Supporting Information for

Seeing Luminescence Appear as Crystals Crumble. Isolation and Subsequent Self-Association of Individual $[(C_6H_{11}NC)_2Au]^+$ Ions in Crystals

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Table SI-1. A summary of properties of crystals of $[(C_6H_{11}NC)_2Au^I](EF_6)$ (E = P, As, Sb)

Compound	$[(C_6H_{11}NC)_2Au^I](PF_6)$ **(1)** Form I	$[(C_6H_{11}NC)_2Au^I](PF_6)$ **(2)** Form II	$[(C_6H_{11}NC)_2Au^I](AsF_6)$ **(3)** Form I	$[(C_6H_{11}NC)_2Au^I](AsF_6)$ **(4)** Form III	$[(C_6H_{11}NC)_2Au^I](SbF_6)$ **(5)** Form IV
Color Form	colorless needle	yellow plate	colorless block	yellow needle	pale yellow needle
Space group	$P2_1/c$	$P2_12_12_1$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
Volume (Å^3); Z; T (K)	1805; 4; 91	7247; 16; 91	1838; 4; 90	1887; 4; 180	7609; 16; 100
REFCODE References	LUVJER01 [36], [37]	LUVJER [36], [37]	MEGFIP [37]	MEGFIP01 [37]	LUGLUX [38]
m.p. (°C)	115-120	110-115	123-125	123-126	113-115
Luminescence, 298K	blue	green	blue	green	blue
Excitation; emission (nm);77 K			373; 439	370; 438 436; 487, 530	421; 452, 495
Excitation; emission (nm); 298 K	353; 424	394; 480	369; 427	358; 422 419; 484	398; 477
Range Au—Au, Å	3.1822(3)	2.9643(6)- 2.9803(6)	3.1983(8)	3.0097(6)- 3.0230(5)	3.0296(7) – 3.0826(7)

Table SI-2. Crystallographic Data for New Gold(I) Complexes.

	$[(C_6H_{11}NC)_2Au](BArF_{24})$ (**6**)	$C_6H_6 \cdot [(C_6H_{11}NC)_2Au](SbF_6)$ (**7**)	$C_6H_6 \cdot [(C_6H_{11}NC)_2Au](AsF_6)$ (**8**)
color/habit	colorless block	colorless block	colorless block
chemical formula	$C_{46}H_{34}AuBF_{24}N_2$	$C_{20}H_{28}AuF_6N_2Sb$	$C_{20}H_{28}AsAuF_6N_2$
formula weight	1278.53	729.16	682.33
crystal system	monoclinic	tetragonal	tetragonal
space group	$C2/c$	$P4/mnc$	$P4/mnc$
a (Å)	23.708(3)	12.948(4)	12.714(4)
b (Å)	9.1838(10)	12.948(4)	12.714(4)
c (Å)	23.708(3)	13.943(4)	13.871(4)
α *(deg)*	90	90	90
β (deg)	114.129(2)	90	90
γ *(deg)*	90	90	90
V (Å^3)	4698.0(9)	2337.6(14)	2251.7(16)
Z	4	4	4
T (K)	90(2)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073
ρ (g/cm^3)	1.808	2.072	2.013
μ (mm^{-1})	3.264	7.481	8.050
R_1 (obsd data)[a]	0.0192	0.0357	0.0304
wR_2 (all data, F^2 refinement)[b]	0.0469	0.0946	0.0984

[a] $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$
[b] $wR_2 = ((\Sigma[w(F_o^2 - F_c^2)^2])/\Sigma[w(F_o^2)^2])^{1/2}$

Infrared Spectra

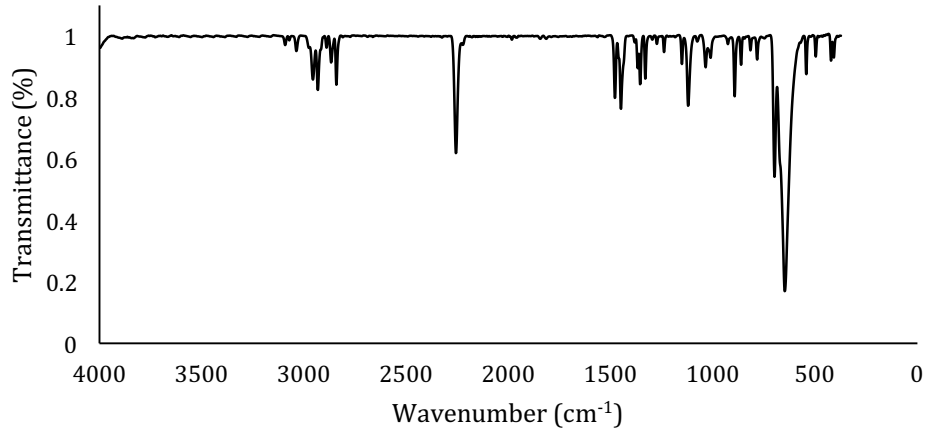


Fig. SI-1 C_6H_6•[$(C_6H_{11}NC)_2Au$](SbF_6) (**7**)
Isocyanide peak at 2256 cm^{-1}
Peaks above 3000 cm^{-1} correspond to C-H stretches of the benzene molecule

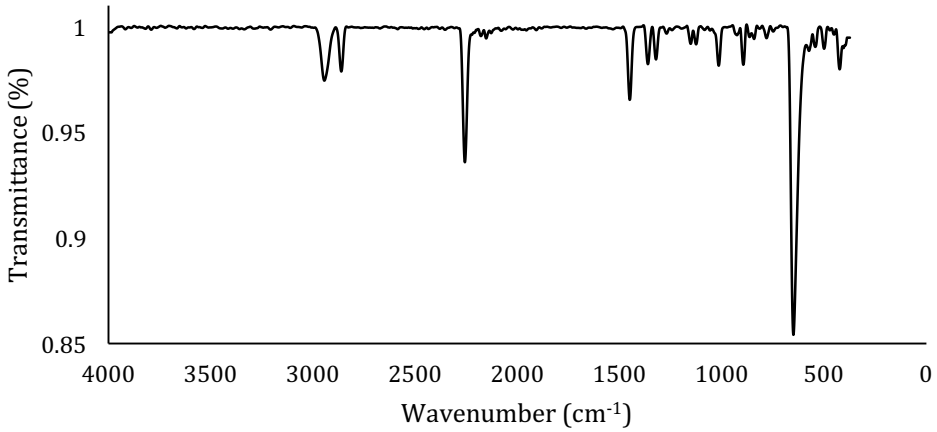


Fig. SI-2 C_6H_6•[$(C_6H_{11}NC)_2Au$](SbF_6) (**7**) after standing in air
Isocyanide peak at 2256 cm^{-1}
No peaks above 3000 cm^{-1}

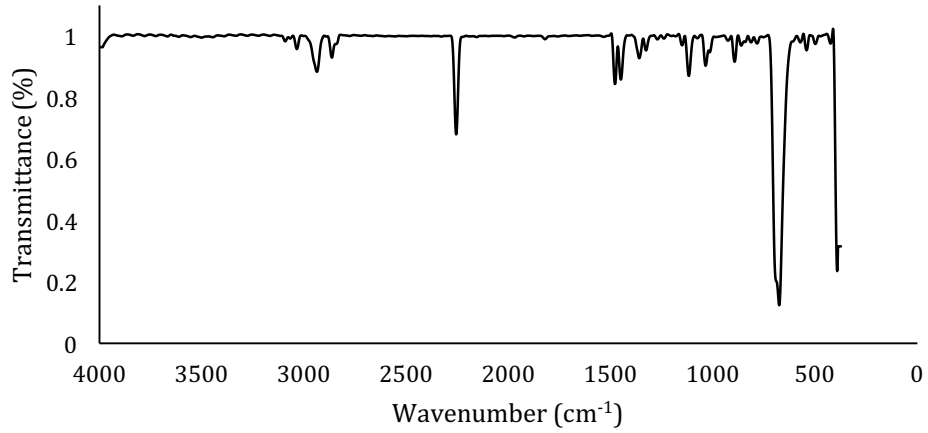


Fig. SI-3 C_6H_6•[$(C_6H_{11}NC)_2Au$](AsF_6) (**8**)
Isocyanide peak at 2255 cm^{-1}
Peaks above 3000 cm^{-1} correspond to C-H vibration of the benzene molecule

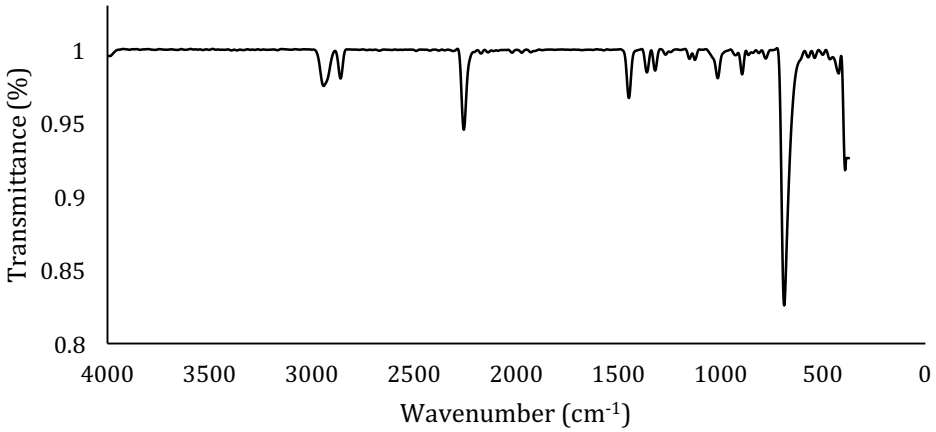


Fig. SI-4 C_6H_6•[$(C_6H_{11}NC)_2Au$](AsF_6) (**8**) after standing in air
Isocyanide peak at 2257 cm^{-1}
No peaks above 3000 cm^{-1}

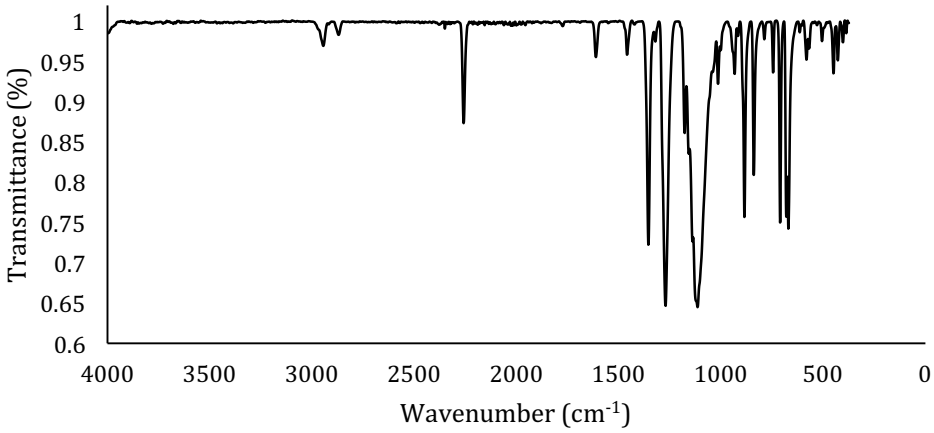


Fig. SI-5 $[(C_6H_{11}NC)_2Au](BArF_{24})$ (**6**)
Isocyanide peak at 2258 cm^{-1}

Simulated Powder X-Ray Diffraction from Single Crystal Data

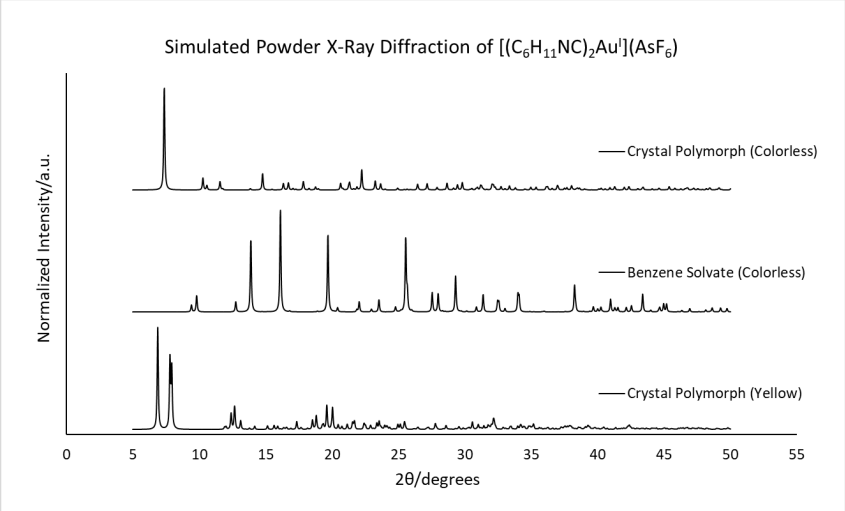


Fig. SI-6 Simulated Powder Diffraction Data Calculated from the Single Crystal Data Taken at 90 K.

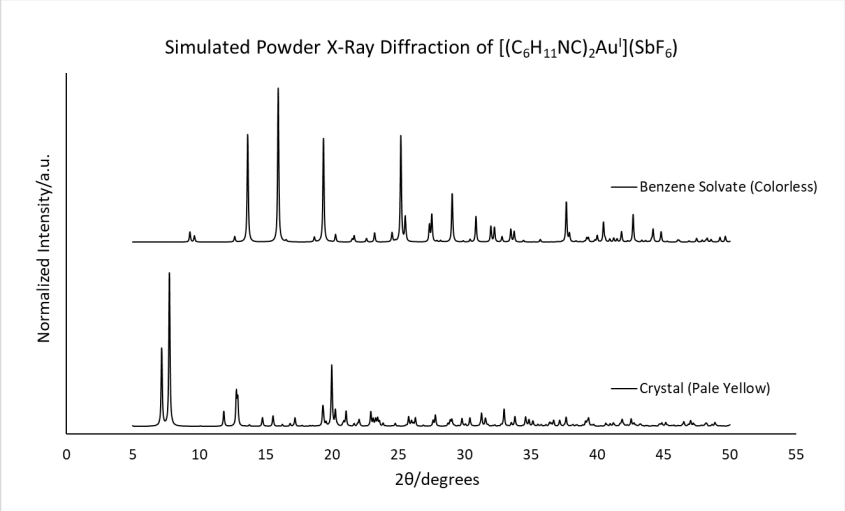
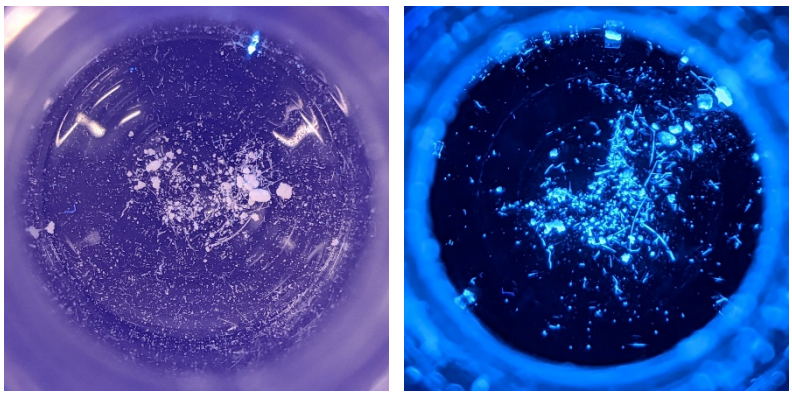
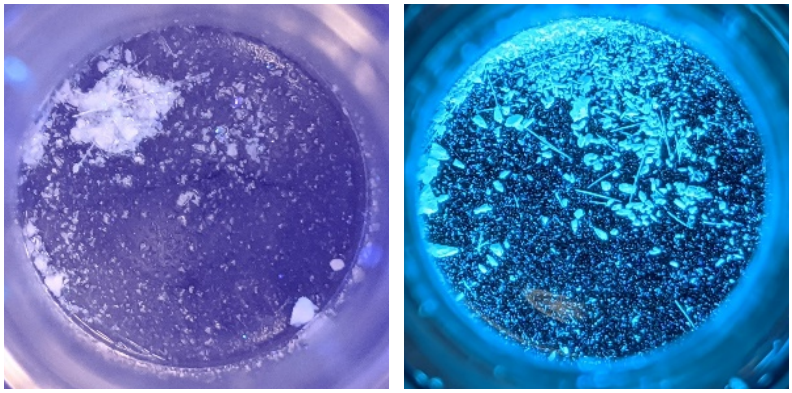


Fig. SI-7 Simulated Powder Diffraction Data Calculated from the Single Crystal Data Taken at 90 K.



A **B**

Fig. SI-8 Photographs of crystals of $[(C_6H_{11}NC)_2Au](SbF_6)\bullet C_6H_6$ (**7**) under UV irradiation. **A** shows the colorless, non-luminescent solvates still wet with pentane from a wash after removal of mother liquor. **B** shows the solvates that have been left to air dry, resulting in the pale-yellow, blue-luminescence solid.



A **B**

Fig. SI-9 Photographs of crystals of $[(C_6H_{11}NC)_2Au](AsF_6)\bullet C_6H_6$ (**8**) under UV irradiation. **A** shows the colorless, non-luminescent solvates still wet with pentane from a wash after removal of mother liquor. **B** shows the solvates that have been left to air dry, resulting in only the yellow, green-luminescent form.