

Supplementary Information

Negative linear compressibility and strong enhancement of emission in Eu[Ag(CN)₂]₃·3H₂O under pressure

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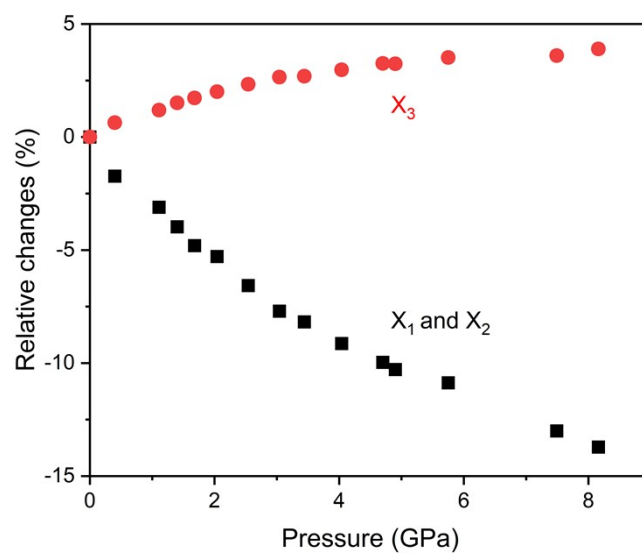


Figure S1. The changes of principal axes X_1 , X_2 and X_3 of phase I as a function of pressure.

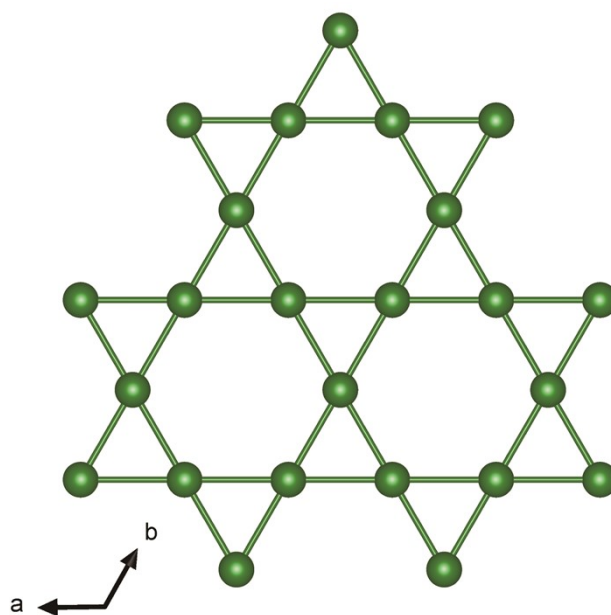


Figure S2. The Kagome net of Ag atoms in $\text{Eu}[\text{Ag}(\text{CN})_2]_3 \cdot 3\text{H}_2\text{O}$. Each Ag atom is connected to four other Ag atoms around it by argentophilic interactions.

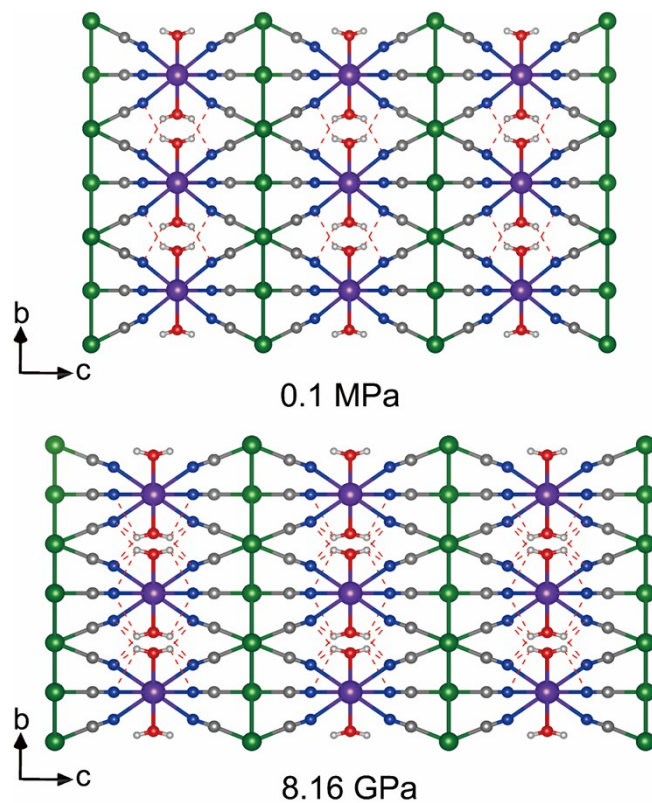


Figure S3. Crystal structure of $\text{Eu}[\text{Ag}(\text{CN})_2]_3 \cdot 3\text{H}_2\text{O}$. The O-H \cdots N hydrogen bonds are represented by red dashed lines. Colour code of atoms: Eu purple, Ag green, N blue, C gray, O red, H light grey.

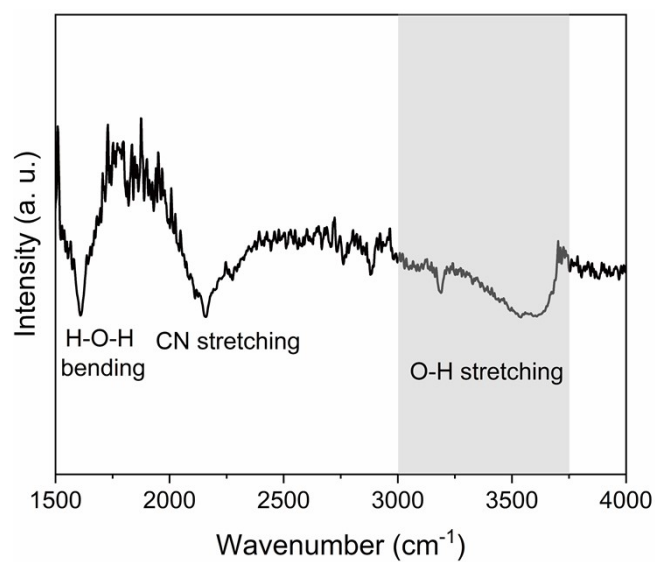


Figure S4. FT-IR spectra of $\text{Eu}[\text{Ag}(\text{CN})_2]_3 \cdot 3\text{H}_2\text{O}$ at ambient pressure.

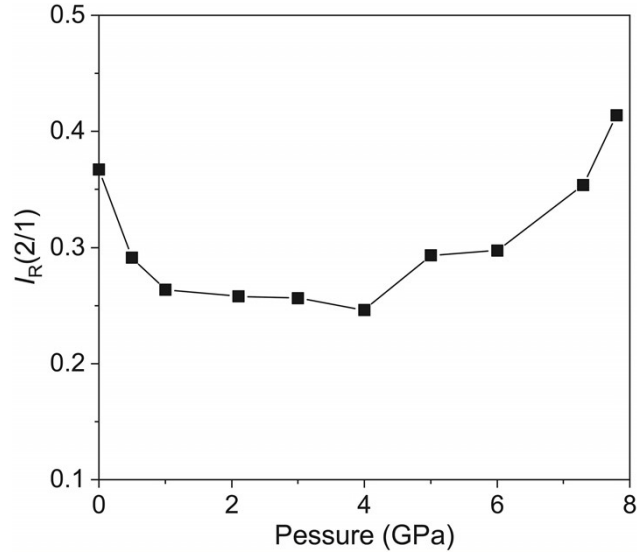


Figure S5. Evolution of intensity ratios of ${}^5D_0 \rightarrow {}^7F_2$ to ${}^5D_0 \rightarrow {}^7F_1$, $I_R(2/1)$ at different pressures.

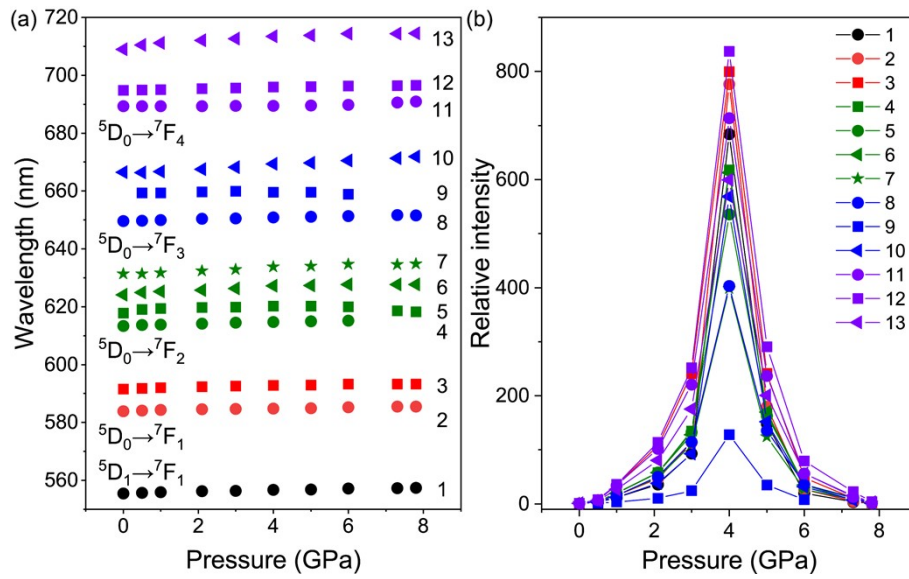


Figure S6. (a) The plot of wavelength of $\text{Eu}[\text{Ag}(\text{CN})_2]_3 \cdot 3\text{H}_2\text{O}$ single crystal as a function of pressure. (b) Relative intensity to ambient pressure data at different pressures.

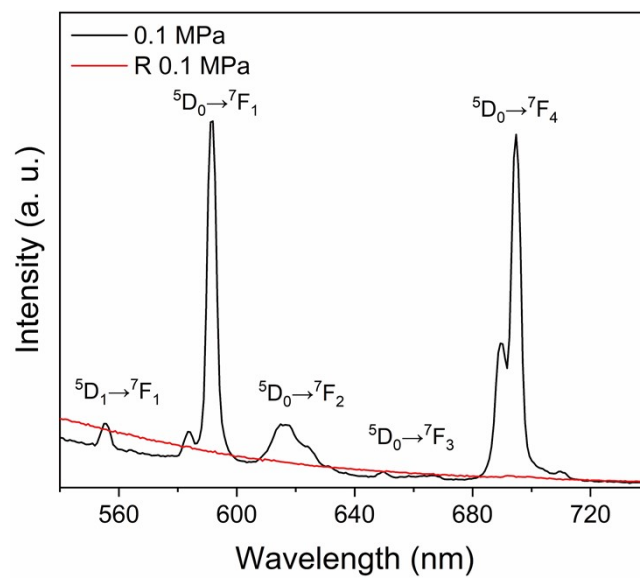


Figure S7. The emission spectra of Eu[Ag(CN)₂]₃·3H₂O single crystal under ambient pressure and released to ambient pressure.

Table S1. Selected crystallographic data of $\text{Eu}[\text{Ag}(\text{CN})_2]_3 \cdot 3\text{H}_2\text{O}$ single crystal compressed in ME mixture at RT.

Pressure (GPa)	0.0001 ^a	0.40	1.11	1.40	1.68
CCDC	2303078	2303077	2303079	2303080	2303081
Crystal system	hexagonal	hexagonal	hexagonal	hexagonal	hexagonal
Space group	$P6_3/mcm$	$P6_3/mcm$	$P6_3/mcm$	$P6_3/mcm$	$P6_3/mcm$
Phase	I	I	I	I	I
Radiation type	MoK α	AgK α	AgK α	AgK α	AgK α
Crystal size (mm)	0.17×0.17×0.12	0.17×0.15×0.10	0.18×0.15×0.12	0.16×0.12×0.08	0.17×0.15×0.09
a (Å)	6.6933(4)	6.5784(4)	6.4884(3)	6.4324(4)	6.3792(2)
b (Å)	6.6933(4)	6.5784(4)	6.4884(3)	6.4324(4)	6.3792(2)
c (Å)	18.4866(11)	18.6044(9)	18.7079(9)	18.7687(9)	18.8082(8)
α (°)	90	90	90	90	90
β (°)	90	90	90	90	90
γ (°)	120	120	120	120	120
V (Å ³)	717.25(10)	697.25(9)	682.07(7)	672.53(9)	662.84(5)
Z	2	2	2	2	2
ρ_{calc} (g/cm ³)	3.175	3.266	3.339	3.386	3.436
μ (mm ⁻¹)	4.432	4.559	4.660	4.675	4.743
Index ranges	$-10 \leq h \leq 11$	$-6 \leq h \leq 6$	$-5 \leq h \leq 5$	$-4 \leq h \leq 4$	$-9 \leq h \leq 9$
	$-11 \leq k \leq 9$	$-7 \leq k \leq 7$	$-7 \leq k \leq 7$	$-7 \leq k \leq 7$	$-7 \leq k \leq 7$
	$-28 \leq l \leq 27$	$-28 \leq l \leq 29$	$-28 \leq l \leq 28$	$-28 \leq l \leq 28$	$-21 \leq l \leq 21$
R_{int}	0.0351	0.0392	0.0341	0.0299	0.0823
GOOF	1.249	1.171	1.043	1.087	1.134
R_1/wR_2 [$I > 2\sigma(I)$] ^b	0.0279/0.0518	0.0218/0.0498	0.0164/0.0372	0.0172/0.0383	0.0359/0.1033
R_1/wR_2 [all data]	0.0384/0.0607	0.0267/0.0524	0.0207/0.0394	0.0217/0.0410	0.0511/0.1033
Largest peak/hole (e ⁻ ·Å ⁻³)	1.75/-1.38	0.46/-0.90	0.27/-0.27	0.48/-0.69	1.51/-2.69

Table S1 (continued)

Pressure (GPa)	2.04	2.54	3.04	3.44	4.04
CCDC	2303082	2303083	2303084	2303085	2303086
Crystal system	hexagonal	hexagonal	hexagonal	hexagonal	hexagonal
Space group	<i>P6₃/mcm</i>	<i>P6₃/mcm</i>	<i>P6₃/mcm</i>	<i>P6₃/mcm</i>	<i>P6₃/mcm</i>
Phase	I	I	I	I	I
Radiation type	AgK α	AgK α	AgK α	AgK α	AgK α
Crystal size (mm)	0.15×0.13×0.12	0.17×0.14×0.12	0.16×0.15×0.10	0.15×0.15×0.07	0.18×0.15×0.12
<i>a</i> (Å)	6.3456(17)	6.2669(5)	6.1962(4)	6.1668(10)	6.1073(11)
<i>b</i> (Å)	6.3456(17)	6.2669(5)	6.1962(4)	6.1668(10)	6.1073(11)
<i>c</i> (Å)	18.861(4)	18.9227(16)	18.9835(13)	18.993(3)	19.045(3)
α (°)	90	90	90	90	90
β (°)	90	90	90	90	90
γ (°)	120	120	120	120	120
<i>V</i> (Å ³)	657.7(4)	643.6(12)	631.19(9)	625.5(2)	615.2(2)
<i>Z</i>	2	2	2	2	2
ρ_{calc} (g/cm ³)	3.460	3.538	3.608	3.642	3.702
μ (mm ⁻¹)	4.829	4.885	5.036	5.083	5.167
Index ranges	$-3 \leq h \leq 3$	$-9 \leq h \leq 9$	$-9 \leq h \leq 9$	$-8 \leq h \leq 8$	$-4 \leq h \leq 4$
	$-5 \leq k \leq 5$	$-7 \leq k \leq 7$	$-7 \leq k \leq 7$	$-4 \leq k \leq 4$	$-7 \leq k \leq 8$
	$-29 \leq l \leq 29$	$-22 \leq l \leq -22$	$-22 \leq l \leq 22$	$-27 \leq l \leq 28$	$-28 \leq l \leq 28$
R_{int}	0.0723	0.0606	0.0436	0.0965	0.1027
GOOF	1.139	1.123	1.174	1.071	1.086
R_1/wR_2 [$I > 2\sigma(I)$] ^b	0.0476/0.0974	0.0315/0.0703	0.0312/0.0671	0.0420/0.0814	0.0444/0.0752
R_1/wR_2 [all data]	0.0654/0.1061	0.0408/0.0753	0.0393/0.0715	0.0871/0.0952	0.0863/0.0905
Largest peak/hole (e ⁻ Å ⁻³)	1.48/-1.85	1.54/-1.38	0.61/-0.52	1.01/-1.44	1.49/-0.98

Table S1 (continued)

Pressure (GPa)	4.70	5.75	7.49	8.16
CCDC	2303087	2303088	2303089	2303090
Crystal system	hexagonal	hexagonal	hexagonal	hexagonal
Space group	<i>P6₃/mcm</i>	<i>P6₃/mcm</i>	<i>P6₃/mcm</i>	<i>P6₃/mcm</i>
Phase	I	I	I	I
Radiation type	AgK α	AgK α	AgK α	AgK α
Crystal size (mm)	0.14×0.12×0.08	0.17×0.13×0.09	0.15×0.13×0.10	0.15×0.14×0.12
<i>a</i> (Å)	6.0562(5)	6.001(2)	5.8722(6)	5.8288(3)
<i>b</i> (Å)	6.0562(5)	6.001(2)	5.8722(6)	5.8288(3)
<i>c</i> (Å)	19.0992(18)	19.149(8)	19.171(2)	19.214(2)
α (°)	90	90	90	90
β (°)	90	90	90	90
γ (°)	120	120	120	120
<i>V</i> (Å ³)	606.66(12)	597.2(5)	572.50(14)	565.35(8)
<i>Z</i>	2	2	2	2
ρ_{calc} (g/cm ³)	3.754	3.813	3.978	4.028
μ (mm ⁻¹)	5.240	5.265	5.492	5.561
Index ranges	$-9 \leq h \leq 9$	$-9 \leq h \leq 9$	$-8 \leq h \leq 8$	$-8 \leq h \leq 8$
	$-3 \leq k \leq 3$	$-7 \leq k \leq 8$	$-8 \leq k \leq 8$	$-6 \leq k \leq 6$
	$-22 \leq l \leq 22$	$-17 \leq l \leq 15$	$-21 \leq l \leq 20$	$-16 \leq l \leq 16$
R_{int}	0.0464	0.4479	0.0910	0.0651
GOOF	1.111	1.141	1.043	1.024
$R_1/wR_2 [I > 2\sigma(I)]^b$	0.0311/0.0695	0.0325/0.0733	0.0482 /0.1193	0.0464/0.1125
R_1/ wR_2 [all data]	0.0399/0.0757	0.0413/0.0798	0.0869/0.1400	0.0815/0.1325
Largest peak/hole (e·Å ⁻³)	0.92/-1.31	0.97/-1.48	1.20/-1.34	1.52/-1.08

Table S1 (continued)

Pressure (GPa)	8.40 ^c	8.88 ^c	9.34 ^c	10.10 ^c	10.60 ^c
Crystal system	hexagonal	hexagonal	hexagonal	hexagonal	hexagonal
Space group	<i>P6₃/mcm</i>	<i>P6₃/mcm</i>	<i>P6₃/mcm</i>	<i>P6₃/mcm</i>	<i>P6₃/mcm</i>
Phase	II	II	II	II	II
Radiation type	AgK α	AgK α	AgK α	AgK α	AgK α
Crystal size (mm)	0.17×0.14×0.05	0.14×0.14×0.06	0.16×0.13×0.09	0.15×0.14×0.10	0.15×0.14×0.12
<i>a</i> (Å)	5.891(5)	5.862(4)	5.835(2)	5.812(5)	5.791(5)
<i>b</i> (Å)	5.891(5)	5.862(4)	5.835(2)	5.812(5)	5.791(5)
<i>c</i> (Å)	17.985(13)	18.051(19)	18.074(9)	18.051(5)	18.032(19)
α (°)	90	90	90	90	90
β (°)	90	90	90	90	90
γ (°)	120	120	120	120	120
<i>V</i> (Å ³)	540.4(8)	537.2(7)	532.9(4)	528.1(5)	523.5(8)
<i>Z</i>	2	2	2	2	2

[a] Ambient pressure data were collected with MoK α ($\lambda = 0.71073$ Å) radiation, other high pressure data were collected with AgK α radiation ($\lambda = 0.56086$ Å)

[b] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ for $F_o^2 > 2\sigma(F_o^2)$; $wR_2 = \sum [w(F_o^2 - F_c^2)] / \sum [w(F_o^2)^2]^{1/2}$, where $w = 1 / [\sigma^2 F_o^2 + (A P)^2 + B P]$, and $P = (F_o^2 + 2F_c^2) / 3$

[c] Due to low quality of the crystal data, only lattice parameters were obtained.

Table S2. Principal axes of the strain tensor and their mean linear compressibility coefficients of Eu[Ag(CN)₂]₃·3H₂O-I (0–8.16 GPa) (TPa⁻¹, ×10⁻³ GPa⁻¹).

Axes	eigenvalue	Direction		
		<i>a</i>	<i>b</i>	<i>c</i>
X ₁	14.63(5)	0.7071	-0.7071	0
X ₂	14.63(5)	0.7071	0.7071	0
X ₃	-4.2(1)	0	0	-1
V	25.6(15)			

Table S3. Assignments of Raman spectra of Eu[Ag(CN)₂]₃·3H₂O single crystal.

Phase I 0.1 MPa	Raman shift (cm ⁻¹)	Assignments	Phase II (8.30 GPa)	Raman shift (cm ⁻¹)	Assignments
ν_1	119.80 w	Ag-Ag stretch	ν_1	163.60 w	Ag-Ag stretch
ν_2	202.90 w	Eu-O stretch	ν_2	250.40 w	Eu-O stretch
ν_3	273.80 w	Ag-CN bend (in plane)	ν_3	276.10 w	Ag-CN bend (in plane)
ν_4	294.90 m	Ag-CN bend (in plane)	ν_4	305.50 s	Ag-CN bend (in plane)
ν_5	414.30 vw	Ag-C stretch			
ν_6	805.88 s	Eu-O stretch	ν_6	771.43 m	Eu-O stretch
ν_7	819.34 s	Eu-O stretch	ν_7	828.90 m	Eu-O stretch
ν_8	833.53 s	Eu-O stretch	ν_8	885.58 m	Eu-O stretch
ν_9	2162.90 w	CN stretch	ν_9	2194.10 w	CN stretch
ν_{10}	3399.30 m	O-H stretch	ν_{10}	3431.30 m	O-H stretch
ν_{11}	3422.80 m	O-H stretch	ν_{11}	3446.50 m	O-H stretch

s = strong; m = medium; vw = very weak;

Table S4. Assignments of emission bands of Eu[Ag(CN)₂]₃·3H₂O single crystal at ambient pressure.

Emission band	λ (nm)	assignment	$\Delta\nu/\Delta p$ (nm/GPa) ^a
1	555.51	⁵ D ₁ → ⁷ F ₁	0.31±0.02
2	583.97	⁵ D ₀ → ⁷ F ₁	0.21±0.03
3	591.53		0.32±0.02
4	613.38		0.35±0.02
5	617.77	⁵ D ₀ → ⁷ F ₂	0.50±0.14
6	624.17		0.68±0.06
7	631.41		0.59±0.05
8	649.68		0.31±0.02
9	659.39	⁵ D ₀ → ⁷ F ₃	0.10±0.08
10	666.49		0.74±0.07
11	689.40		0.04±0.01
12	694.75	⁵ D ₀ → ⁷ F ₄	0.30±0.01
13	708.94		1.02±0.14

^a Linear fit of the emission data in the range of 0-4.0 GPa.