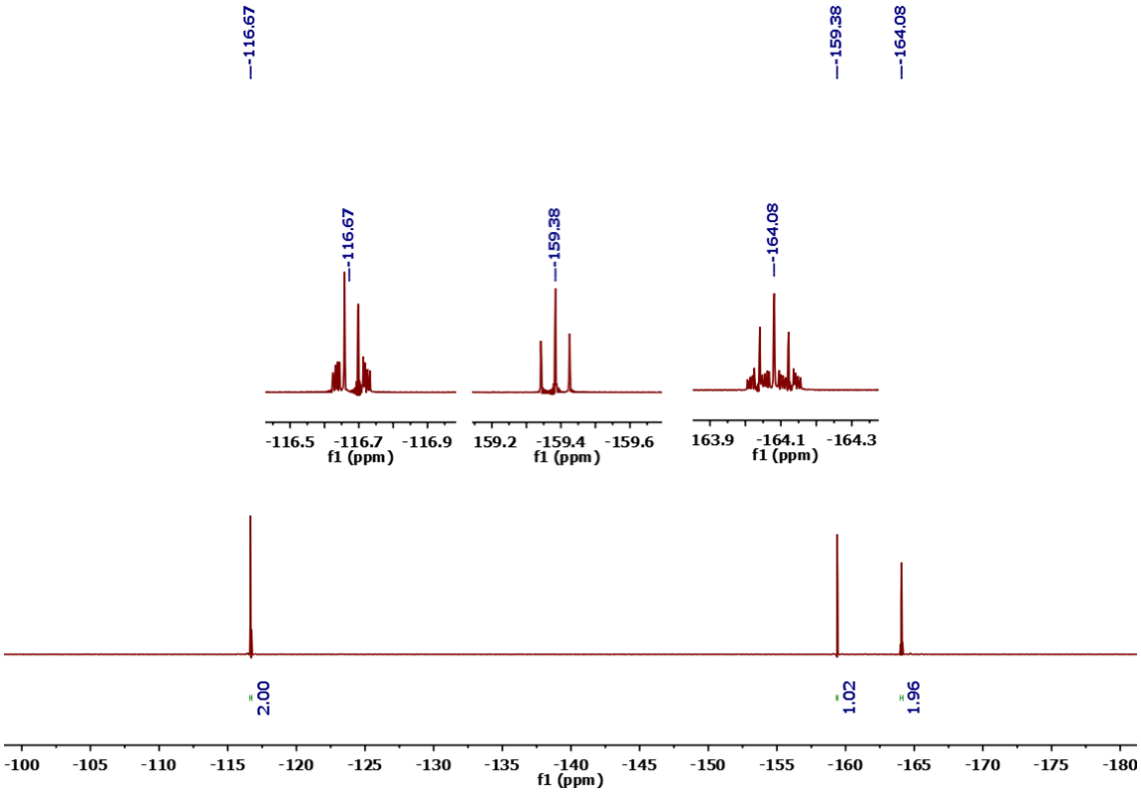


Figure ESI2. ^{19}F NMR spectra of **1** at 298 K in acetone-d_6

[Au(C$_6$F$_3$Cl$_2$-3,5)(CNPy-4)] (2)

In a flask under nitrogen, [Au(C$_6$F$_3$Cl$_2$-3,5)(tht)] (233 mg, 0.48 mmol), the ligand CNPy-4 (50 mg, 0.48 mmol) and 15 mL of dry CH_2Cl_2 were added. The mixture was stirred for 2 hours and the solvent was reduced in vacuum, then *n*-hexane was added (10 mL). The pale yellow solid obtained was washed with *n*-hexane (3 × 5 mL). Yield: 197 mg, 82 %.

^{1}H NMR (499.72 MHz, $CDCl_3$, 298 K, Figure ESI3): δ 8.88 (m, 2H, C*H*–N, Py), 7.47 (m, 2H, C*H*–C, Py).

^{19}F NMR (470.15 MHz, $CDCl_3$; 298 K, Figure ESI4): δ –89.71 (s, 2F$_o$), –114.48 (s, 1F$_p$).

^{13}C {^{1}H} NMR (125.67 MHz, $CDCl_3$ 298 K, Figure ESI5 and ESI6): δ 161.21 (ddd, $^1J_{C–Fo}$ = 234.5 Hz, $^3J_{C–Fp}$ = 24.5 Hz, $^3J_{C–Fo'}$ = 5.2 Hz, 2C*Fo*), 160.82 (br, 1C, Au–*C*N), 153.72 (dt, $^1J_{C–Fp}$ = 247.0 Hz, $^3J_{C–Fo}$ = 5.2 Hz), 152.08 (2C, *C*H–N, Py), 131.78 (br, 1C, *C*$_{Py}$–NCAu), 128.05 (td, $^2J_{C–Fo}$ = 57.6 Hz, $^4J_{C-F}$ = 3.2 Hz, *C*$_{Rf}$–Au), 120.19 (2C, *C*H–C, Py), 105.74 (ddd, $^2J_{C–F}$ = 26.2 Hz, $^2J_{C–F}$ = 20.6 Hz, $^4J_{C–Fo'}$ = 5.9 Hz, 2C, *C*$_{Rf}$–Cl).

NMR data of **2** in acetone-d_6:

^{1}H NMR (499.72 MHz, acetone-d_6, 298 K, Figure ESI7): δ 8.91 (m, 2H, C*H*–N, Py), 7.91 (m, 2H, C*H*–N, Py).

^{19}F NMR (470.15 MHz, acetone-d_6, 298 K, Figure ESI8): δ –90.12 (s, 2F$_o$), –116.67 (s, 1F$_p$).

IR (ATR, neat): 2214 cm^{-1} ($\nu_{C\equiv N}$). *Anal*. calcd for $C_{12}H_4AuCl_2F_3N_2$: C 28.77, H 0.80, N 5.59; found C 29.03, H 0.96, N 5.42.

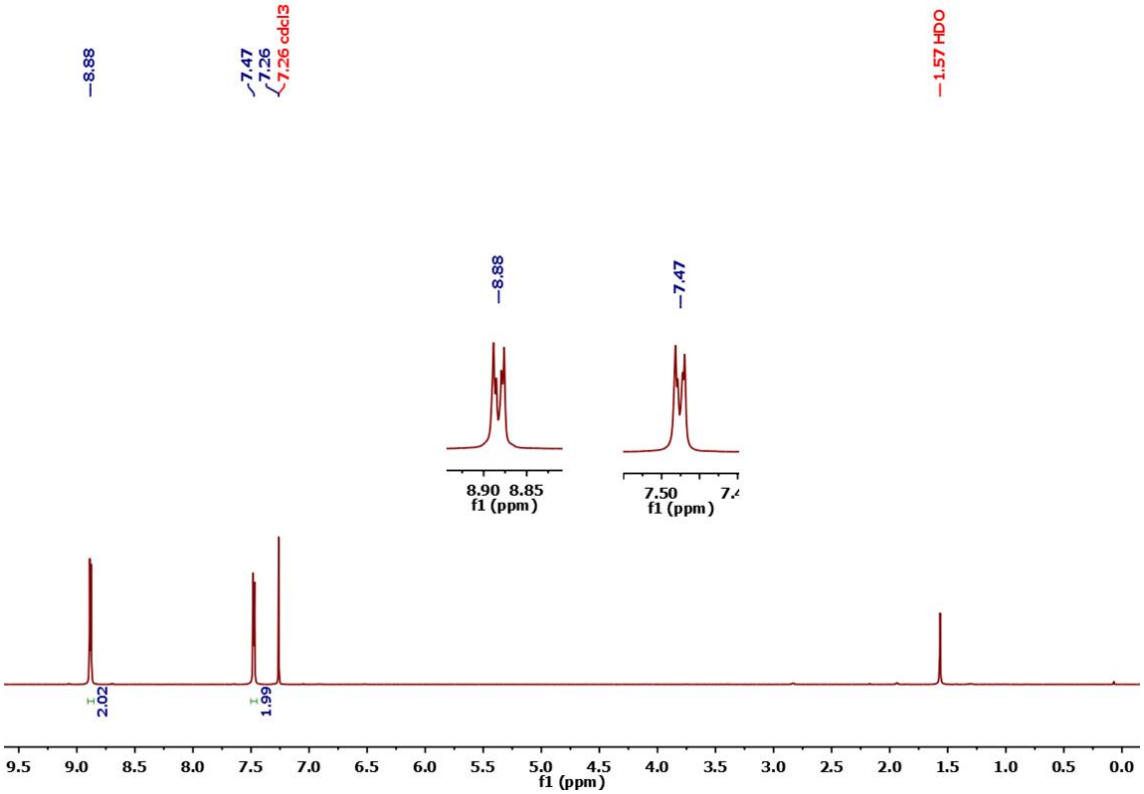


Figure ESI3. ^{1}H NMR spectrum of **2** at 298 K in $CDCl_3$

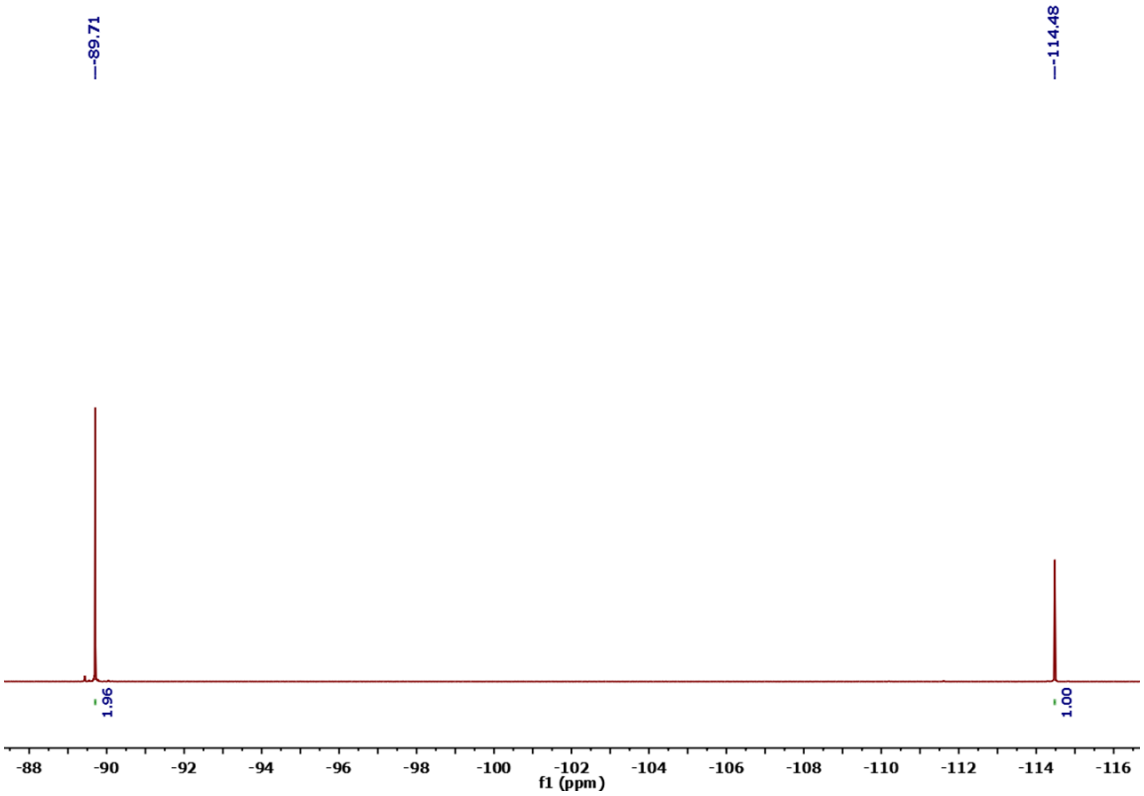


Figure ESI4. ^{19}F NMR spectrum of **2** at 298 K in $CDCl_3$

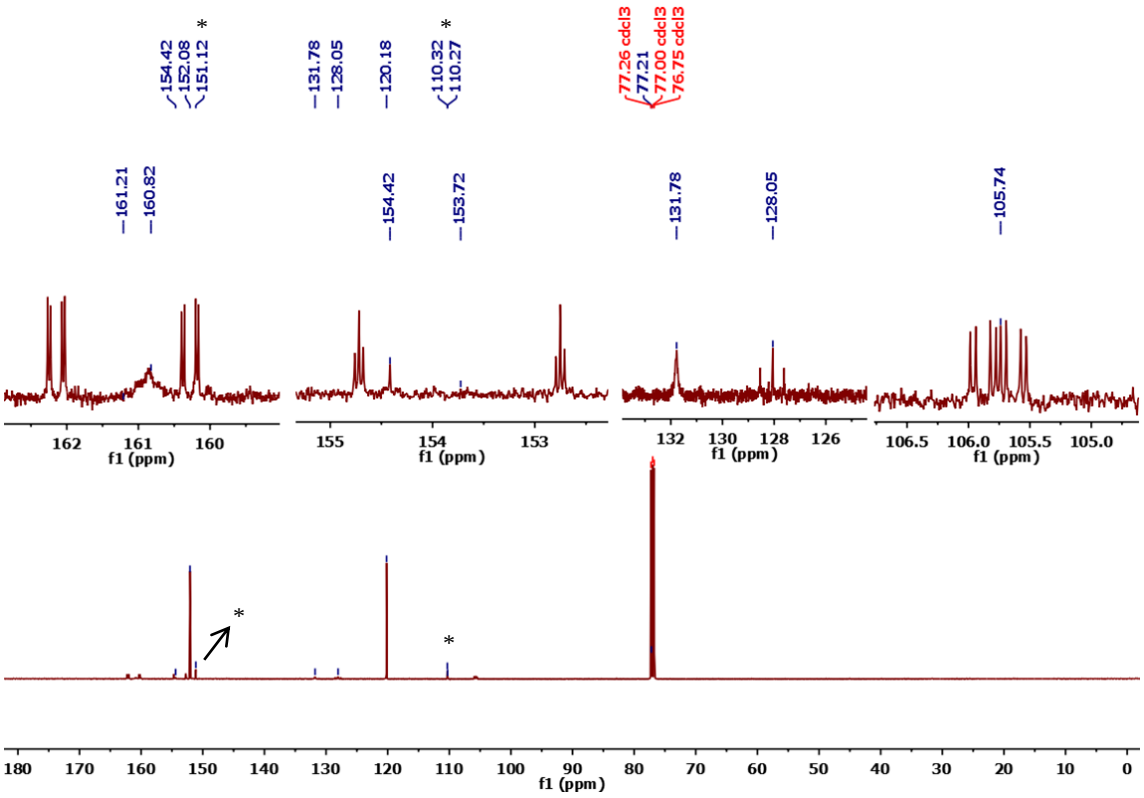


Figure ESI5. $^{13}C\{^1H\}$ NMR spectrum of **2** at 298 K in $CDCl_3$. *Impurity observed in long standing solutions.

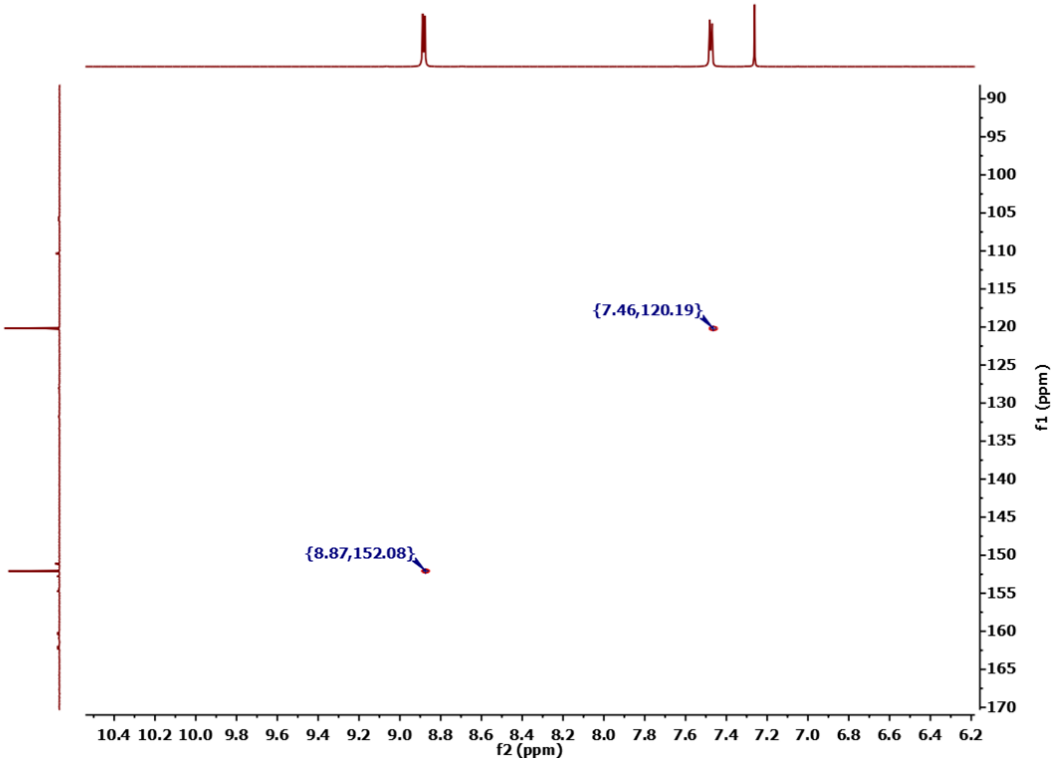


Figure ESI6. 2D-HSQC NMR spectrum of **2** at 298 K in $CDCl_3$

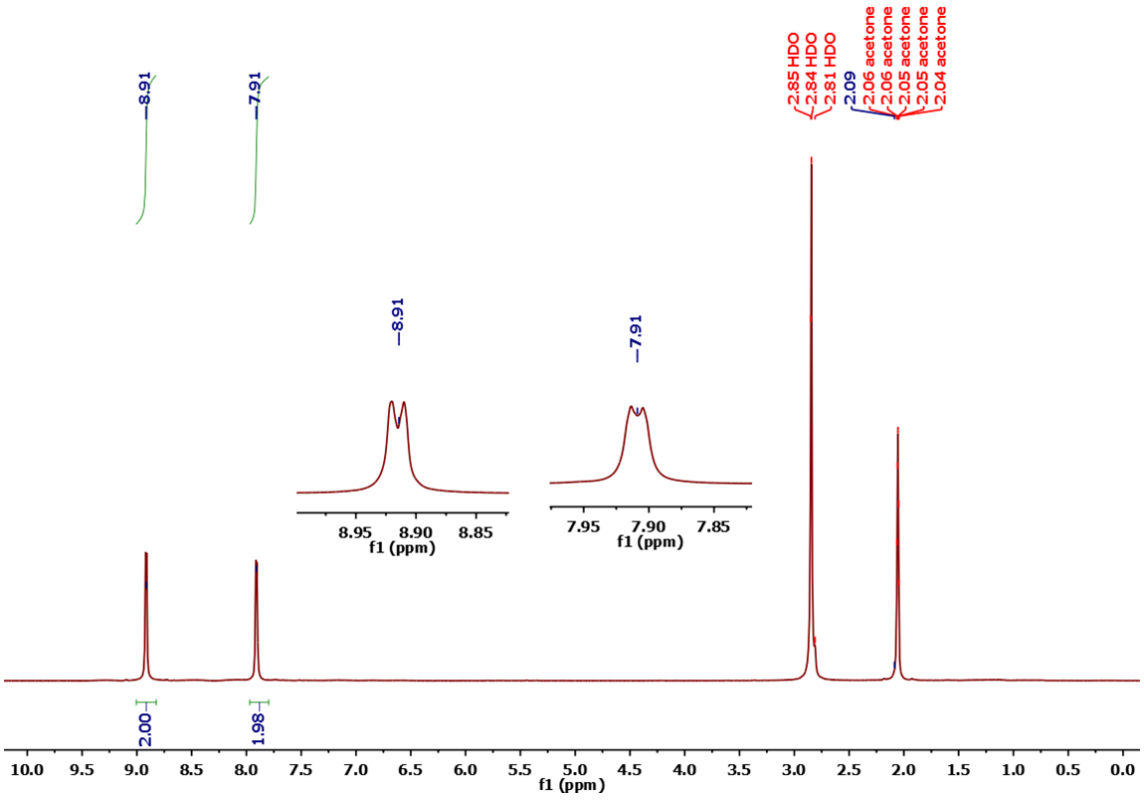


Figure ESI7. ^{1}H NMR spectrum of **2** at 298 K in acetone-d_6

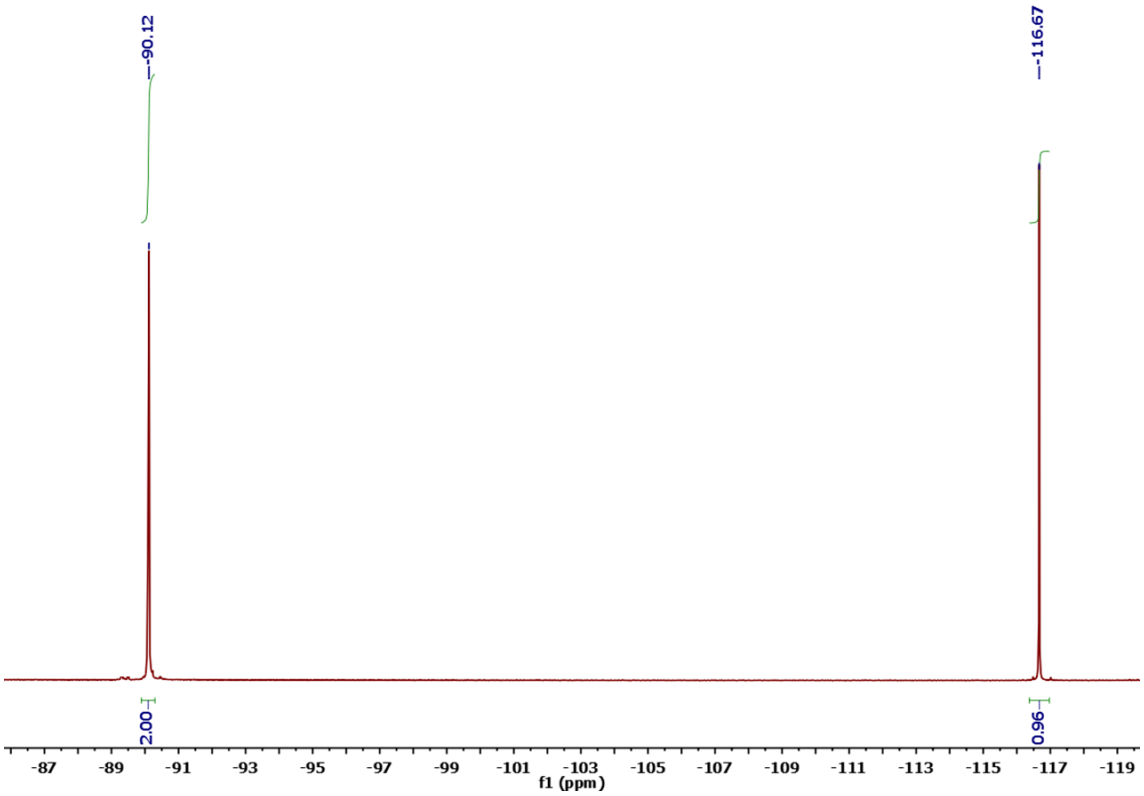


Figure ESI8. ^{19}F NMR spectra of **2** at 298 K in acetone-d_6

[Ag[AuPf(CNPy-4)]$_2$](BF$_4$) (3)

To a solution of [Au(C$_6$F$_5$)(CNPy-4)] (**1**) (50 mg, 0.106 mmol) in 15 mL of dry CH$_2$Cl$_2$, a solution of Ag(BF$_4$) in dry acetone (0.053 mmol: 950 μL, 5.6×10^{-2} M) was added. The mixture was stirred at room temperature during 1 hour in the darkness. Then, the suspension was concentrated under vacuum and *n*-hexane was added (5 mL). The yellow solid was filtered off and washed with *n*-hexane (3 × 5 mL). Yield: 48 mg, 80 %.

^{1}H NMR (499.72 MHz, acetone-d_6, 298 K, Figure ESI9): δ 9.05 (m, 4H, C*H*–N, Py), 8.10 (m, 4H, C*H*–N, Py).

^{19}F NMR (470.15 MHz, acetone-d_6, 298 K, Figure ESI10): δ –116.68 (m, 4F$_o$), –151.87 (s, ^{10}BF$_4$), –151.92 (s, ^{11}BF$_4$), –159.30 (t, $^3J_{Fm\text{-}Fp}$ = 20.0 Hz, 2F$_p$), –164.05 (m, 4F$_m$).

IR (ATR, neat): 2222 cm^{-1} ($\nu_{C\equiv N}$). *Anal*. calcd for C$_{24}$H$_8$AgAu$_2$BF$_{14}$N$_4$: C 25.49, H 0.71, N 4.95; found C 25.48, H 0.72, N 4.87.

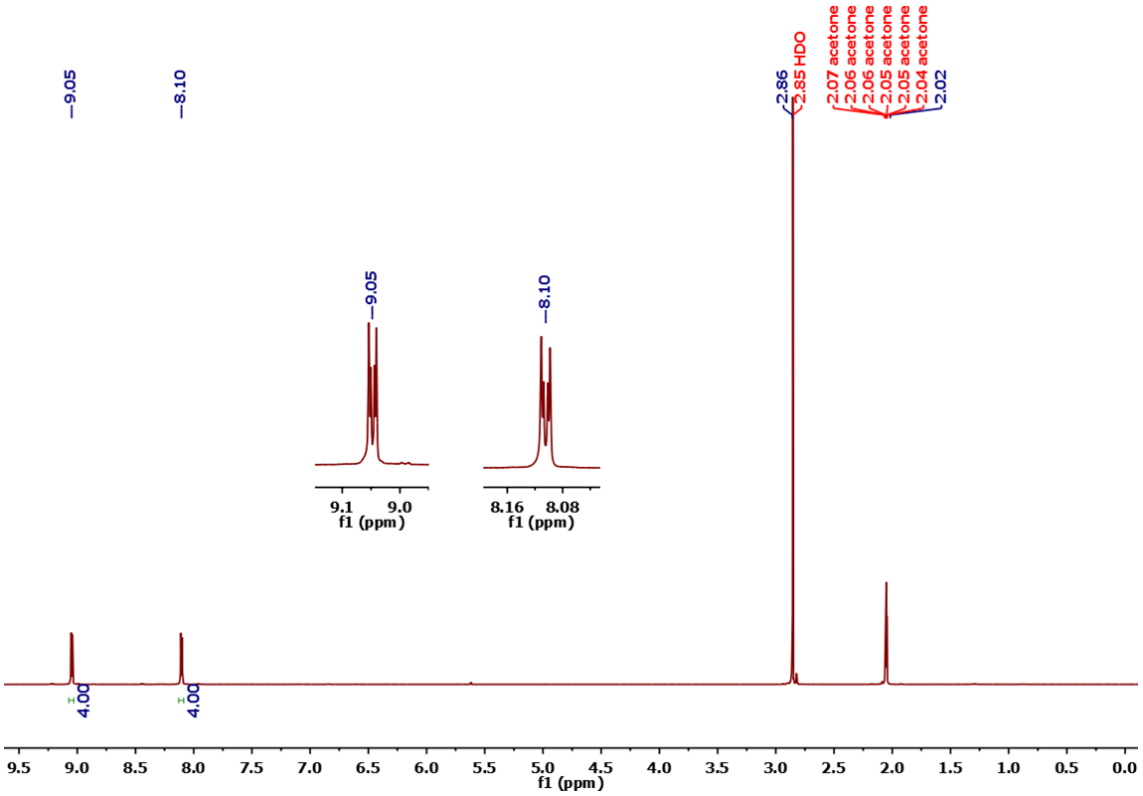


Figure ESI9. ^{1}H NMR spectra of **3** at 298 K in acetone-d_6

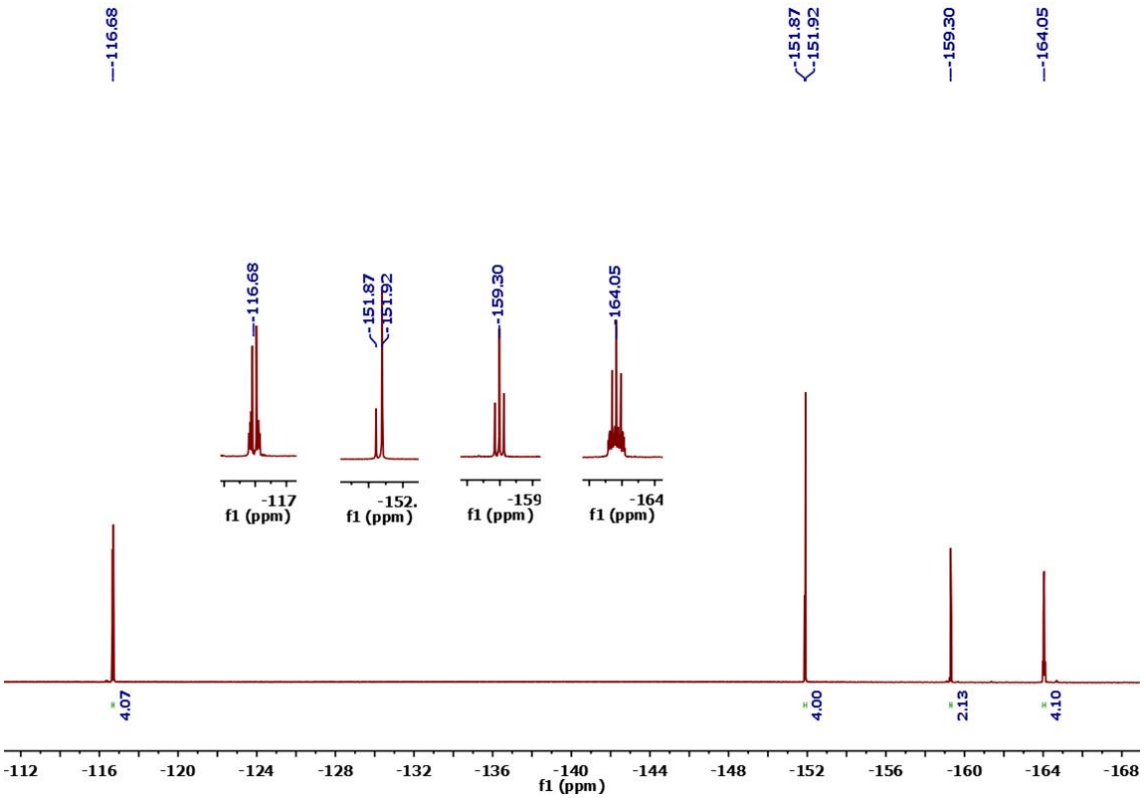


Figure ESI10. ^{19}F NMR spectra of **3** at 298 K in acetone-d_6

[Ag[AuRf(CNPy-4)]$_2$](BF$_4$) (4)

To a stirred solution of [Au(C$_6$F$_3$Cl$_2$-3,5)(CNPy-4)] (**2**) (50 mg, 0.098 mmol) in 15 mL of dry CH$_2$Cl$_2$, a solution of Ag(BF$_4$) in dry acetone (0.049 mmol: 870 µL, 5.6×10^{-2} M) was added. The mixture was stirred at room temperature for 1 hour in the darkness. Then, the suspension formed was concentrated under vacuum, and *n*-hexane (3 × 5 mL) was added. The resulting dark yellow solid was filtered and recrystallized from acetone/*n*-hexane to obtain a yellow solid. Yield: 34 mg, 58 %.

^{1}H NMR (499.72 MHz, acetone-*d*$_6$, 298 K, Figure ESI11): δ 8.95 (m, 4H, C*H*–N, Py), 7.97 (m, 4H, C*H*–N, Py).

^{19}F NMR (470.15 MHz, acetone-*d*$_6$, 298 K, Figure ESI12): δ –90.22 (s, 4F$_o$), –116.65 (s, 2F$_p$), –151.82 (s, ^{10}BF$_4$), –151.87 (s, ^{11}BF$_4$).

IR (ATR, neat): 2213 cm^{-1} ($\nu_{C\equiv N}$). *Anal.* calcd for C$_{24}$H$_8$AgAu$_2$BCl$_4$F$_{10}$N$_4$: C 24.09, H 0.67, N 4.68; found C 24.10, H 0.78, N 4.60.

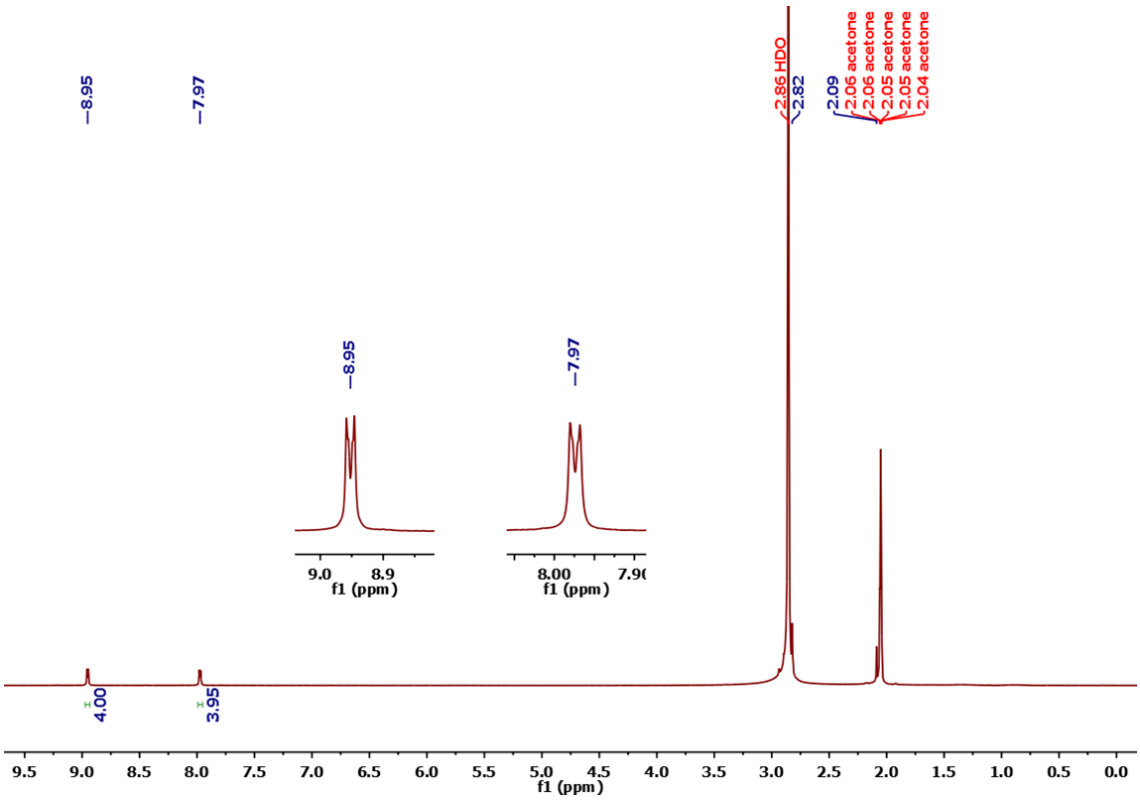


Figure ESI11. ^{1}H NMR spectra of **4** at 298 K in acetone-*d*$_6$

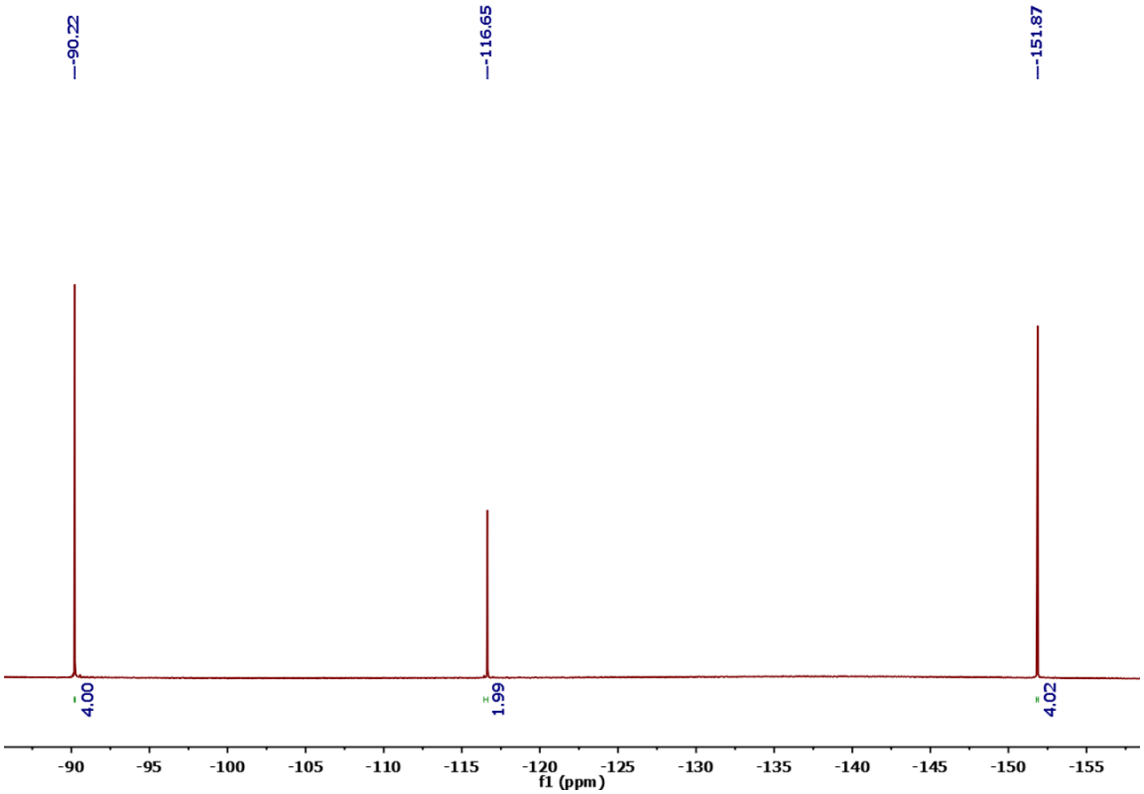


Figure ESI12. ^{19}F NMR spectra of **4** at 298 K in acetone-d_6

REFINEMENT DATA AND EXTRA DETAILS OF THE X-RAY STRUCTURES

Table ESI1. Crystal data and structure refinements for complexes **1** and **2$_\alpha$**.

	[AuPf(CNPy-4] (**1**)	[AuRf(CNPy-4] (**2$_\alpha$**)
Empirical formula	$C_{12}H_4N_2F_5Au$	$C_{12}H_4N_2F_3Cl_2Au$
Formula weight	468.14	501.04
Temperature/K	298.15	294
Crystal system	monoclinic	triclinic
Space group	Pc	P-1
a/Å	3.8166(6)	10.0232(5)
b/Å	12.7293(14)	11.4385(6)
c/Å	12.1037(8)	13.5702(7)
α/°	90	71.133(5)
β/°	94.088(10)	87.315(4)
γ/°	90	66.146(5)
Volume/Å^3	586.53(12)	1340.13(13)
Z	2	4
ρ_{calc}g/cm^3	2.651	2.483
μ/mm^{-1}	12.595	11.399
F(000)	428	920
Crystal size/mm^3	0.35 × 0.121 × 0.034	0.248 × 0.141 × 0.14
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	6.75 to 59.484	7.102 to 59.088
Index ranges	$-4 \le h \le 5$, $-12 \le k \le 16$, $-11 \le l \le 16$	$-10 \le h \le 12$, $-15 \le k \le 14$, $-17 \le l \le 13$
Reflections collected	2349	10395
Independent reflections	1729 [R_{int} = 0.0318, R_{sigma} = 0.0667]	6239 [R_{int} = 0.0661, R_{sigma} = 0.0759]
Data/restraints/parameters	1729/59/181	6239/0/361
Goodness-of-fit on F^2	1.045	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0697, wR_2 = 0.1693	R_1 = 0.0483, wR_2 = 0.0927
Final R indexes [all data]	R_1 = 0.0894, wR_2 = 0.1843	R_1 = 0.0759, wR_2 = 0.1114
Largest diff. peak/hole / eÅ^{-3}	3.65/-1.62	1.10/-1.79

Suitable colorless single crystals of **1** and **2$_\alpha$** for X-ray Crystallography were obtained by slow diffusion of n-hexane in a CH_2Cl_2 solution of the corresponding compound. Figures ESI13 and ESI14 show a view of the extended packing of **1** and **2$_\alpha$** respectively. Figure ESI15 shows the asymmetric unit of **2$_\alpha$**.

Table ESI2. Crystal data and structure refinements for complexes **2β** and **4**.

	[AuRf(CNPy-4] (**2β**)	[Ag[AuRf(CNPy-4)]$_2$](BF$_4$) ·0.5(Me$_2$CO) (**4**)
Empirical formula	$C_{12}H_4N_2F_3Cl_2Au$	$C_{51}H_{22}Ag_2Au_4B_2Cl_8F_{20}N_8O$
Formula weight	501.04	2451.59
Temperature/K	294	294
Crystal system	orthorhombic	orthorhombic
Space group	P21212	Pbcn
a/Å	35.8917(7)	26.9355(9)
b/Å	38.9207(10)	13.2083(5)
c/Å	13.6252(3)	18.8465(6)
α/°	90	90
β/°	90	90
γ/°	90	90
Volume/Å^3	19033.5(7)	6705.1(4)
Z	48	4
ρ_{calc}g/cm^3	2.098	2.429
μ/mm^{-1}	9.631	9.711
F(000)	11040	4512
Crystal size/mm^3	? × ? × ?	0.248 × 0.154 × 0.093
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	6.482 to 59.556	6.71 to 59.5
Index ranges	-49 ≤ h ≤ 39, -38 ≤ k ≤ 49, -14 ≤ l ≤ 18	-20 ≤ h ≤ 37, -16 ≤ k ≤ 15, -24 ≤ l ≤ 19
Reflections collected	88140	20339
Independent reflections	44775 [R_{int} = 0.0642, R_{sigma} = 0.1524]	7851 [R_{int} = 0.0313, R_{sigma} = 0.0431]
Data/restraints/parameters	44775/0/1971	7851/0/435
Goodness-of-fit on F^2	0.91	1.01
Final R indexes [I>=2σ (I)]	R_1 = 0.0637, wR_2 = 0.1415	R_1 = 0.0520, wR_2 = 0.1011
Final R indexes [all data]	R_1 = 0.1830, wR_2 = 0.1918	R_1 = 0.1129, wR_2 = 0.1289
Largest diff. peak/hole / eÅ^{-3}	1.29/-1.61	1.06/-1.02

Colorless crystals of **2β** were obtained by slow evaporation of a solution of **2** in dichloromethane/n-hexane. The structure has some disorder problems mostly affecting one molecule. However, the errors of the Au···Au distances are negligible. Figure ESI16 shows the asymmetric unit of **2β**, with twelve different molecules (Z´=12).

Suitable orange single crystals of **4** (Figure 4 and packing in ESI17) were obtained by diffusion, in the dark at room temperature, of a solution of AgBF$_4$ in acetone layered on top of a solution of complex **2** in dichloromethane. After 24 h, orange crystals had been formed at the interphase.

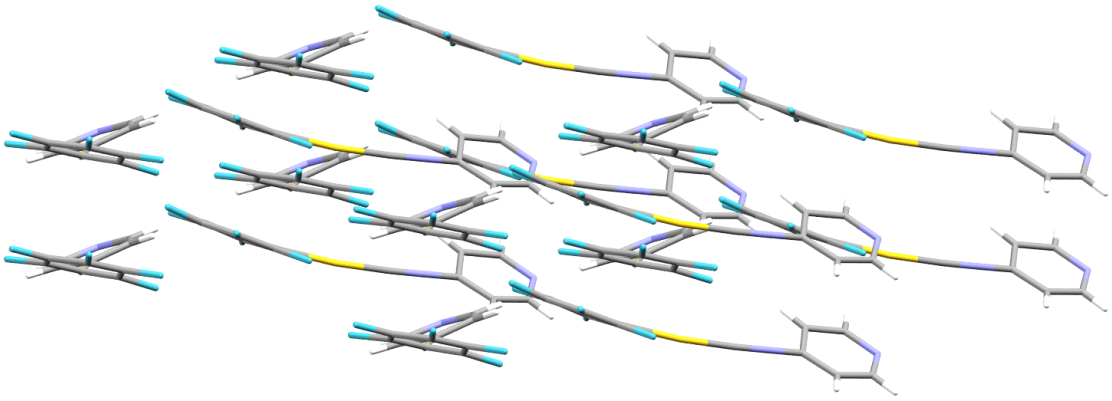


Figure ESI13. Packing of complex **1**

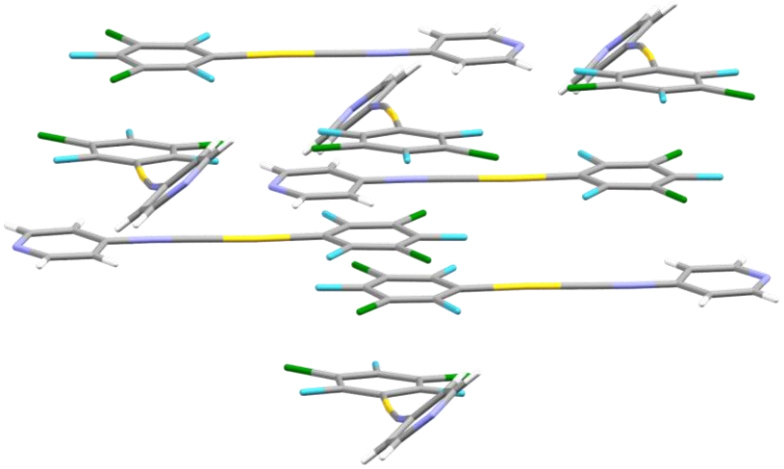


Figure ESI14. Packing of complex $\mathbf{2}_{\alpha}$

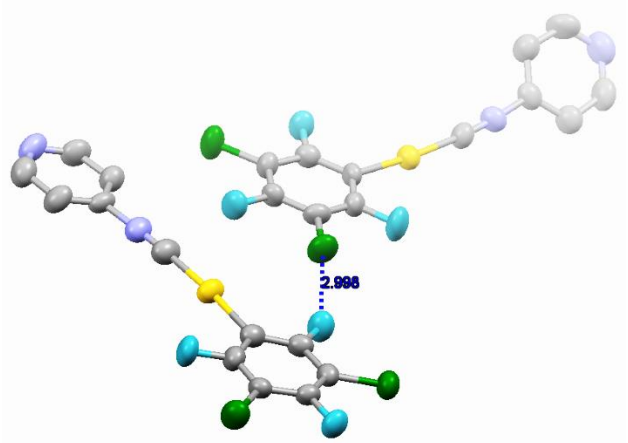


Figure ESI15. Asymmetric unit for the X-Ray structure of [AuRf(CNPy-4](**2**$_{\alpha}$). Hydrogen atoms were omitted for clarity. The shortest F···Cl distance (2.998 Å) is highlighted.

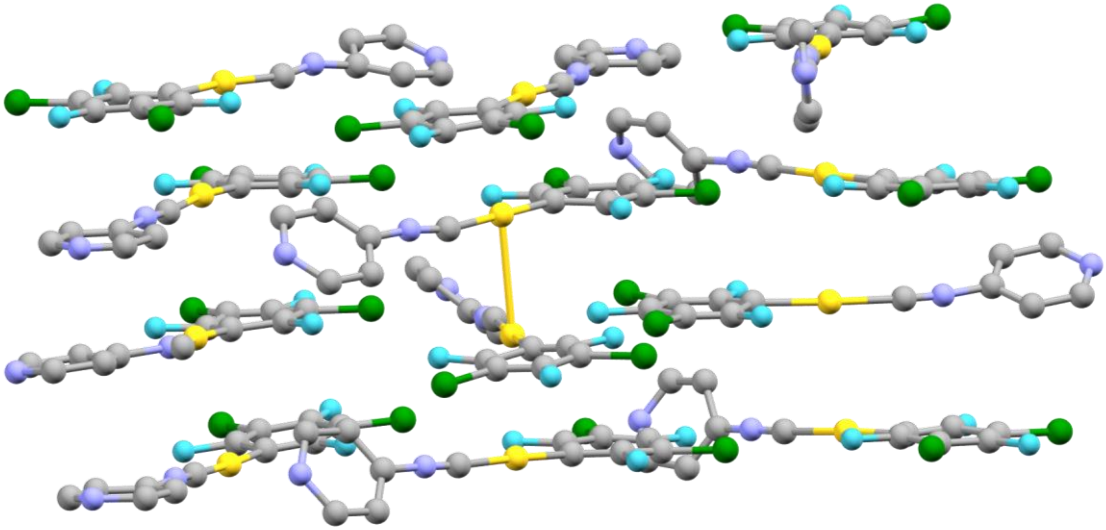


Figure ESI16. Asymmetric unit (Z´=12) for the X-Ray structure of [AuRf(CNPy-4] (**2**$_{\beta}$). The shortest Au···Au distances are 3.2344(16) and 3.2768(16).

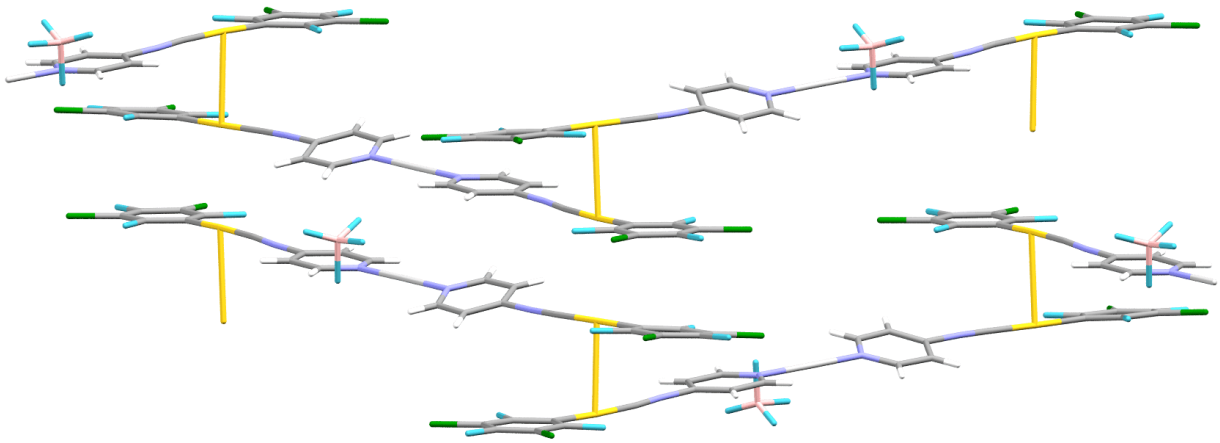


Figure ESI17. Packing of complex **4**. Acetone molecules are omitted for clarity.

POWDER X-RAY DIFFRACTION PATTERNS

PXRD patterns before and after grinding for complexes **1** and **2**. Loss of crystallinity upon grinding can be observed in Figure ESI18.

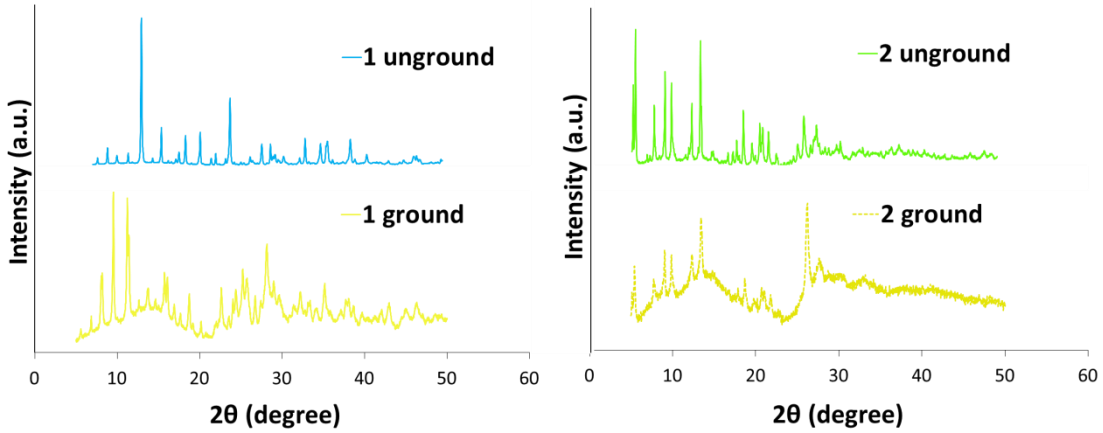


Figure ESI18. PXRD patterns for **1** (left) and **2** (right). Above: unground material; Below: ground material.

Figures ESI19 and ESI20 show the comparison of the PXRD patterns obtained experimentally for the unground material and the simulated one with the single-crystal X-Ray structures for complexes **1** and **2** respectively.

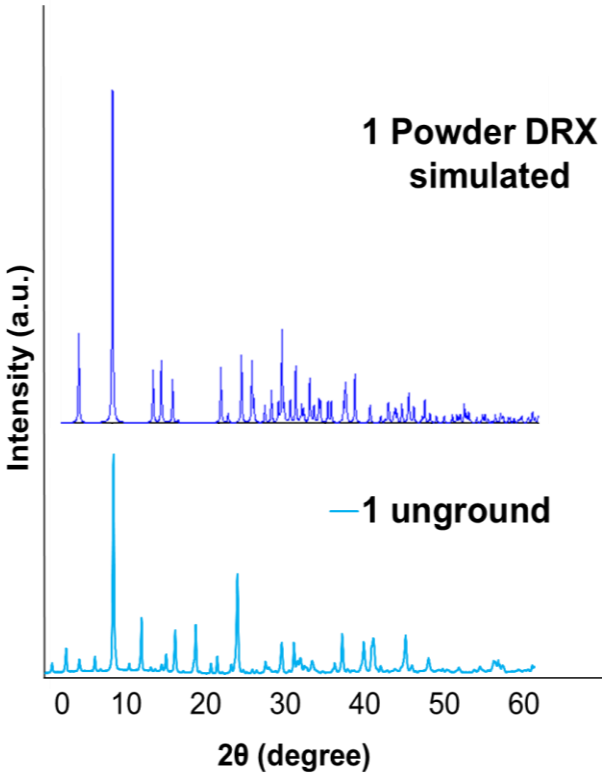


Figure ESI19. Above: simulated PXDR pattern for **1**. Bellow: PXDR for the unground product.

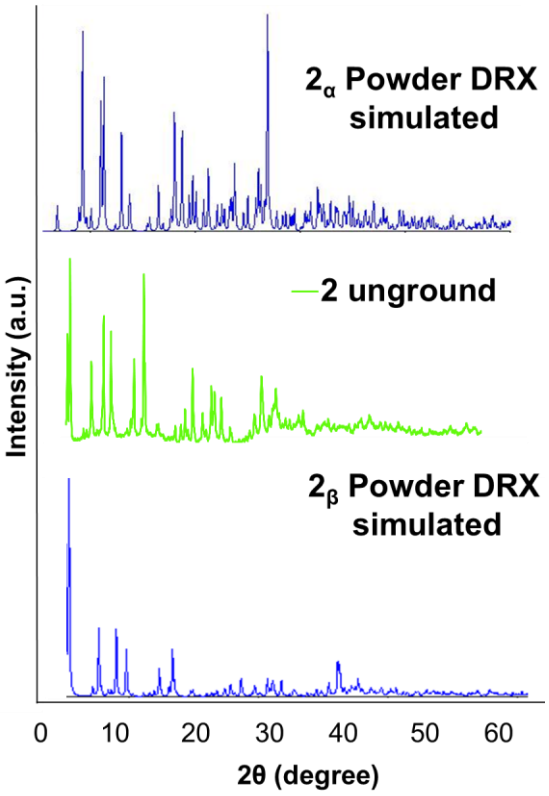


Figure ESI20. Above: simulated PXDR pattern for **2**$_{\alpha}$. Middle: PXDR for the unground bulk product obtained. Below: simulated PXDR pattern for **2**$_{\beta}$.

PHOTOPHYSICAL PROPERTIES

UV-Vis data in solution

Table ESI3 and Figure ESI21 collect all the information of absorption spectra in different solvents.

Table ESI3. UV-Vis data: absorption bands and extinction coefficients (ε) in solution

Comp.	**Absorptions** / nm (**ε** / $M^{-1}cm^{-1}$)
CNPy-4	266 (2.18×10^3)[a]
1	227 (2.36×10^4)[a]; 258 (1.52×10^4)[a]; 273 (1.20×10^4)[a] 209 (1.56×10^4)[b]
2	227 (2.54×10^4)[a]; 260 (1.52×10^4)[a] 210 (2.07×10^4)[b]
3	210 (1.23×10^4)[b]
4	211 (2.92×10^4)[b]

[a] Measurements in dichloromethane. [b] Measurements in acetone.

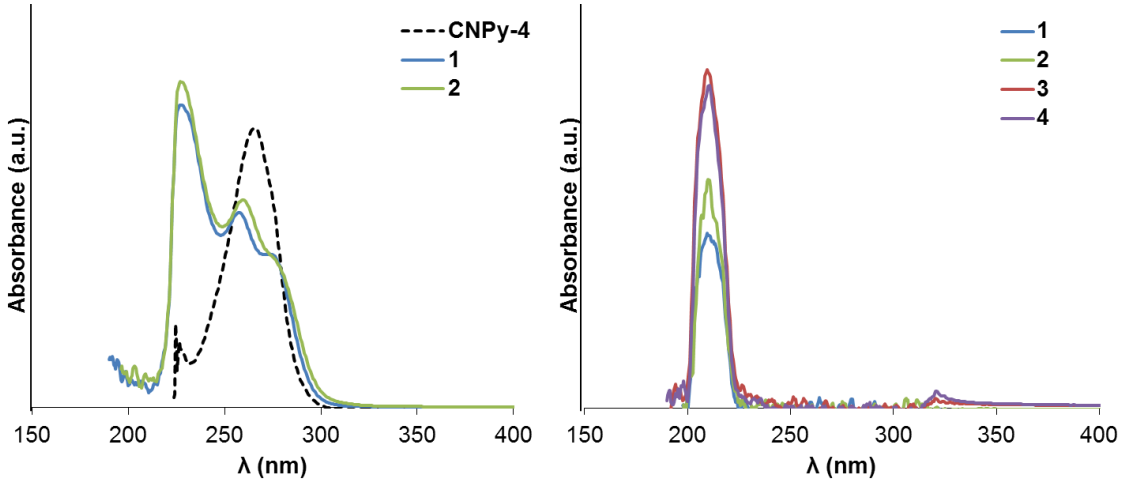


Figure ESI21. Left: UV-Vis absorption spectra in dichloromethane for **CNPy-4** ligand and compounds **1** and **2**. Right: UV-Vis absorption spectra in acetone for **1**-**4** complexes. *Note that the concentrations are different due to their different solubility.

Emission spectra in glassy state

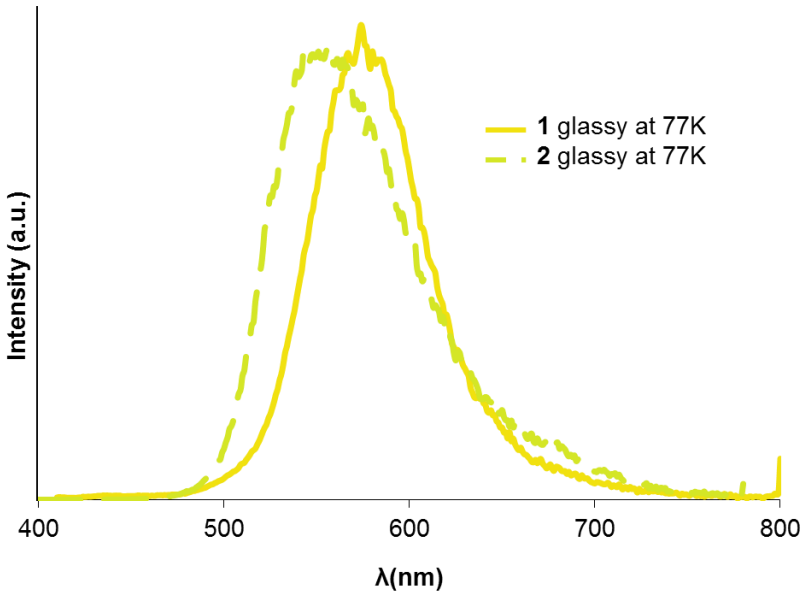


Figure ESI22. Emission spectra of [AuAr(CNPy-4)] (**1** and **2**) in glassy state at 77 K

Emission spectrum of 2_{β}

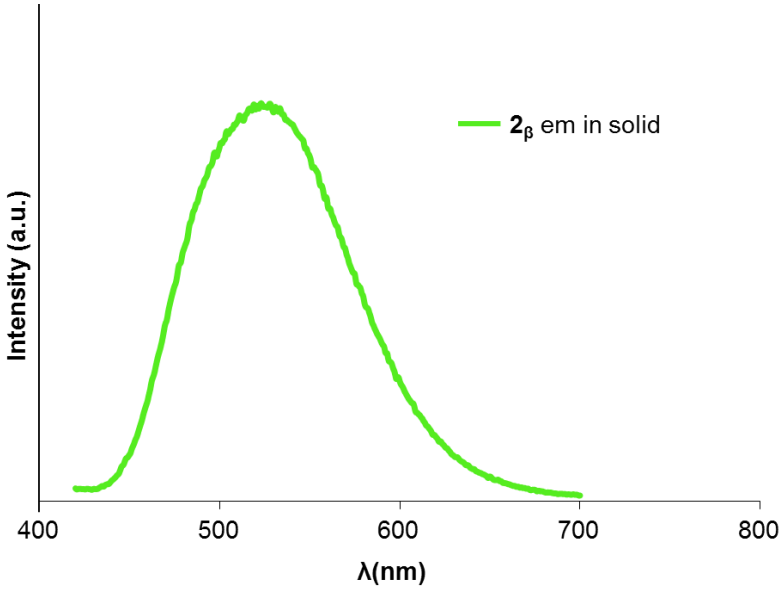


Figure ESI23. Emission spectrum of [AuRf(CNPy-4)] unground enriched in polymorph $\mathbf{2_{\beta}}$ (λ_{exc} = 387 nm)

Emission decay profiles

Table ESI4: Excitation and emission data (nm) before and after grinding (solid state, 298 K).

Comp[a]	λ_{exc}	λ_{emis}	Φ (%)	τ_{av}[c] (ns)	τ_n[d]; A_n[e]
1 u	343	434	21.0	9.65	$\tau_1 = 1.76$; $A_1 = 0.41$ $\tau_2 = 10.56$; $A_2 = 0.59$
1 g	390	540	18.0	677	$\tau_1 = 161.59$; $A_1 = 0.29$ $\tau_2 = 724.23$; $A_2 = 0.71$
1*	401	575	-	712	$\tau_1 = 712$
2$_\alpha$ u	343[b], 387	497	9.9	267	$\tau_1 = 22.25$; $A_1 = 0.03$ $\tau_2 = 267.48$; $A_2 = 0.97$
2 g	397	557	15.9	488	$\tau_1 = 57.78$; $A_1 = 0.03$ $\tau_2 = 489.60$; $A_2 = 0.97$
2*	391	557	-	793	$\tau_1 = 793$
3 u	387	600	2.4	441	$\tau_1 = 71.02$; $A_1 = 0.11$ $\tau_2 = 448.12$; $A_2 = 0.89$
3 g	399	580	5.2	466	$\tau_1 = 82.74$; $A_1 = 0.14$ $\tau_2 = 476.58$; $A_2 = 0.86$
4 u	387	623	42.0	326	$\tau_1 = 326$
4 g	387	620	52.0	388	$\tau_1 = 388$

[a] Unground (**u**) or ground (**g**). [b] Most intense peak. [c] Average lifetime: $\tau_{av} = (A_1\tau_1^2 + A_2\tau_2^2 + \cdots) / (A_1\tau_1 + A_2\tau_2 + \cdots)$. [d] τ_n = Natural lifetime. [e] A_n = Intensity coefficients. [*]Glassy state at 77 K.

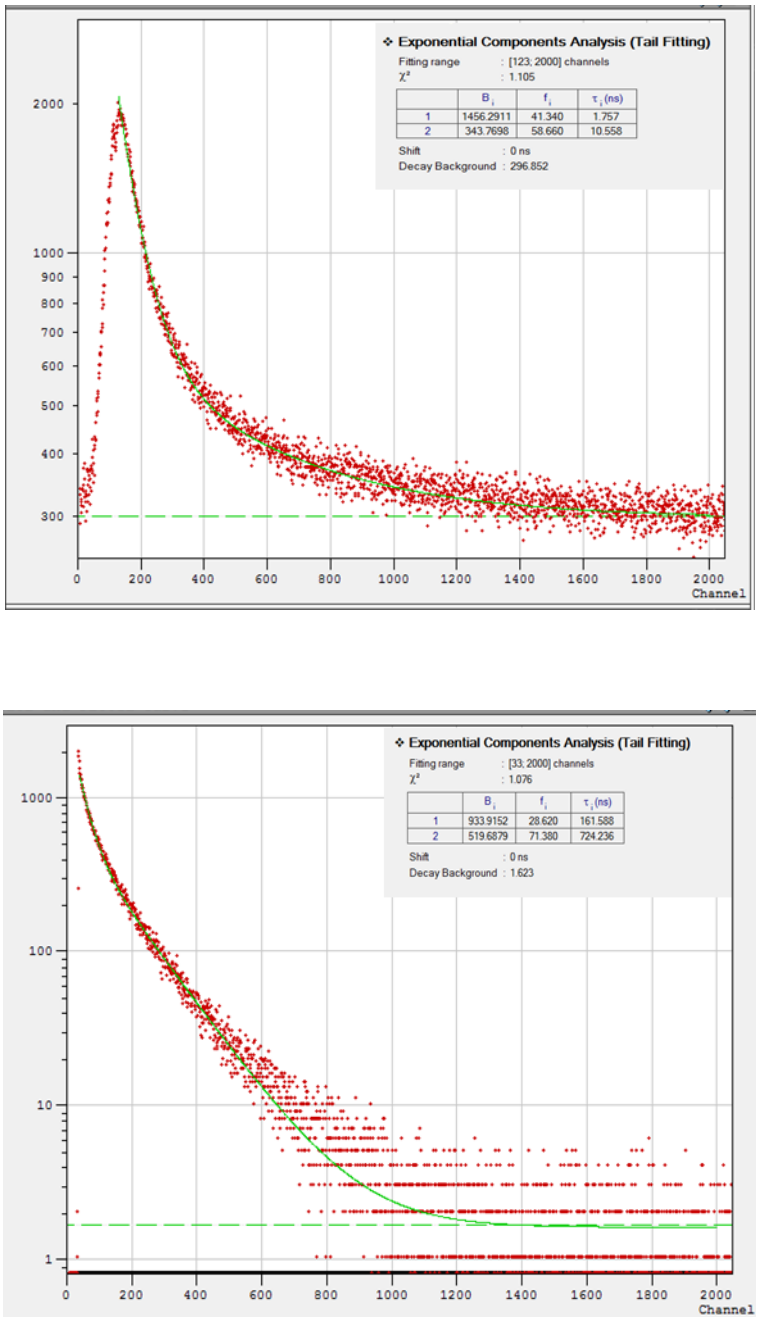


Figure ESI24. Emission Decay profiles of [AuPf(CNPy-4)] (**1**). Above: **1 unground**. Below: **1 ground**.

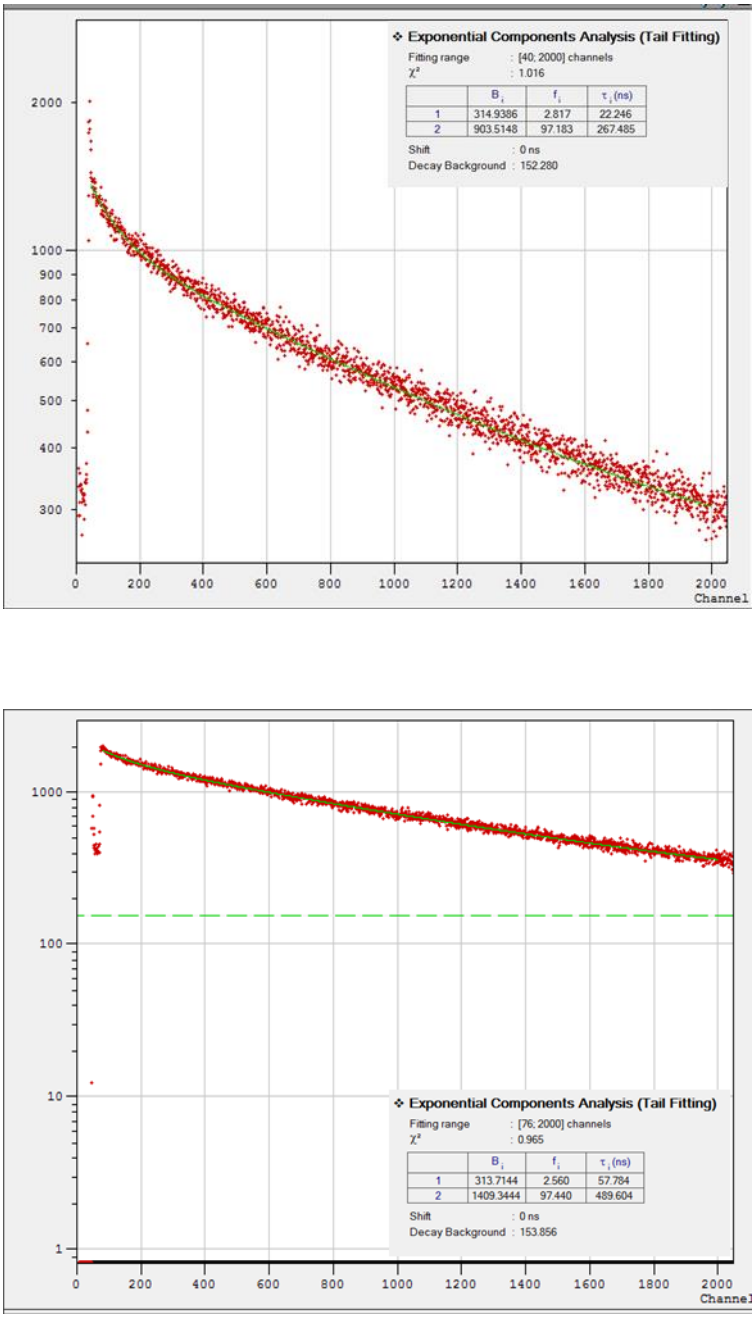


Figure ESI25. Emission Decay profiles of [AuRf(CNPy-4)] (**2**$_{\alpha}$). Above: **2** $_{\alpha}$ **unground**. Below: **2 ground**.

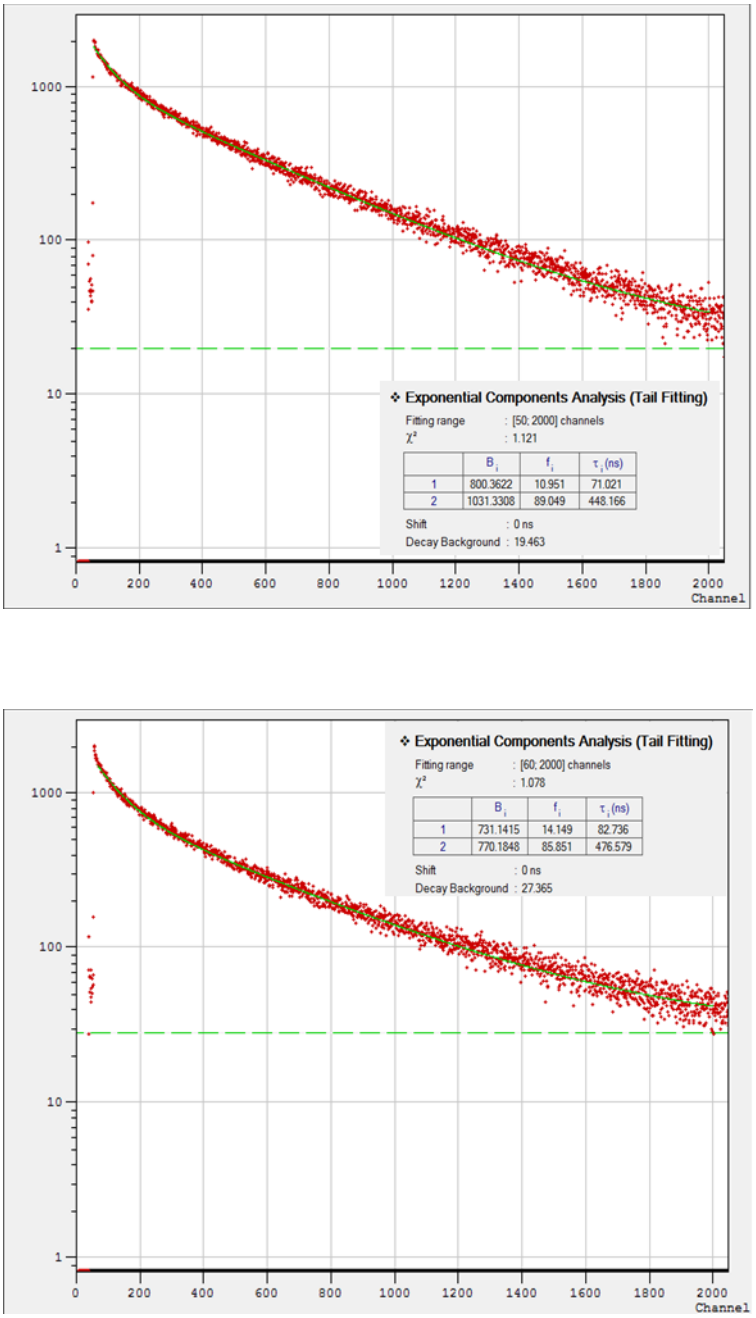


Figure ESI26. Emission Decay profiles of $[Ag[AuPf(CNPy\text{-}4)]_2](BF_4)$ (**3**). Above: **3 unground**. Below: **3 ground**.

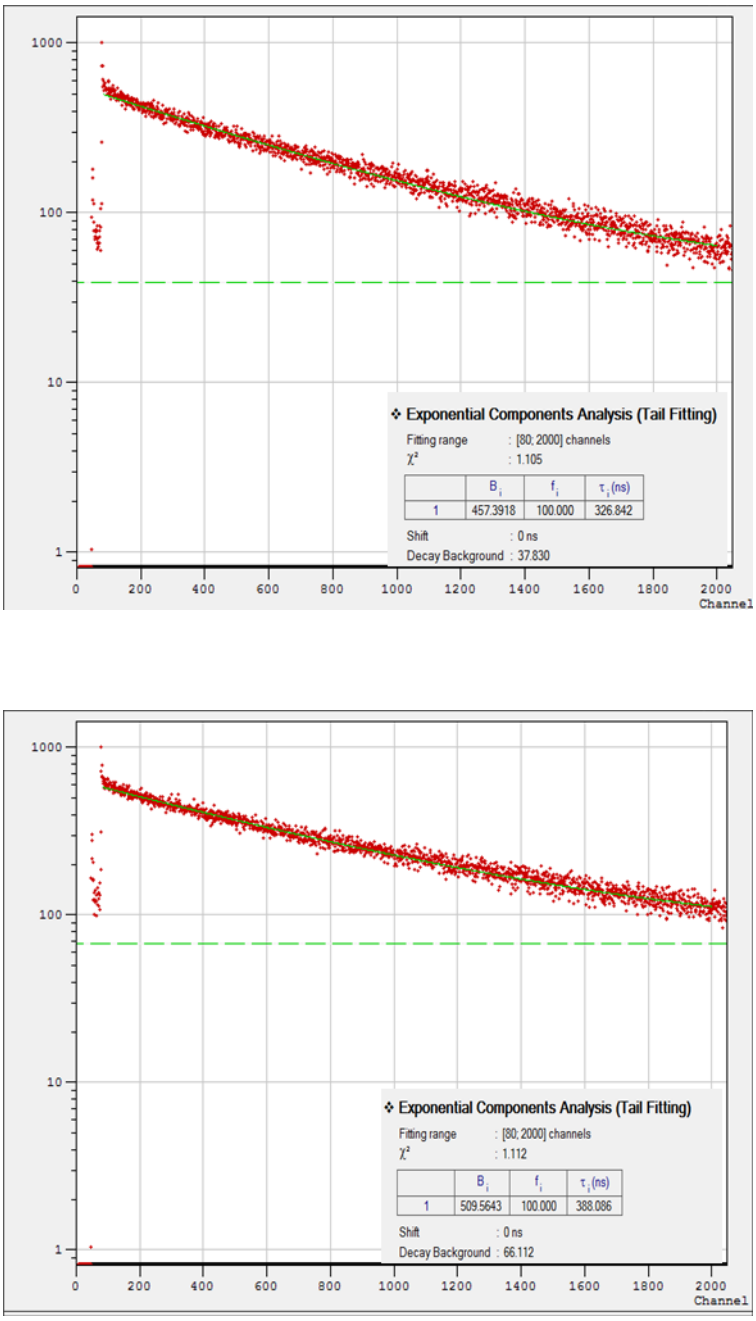
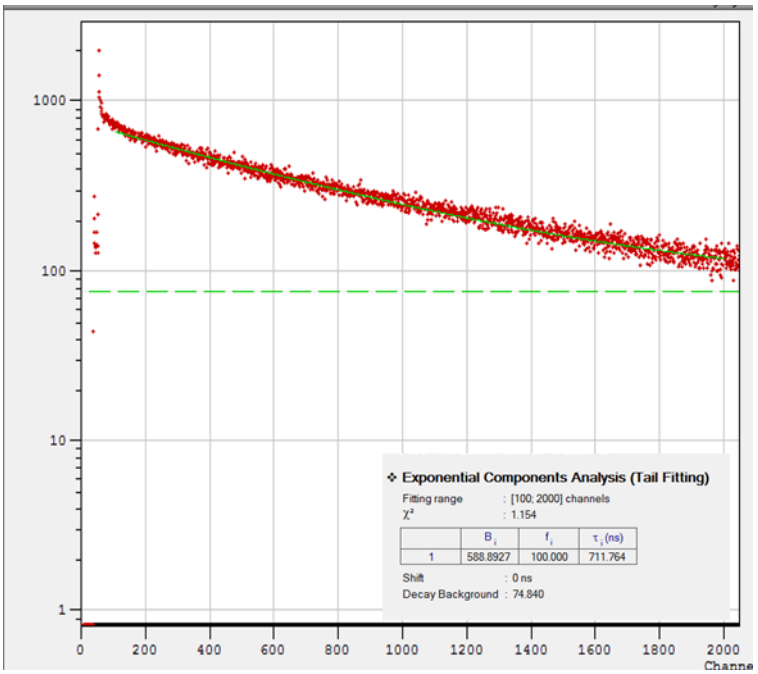


Figure ESI27. Emission Decay profiles of $[Ag[AuRf(CNPy\text{-}4)]_2](BF_4)$ (**4**). Above: **4 unground**. Below: **4 ground**.



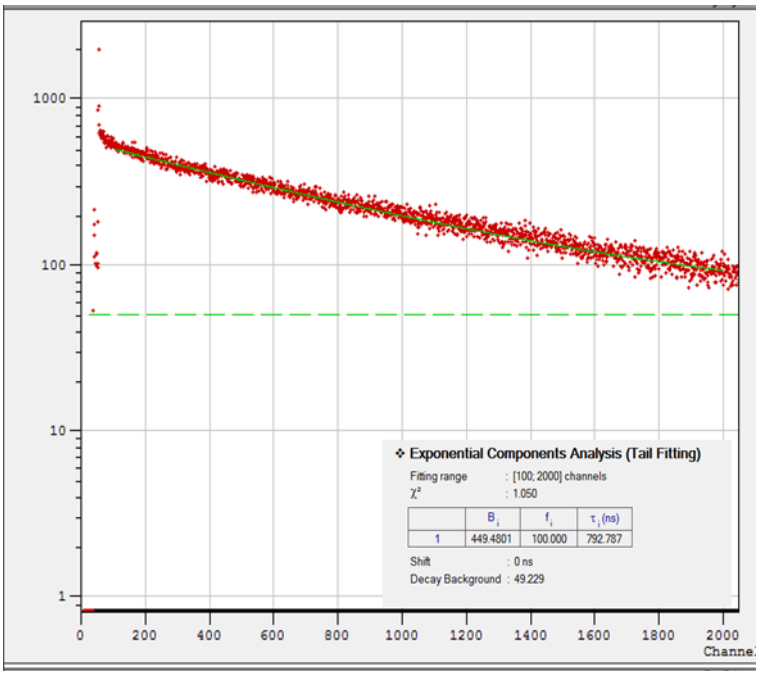


Figure ESI28. Emission Decay profiles of [AuAr(CNPy-4)]. Above: **1 in glassy state** (77 K). Below: **2 in glassy state** (77 K).

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COMPUTACIONAL SECTION

Density functional theory (DFT) calculations reported in this work were carried out using the dispersion corrected hybrid functional ωB97X-D developed by Head-Gordon and Chai,[9] and the Gaussian09 software.[10] The choice of this level of theory is based on the satisfactory results obtained in previous theoretical studies.[11] C, B and H atoms were described using the double-ζ basis set 6-31G(d,p), whereas the same basis set plus diffuse functions was employed to describe the more electronegative N, Cl and F atoms. Au and Ag metals were described using the effective core potential LANL2DZ[12] including f-polarization functions (exponents: 1.050 for Au, 1.611 for Ag).[13]

Time Dependent DFT (TD-DFT) calculations were performed to obtain singlet excitation energy levels for the hexagold structures (at ground state) of $[AuRf(CNPy\text{-}4)]_6$ collected in Figure 7. The geometries were taken from the X-Ray structures of complexes $\mathbf{2_\alpha}$ and **4** respectively. The TD-DFT calculations are qualitatively consistent with the experimental results. Note that the absence of full optimization of the crystalline structures limits the quantitative accuracy of these calculations.

Population analysis using *Chemissian* was used in order to quantify the % of participation of each part of the molecule in the corresponding MOs collected in Figure 7.

Selected relevant Molecular Orbitals (MO)

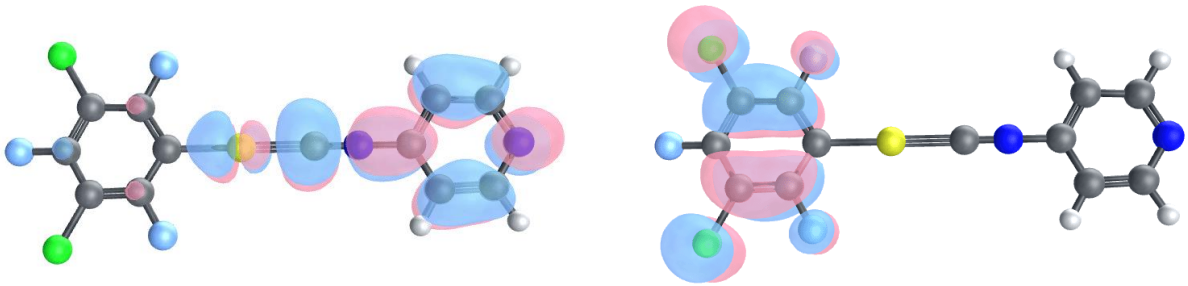

Figure ESI29. Frontier Orbitals (isovalue = 0.07) of $[Au(C_6F_3Cl_2\text{-}3,5)(CNPy\text{-}4)]$ (**2**). Left: LUMO; Right: HOMO.

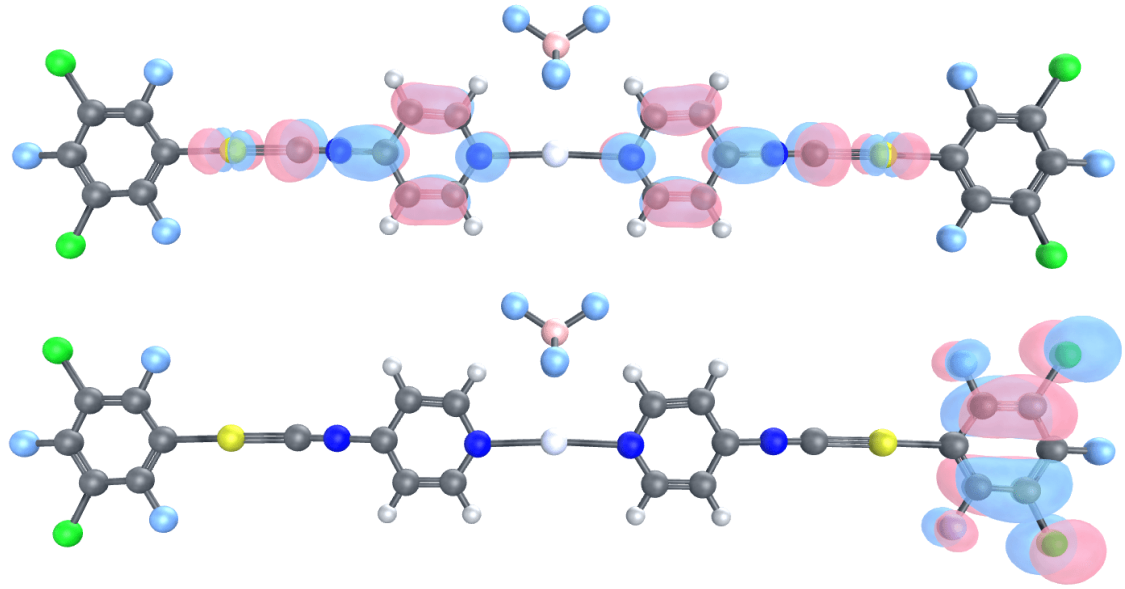

Figure ESI30. Frontier Orbitals (isovalue = 0.07) of $[Ag[Au(C_6F_3Cl_2\text{-}3,5)(CNPy\text{-}4)]_2](BF_4)$ (**4**). Above: LUMO; Below: HOMO. No significant silver contribution can be observed in both cases.

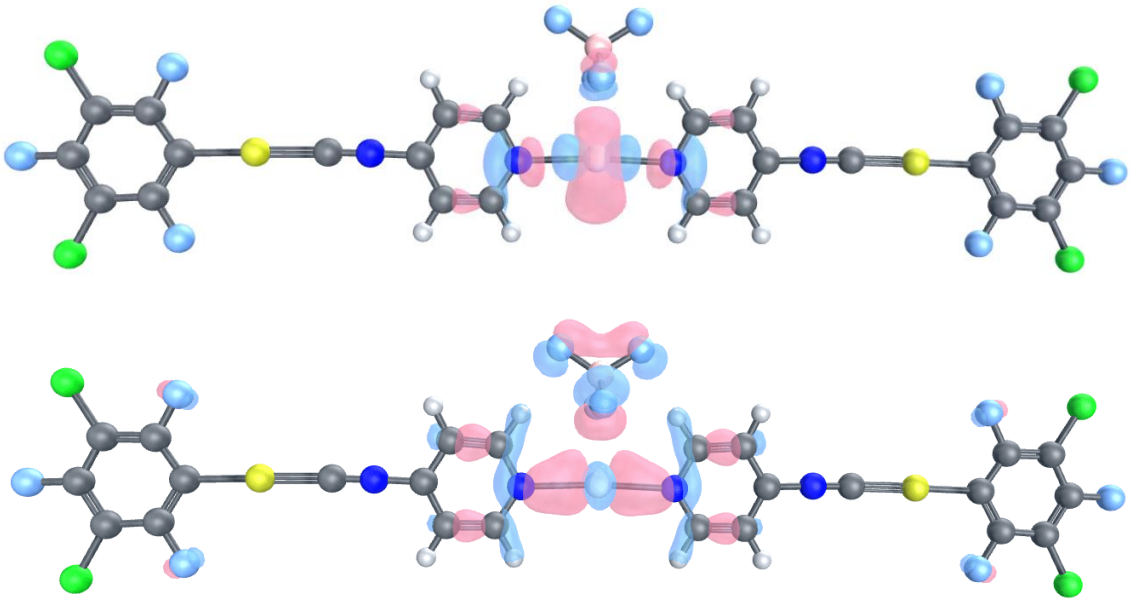

Figure ESI31. Selected Occupied Molecular Orbitals (isovalue = 0.10) of complex **4**. Above: HOMO-6, is the highest orbital with significant silver contribution; Below: bonding orbital between Ag and the nitrogen atoms of the pyridine moieties.

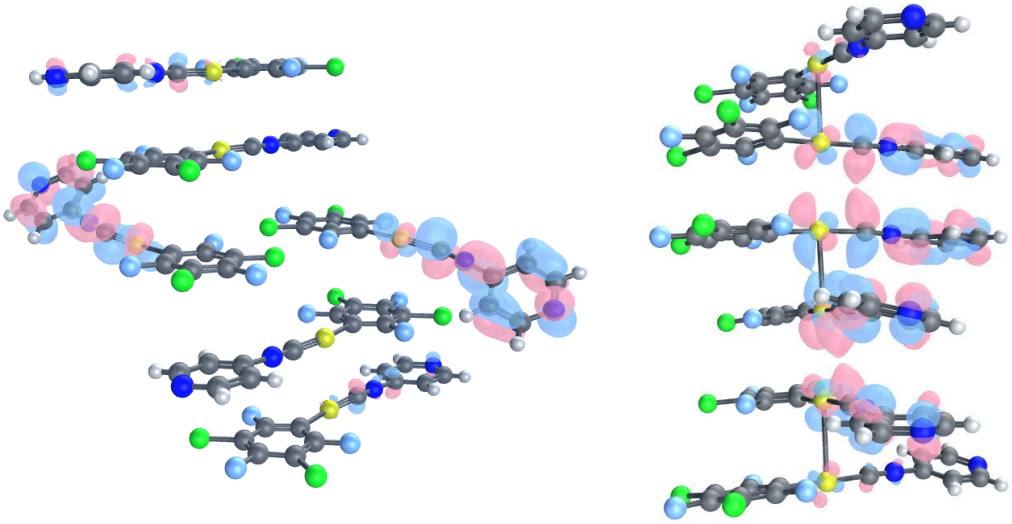

Figure ESI32. Lowest Unoccupied Molecular Orbitals, LUMOs, (isovalue = 0.07) of six ArRf(CNPy-4) fragments taken from X-Ray structures of compounds **2**$_{\alpha}$ (left) and **4** (right).

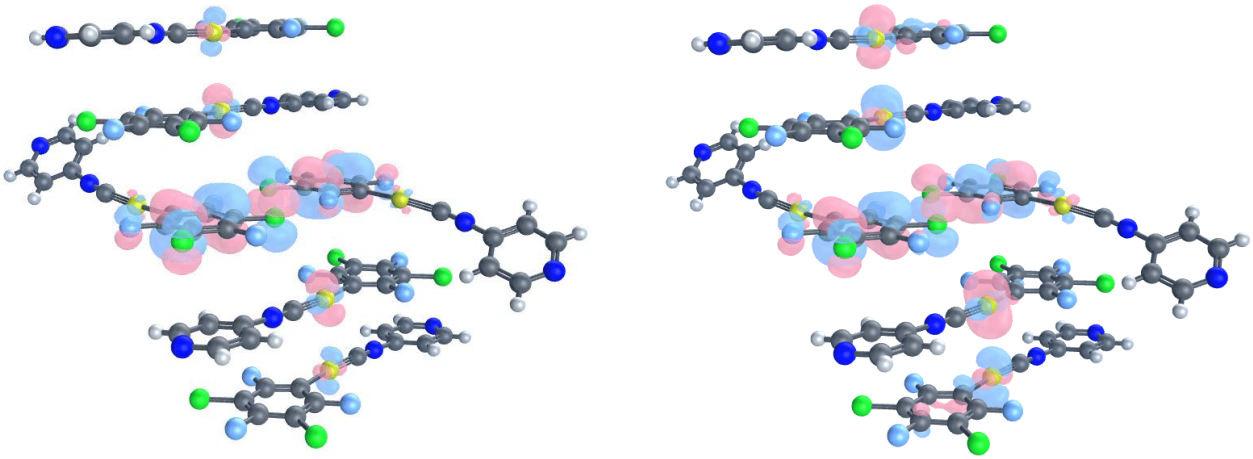

Figure ESI33. Occupied Molecular Orbitals (isovalue = 0.07) of the selected fragment of the structure of **2**$_{\alpha}$. HOMO (left) and HOMO-1 (right). Both orbitals are almost identical.

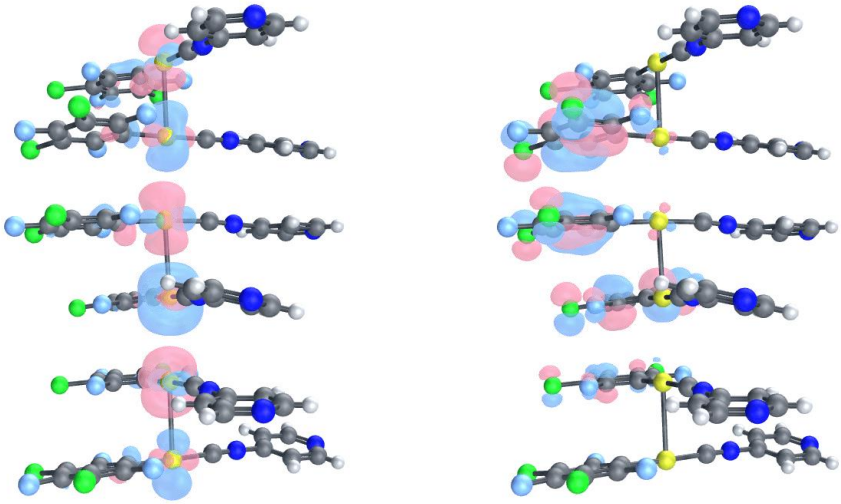

Figure ESI34. Occupied Molecular Orbitals (isovalue = 0.07) of the selected fragment of the structure of **4**. HOMO (left) and HOMO-1 (right). Both orbitals are completely different.

Rest of relevant data

Table ESI5. Energies and oscillator strengths (f) for ten Singlet Excited States calculated by TD-DFT on the selected fragments of the structures of $\mathbf{2}_{\alpha}$ and **4**.

	Complex 2		**Complex 4**	
Excited State	**E (eV)**	**f***	**E (eV)**	**f**
1	**4.6006**	**0.5568**	**3.5608**	**0.7942**
2	4.6117	0.0000	3.8817	0.0002
3	4.7875	0.0000	4.1620	0.0716
4	4.7876	0.0099	4.3121	0.0023
5	4.8111	0.0178	4.3613	0.0278
6	4.8113	0.0000	4.3924	0.0215
7	4.9484	0.0000	4.4189	0.0120
8	4.9485	0.0048	4.4316	0.0015
9	4.9562	0.0000	4.4691	0.0023
10	4.9602	0.0133	4.5038	0.0259

Table ESI6. Composition of the first Excited State calculated for structures $\mathbf{2}_{\alpha}$ and **4**. Orbital transitions and their corresponding coefficients. Note that the HOMO and LUMO are orbitals number 510 and 511 respectively.

	Transitions	**Coefficients**
Excited State 1 of complex **2**	497 → 514	0.14721
	498 → 513	-0.15891
	501 → 513	-0.11243
	502 → 514	-0.12318
	505 → 513	-0.21549
	506 → 514	0.19701
	507 → 514	0.26948
	508 → 513	0.15517
	509 → 513	0.23009
	510 → 514	-0.13202
Excited State 1 of complex **4**	497 → 512	-0.10886
	501 → 512	0.12238
	510 → 511	**0.59311**

Strong participation of the HOMO → LUMO transition in complex **4**, in bold.

Table ESI7. Contribution (%) of the haloaryl (Rf) groups, isocyanide ligands and gold centres in the Molecular Orbitals collected in Figure 7.

	Rf	**CNPy**	**Au**
HOMO (2)	91	1	**8**
LUMO (2)	8	83	9
σ*-HOMO (4)	19	2	**79**
LUMO (4)	6	76	18

Cartesian coordinates of all the calculated species (opt. = optimized geometry)

CNPy-4 (opt.)

6	1.466932	-1.140716	0.000119
1	2.050901	-2.056762	0.000510
6	-0.621788	-0.000074	-0.000164
7	2.161346	-0.000010	-0.000020
6	0.077905	1.203864	-0.000117
1	-0.447048	2.151420	0.000284
7	-2.006737	-0.000026	0.000029
6	0.077866	-1.203868	-0.000136
1	-0.446869	-2.151518	-0.000100
6	-3.182747	0.000028	0.000133
6	1.466813	1.140816	-0.000080
1	2.050866	2.056808	0.000707

[AuRf(CNPy-4)] (opt.)

79	-0.490160	0.000205	0.000036
17	4.550609	-2.706284	-0.000216
17	4.551516	2.705664	0.000096
9	1.646316	-2.352158	0.000040
9	1.647121	2.352529	0.000250
9	5.700607	-0.000502	-0.000152
6	2.292511	1.171585	0.000109
6	2.292115	-1.171432	0.000006
6	1.547428	0.000216	0.000080
6	4.368118	-0.000277	-0.000081
6	3.684427	-1.211480	-0.000099
6	3.684848	1.211153	0.000033
6	-7.096532	-1.142693	0.000393
1	-7.681698	-2.057548	0.000749
6	-5.015987	-0.000063	-0.000011
7	-7.786928	-0.000116	-0.000097
6	-5.707042	1.207536	-0.000515
1	-5.181780	2.154887	-0.000869
7	-3.629935	-0.000005	-0.000002
6	-5.706991	-1.207688	0.000458
1	-5.181682	-2.155013	0.000852
6	-2.465459	0.000098	-0.000041
6	-7.096580	1.142492	-0.000531
1	-7.681780	2.057325	-0.000914

[AuPf(CNPy-4)] (opt.)

79	-0.133981	-0.000047	-0.000171
9	4.703549	-2.356413	-0.000166
9	4.703545	2.356465	0.000404
9	2.018305	-2.368162	-0.000241
9	2.018298	2.368227	0.000361
9	6.065312	0.000034	0.000141
6	2.644746	1.174317	0.000260
6	2.644749	-1.174244	-0.000042
6	1.903223	0.000036	0.000071
6	4.731371	0.000032	0.000142
6	4.033042	-1.199655	-0.000033
6	4.033032	1.199712	0.000273
6	-6.740303	-1.142535	0.000801
1	-7.325509	-2.057364	0.001315
6	-4.659719	0.000006	0.000149
7	-7.430630	0.000084	0.000133
6	-5.350700	1.207647	-0.000528
1	-4.825381	2.154965	-0.001078
7	-3.273665	-0.000041	0.000092
6	-5.350774	-1.207600	0.000862
1	-4.825512	-2.154949	0.001432
6	-2.109208	-0.000070	-0.000315
6	-6.740240	1.142663	-0.000499
1	-7.325394	2.057531	-0.001038

[Ag[AuRf(CNPy-4)]$_2$](BF$_4$) (opt.)

79	9.505543	-0.170802	-0.000575
79	-9.505539	-0.170778	0.000441
47	0.000001	-0.205975	0.000965
17	14.447532	-3.040209	0.000793
17	-14.447509	-3.040233	-0.002132
17	-14.634254	2.368477	-0.000597
17	14.634236	2.368500	-0.000833
9	11.556607	-2.586456	0.000317
9	-11.718237	2.114623	0.000411
7	6.369626	-0.156499	-0.000550
9	-15.688840	-0.375815	-0.001783
9	-11.556582	-2.586456	-0.000927
7	-6.369625	-0.156432	0.001208
6	-4.987968	-0.196953	0.001417
6	7.535651	-0.144884	-0.000611
9	11.718214	2.114625	-0.001070
6	4.987967	-0.196977	-0.000368
6	-4.338471	-1.429863	0.001359
1	-4.894396	-2.359049	0.001181
6	11.540368	-0.232109	-0.000395
7	2.229216	-0.292069	0.000121
6	-7.535650	-0.144832	0.000975
9	15.688841	-0.375774	0.000103
6	-2.953761	-1.421635	0.001506
1	-2.401942	-2.354774	0.001439
6	4.338429	-1.429866	0.000530
1	4.894323	-2.359068	0.001061
7	-2.229218	-0.292143	0.001719
6	-4.255609	0.983829	0.001667
1	-4.740109	1.952114	0.001721
6	12.243804	-1.428977	0.000039
6	13.633468	-1.516957	0.000223
6	-11.540365	-0.232110	-0.000222
6	2.870204	0.888581	-0.000748
1	2.263904	1.788183	-0.001181
6	-2.870166	0.888529	0.001824
1	-2.263827	1.788107	0.002010
6	12.324229	0.913995	-0.000654
6	-12.243792	-1.428983	-0.000833
6	-14.357868	-0.329413	-0.001281
6	4.255650	0.983830	-0.001037
1	4.740185	1.952098	-0.001754
6	2.953720	-1.421588	0.000729
1	2.401870	-2.354709	0.001419
6	-12.324239	0.913988	-0.000163
6	-13.633455	-1.516976	-0.001369
6	14.357867	-0.329388	-0.000060
6	-13.717030	0.905231	-0.000678
6	13.717020	0.905254	-0.000503
9	-0.000943	2.085040	-1.143716
9	0.000847	2.085550	1.144447
9	1.165119	3.709826	-0.000918
9	-1.165068	3.709909	0.000911
5	-0.000014	2.957137	0.000165

[AuRf(CNPy-4)]$_6$ (**4**, from X-Ray)

79	8.253514	-0.017420	0.351422
17	7.907690	-1.237471	-5.183505
17	8.213313	-5.322383	-1.705845
9	8.276481	-3.186535	0.268232
9	8.017341	-4.032798	-4.314164
9	8.090205	0.372425	-2.765745
7	8.115215	2.070628	2.614944
6	8.008192	3.154846	3.522495
6	7.940707	4.402561	3.082012
1	7.945963	4.576286	2.167226
6	8.223316	1.282078	1.811603
6	7.860601	5.438387	3.987928
1	7.802495	6.314191	3.674756
7	7.863775	5.214572	5.302964
6	8.011703	2.878638	4.873713
1	8.065768	2.005742	5.192452

6	8.189820	-1.340638	-1.178921	6	-5.279080	3.845832	5.687462	6	-1.249205	4.716867	2.837729
6	7.928685	3.958017	5.726902	1	-5.288355	3.685642	6.603555	1	-1.010343	4.891253	1.955727
1	7.919409	3.797827	6.642995	6	-5.114967	-1.063520	-2.554032	6	-1.869128	4.322928	5.397333
6	8.092798	-0.951336	-2.514592	6	-5.129719	-3.256626	-3.331380	1	-2.080464	4.165447	6.290012
6	8.078046	-3.144441	-3.291939	6	-4.996341	-2.816596	-1.023879	6	-1.576759	-3.825702	-2.521611
6	8.211424	-2.704412	-0.984439	6	-5.149481	-1.915262	-3.609772	6	-1.679550	-2.579640	-3.056528
6	8.058283	-1.803077	-3.570331	6	-5.046235	-3.740075	-2.050264	79	1.648205	0.103019	0.324114
6	8.161530	-3.627890	-2.010824	79	-8.089477	-0.065829	0.398528	17	1.285929	0.837694	-5.294838
79	5.118287	0.046355	0.437969	17	-7.902382	5.447248	-1.079322	17	1.520900	5.210477	-2.180733
17	5.305382	5.559433	-1.039882	17	-8.541093	1.760647	-4.931612	9	1.618206	3.253347	-0.030720
17	4.666672	1.872832	-4.892172	9	-7.818774	3.084987	0.648542	9	1.348261	3.698746	-4.668638
9	5.388990	3.197171	0.687982	7	-8.021684	-2.302924	2.545055	9	1.493566	-0.555532	-2.747988
7	5.186081	-2.190739	2.584496	6	-8.044604	-1.489711	1.712005	7	1.543069	-1.785123	2.758553
6	5.163161	-1.377527	1.751446	9	-8.347195	-0.080583	-2.705178	6	1.453514	-2.789104	3.755865
9	4.860570	0.031601	-2.665738	6	-8.062200	-3.313099	3.514472	6	1.407290	-4.070864	3.424113
6	5.145565	-3.200915	3.553913	6	-8.111687	1.443425	-0.977795	1	1.416103	-4.322331	2.527604
6	5.096077	1.555610	-0.938355	7	-8.153683	-5.203455	5.468607	6	1.638663	-1.066716	1.890436
7	5.054082	-5.091271	5.508047	9	-8.352127	4.454225	-3.771506	6	1.343742	-5.026430	4.415630
9	4.855637	4.566410	-3.732065	6	-8.366193	-2.959391	4.779147	1	1.300594	-5.926623	4.178800
6	4.841572	-2.847206	4.818587	1	-8.544774	-2.075013	5.000899	7	1.342334	-4.690481	5.706604
1	4.662991	-1.962829	5.040340	6	-8.002428	2.761683	-0.626580	6	1.451543	-2.397951	5.078398
6	5.205336	2.873868	-0.587140	6	-8.038661	3.791301	-1.568863	1	1.490694	-1.500145	5.321022
6	5.169104	3.903485	-1.529423	6	-7.846454	-5.483870	4.217811	6	1.563521	1.288896	-1.314083
6	5.361311	-5.371686	4.257251	1	-7.663883	-6.370408	4.005573	6	1.385948	-3.401375	6.021116
1	5.543882	-6.258223	4.045013	6	-8.274778	1.194514	-2.284370	1	1.373241	-3.163348	6.920091
6	4.932986	1.306699	-2.244929	6	-7.776014	-4.558490	3.214301	6	1.473873	0.784754	-2.611349
6	5.431750	-4.446306	3.253742	1	-7.533540	-4.803901	2.350345	6	1.423058	2.902617	-3.574005
1	5.674224	-4.691716	2.389785	6	-8.404166	-3.956782	5.731108	6	1.562109	2.664496	-1.237354
6	4.803599	-3.844597	5.770548	1	-8.618744	-3.726735	6.607128	6	1.425897	1.542170	-3.736259
1	4.589021	-3.614551	6.646569	6	-8.242327	3.486044	-2.858039	6	1.497638	3.495537	-2.339157
6	4.965437	3.598228	-2.818599	6	-8.323812	2.197237	-3.283995				
6	4.883953	2.309421	-3.244554	79	-1.485681	-0.005441	0.418064				
79	-4.954250	-0.129604	0.311982	17	-1.205389	-5.621098	-0.581415				
17	-5.300074	-1.349655	-5.222946	17	-1.902808	-2.289724	-4.735375				
17	-4.994451	-5.434567	-1.745285	9	-1.162481	-3.118122	0.937315				
9	-4.931284	-3.298719	0.228792	7	-1.456795	2.408506	2.364664				
9	-5.190424	-4.144982	-4.353604	6	-1.465434	1.526444	1.604487				
9	-5.117560	0.260240	-2.805186	9	-1.741282	-0.261263	-2.675280				
7	-5.092550	1.958444	2.575503	6	-1.514871	3.497319	3.243856				
6	-5.199573	3.042662	3.483054	6	-1.481597	-1.627385	-0.823664				
6	-5.267058	4.290376	3.042572	7	-1.639311	5.546588	5.028645				
1	-5.261801	4.464102	2.127785	9	-1.669821	-4.870392	-3.348553				
6	-4.984449	1.169894	1.772163	6	-1.813822	3.248305	4.534439				
6	-5.347164	5.326202	3.948488	1	-1.977769	2.383459	4.831382				
1	-5.405170	6.202007	3.635316	6	-1.350592	-2.908636	-0.360708				
7	-5.343989	5.102387	5.263523	6	-1.369051	-4.015671	-1.211147				
6	-5.196061	2.766453	4.834273	6	-1.335808	5.723635	3.758185				
1	-5.141997	1.893557	5.153012	1	-1.168015	6.591615	3.470528				
6	-5.017944	-1.452823	-1.218361	6	-1.647885	-1.494162	-2.146665				

[AuRf(CNPy-4)]$_6$ (2$_\alpha$, from X-Ray)

79	-1.923591	1.174662	5.015863
17	-1.082239	-1.374345	0.051122
17	-5.145679	-3.168461	3.076283
9	-0.758727	0.531675	2.196980
9	-3.363144	-3.081553	0.770668
9	-4.188082	-1.153323	4.944803
6	-1.771455	-0.352965	2.461538
6	-2.026779	-1.277031	1.483824
6	-3.073966	-2.160125	1.711318
6	-2.419143	-0.263608	3.652687
6	-3.824078	-2.108665	2.869238
6	-3.441244	-1.180675	3.804776
7	-1.279166	3.600420	6.854220
6	-1.460571	2.669375	6.235640
6	-1.046931	4.785057	7.521365
7	-0.571522	7.177253	8.819871

6	-0.793002	6.063637	9.475515	1	0.949967	4.165247	-3.887849	7	-6.137404	5.329110	1.506829
1	-0.787502	6.098509	10.405940	7	0.740018	5.132301	-1.506829	6	-8.040623	4.068484	2.294112
6	-1.033317	4.853034	8.879940	6	2.643238	6.392927	-2.294112	1	-8.092011	3.618457	1.482546
1	-1.183529	4.093090	9.393719	1	2.694626	6.842955	-1.482546	6	-5.341453	5.619583	0.745107
6	-0.846731	5.926635	6.814600	6	-0.055932	4.841828	-0.745107	6	-7.935738	5.324581	4.678967
1	-0.866958	5.924194	5.884174	6	2.538352	5.136830	-4.678967	1	-7.912609	5.772825	5.494367
6	-0.614285	7.089254	7.520087	1	2.515224	4.688586	-5.494367	79	1.450239	-4.265883	-0.508028
1	-0.477284	7.868242	7.030592	79	3.947146	-6.195528	0.508028	17	4.416299	-4.110162	-5.431231
79	1.923591	-1.174662	-5.015863	17	0.981086	-6.351249	5.431231	17	5.690155	-0.661172	-1.530345
17	1.082239	1.374345	-0.051122	17	-0.292770	-9.800239	1.530345	9	2.340147	-4.958304	-3.547886
17	5.145679	3.168461	-3.076283	9	3.057239	-5.503107	3.547886	9	3.505285	-1.965529	-0.106079
9	0.758727	-0.531675	-2.196980	9	1.892100	-8.495882	0.106079	9	5.896722	-1.970719	-4.134514
9	3.363144	3.081553	-0.770668	9	-0.499336	-8.490692	4.134514	6	3.686327	-2.486918	-1.344516
9	4.188082	1.153323	-4.944803	6	1.711058	-7.974493	1.344516	6	3.131430	-3.982414	-3.039220
6	1.771455	0.352965	-2.461538	6	2.265956	-6.478997	3.039220	6	2.861639	-3.519064	-1.763719
6	2.026779	1.277031	-1.483824	6	2.535746	-6.942347	1.763719	6	4.910509	-2.488918	-3.360012
6	3.073966	2.160125	-1.711318	6	0.486876	-7.972493	3.360012	6	4.099952	-3.475960	-3.846952
6	2.419143	0.263608	-3.652687	6	1.297433	-6.985452	3.846952	6	4.700364	-1.936099	-2.103682
6	3.824078	2.108665	-2.869238	6	0.697021	-8.525312	2.103682	6	-3.508532	-6.659728	3.306333
6	3.441244	1.180675	-3.804776	6	8.905918	-3.801684	-3.306333	1	-4.170274	-7.295586	3.152967
7	1.279166	-3.600420	-6.854220	1	9.567660	-3.165825	-3.152967	6	-1.694260	-5.437665	2.516494
6	1.460571	-2.669375	-6.235640	6	7.091645	-5.023746	-2.516494	7	-3.474987	-6.080491	4.492370
6	1.046931	-4.785057	-7.521365	7	8.872373	-4.380920	-4.492370	6	-1.609030	-4.800392	3.721702
7	0.571522	-7.177253	-8.819871	6	7.006416	-5.661019	-3.721702	1	-0.949967	-4.165247	3.887849
6	0.793002	-6.063637	-9.475515	1	6.347353	-6.296164	-3.887849	7	-0.740018	-5.132301	1.506829
1	0.787502	-6.098509	-10.405940	7	6.137404	-5.329110	-1.506829	6	-2.643238	-6.392927	2.294112
6	1.033317	-4.853034	-8.879940	6	8.040623	-4.068484	-2.294112	1	-2.694626	-6.842955	1.482546
1	1.183529	-4.093090	-9.393719	1	8.092011	-3.618457	-1.482546	6	0.055932	-4.841828	0.745107
6	0.846731	-5.926635	-6.814600	6	5.341453	-5.619583	-0.745107	6	-2.538352	-5.136830	4.678967
1	0.866958	-5.924194	-5.884174	6	7.935738	-5.324581	-4.678967	1	-2.515224	-4.688586	5.494367
6	0.614285	-7.089254	-7.520087	1	7.912609	-5.772825	-5.494367				
1	0.477284	-7.868242	-7.030592	79	-3.947146	6.195528	-0.508028				
79	-1.450239	4.265883	0.508028	17	-0.981086	6.351249	-5.431231				
17	-4.416299	4.110162	5.431231	17	0.292770	9.800239	-1.530345				
17	-5.690155	0.661172	1.530345	9	-3.057239	5.503107	-3.547886				
9	-2.340147	4.958304	3.547886	9	-1.892100	8.495882	-0.106079				
9	-3.505285	1.965529	0.106079	9	0.499336	8.490692	-4.134514				
9	-5.896722	1.970719	4.134514	6	-1.711058	7.974493	-1.344516				
6	-3.686327	2.486918	1.344516	6	-2.265956	6.478997	-3.039220				
6	-3.131430	3.982414	3.039220	6	-2.535746	6.942347	-1.763719				
6	-2.861639	3.519064	1.763719	6	-0.486876	7.972493	-3.360012				
6	-4.910509	2.488918	3.360012	6	-1.297433	6.985452	-3.846952				
6	-4.099952	3.475960	3.846952	6	-0.697021	8.525312	-2.103682				
6	-4.700364	1.936099	2.103682	6	-8.905918	3.801684	3.306333				
6	3.508532	6.659728	-3.306333	1	-9.567660	3.165825	3.152967				
1	4.170274	7.295586	-3.152967	6	-7.091645	5.023746	2.516494				
6	1.694260	5.437665	-2.516494	7	-8.872373	4.380920	4.492370				
7	3.474987	6.080491	-4.492370	6	-7.006416	5.661019	3.721702				
6	1.609030	4.800392	-3.721702	1	-6.347353	6.296164	3.887849				

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