Supporting Information

Pressure Induced Blue Shift Emission and Its Influence on the Band Gap in an Emerging 3D Semiconductor †

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Experimentals

Instrumentation and Characterizations

Powder X-ray diffraction (PXRD) patterns of the samples were collected at room temperature using a D/MAX-3D diffractometer (Cu-Kα radiation, λ =1.54178 Å, voltage =20-40 kV, current =2-15 mA) over the range of 2θ =3 to 50 at a scan speed of 2θ =10 min^{-1}. Elemental percentage of C, H, N and S were analyzed by a Perkin-Elmer 240 elemental analyzer. Thermogravimetric analyses (TGA) were carried out with a TA Q50 system from room temperature to 500 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. UV-vis measurements were performed using a Hitachi UH4150 UV-visible spectrophotometer. Fourier transforms infrared (FT-IR) spectra were recorded on a Nexus 870 FT-IR spectrometer. Emission and excitation spectra at room temperature were recorded on a HORIBA FluoroLog-3 fluorescence spectrometer. Luminescence decay was measured on a HORIBA FluoroLog-3 fluorescence spectrometer equipped with a 355 nm laser operating in time correlated single-photon counting mode (TCSPC) with a time resolution of 340 μs. The photoluminescence quantum yield (PLQY) was measured on a HORIBA Scientific Fluorolog-3 spectrofluorometer equipped with 450 W xenon lamp and an integrating sphere. Scanning electron microscopy (SEM) was carried out by field emission Zeiss Sigma 500.

Single crystal X-ray diffraction analysis (SCXRD)

SCXRD measurements of $\{Ag_{10}[(CH_3)_2CHS]_8(CN)_2\}_n$ (compound **1**) were carried on a Rigaku XtaLAB pro diffractometer with Cu-Kα radiation (λ=1.54184 Å) at 200 K. Date collection and reduction were processed using the program CrysAlisPro.[1] The structure was assessed with intrinsic phasing methods (SHELXT-2015)[2] and refined by full-matrix least squares on F^2 using *OLEX2*.[3] All non-hydrogen atoms were located in difference-Fourier maps and refined anisotropically. Hydrogen atoms were placed in calculated positions refined using idealized geometries

and assigned fixed isotropic displacement parameters. The crystal structures were visualized by DIAMOND 3.2.[4] The X-ray crystallographic data were deposited in the Cambridge Crystallographic Data Centre (CCDC). The data can be obtained free of charge from the CCDC *via* http://www.ccdc.cam.ac.uk.

Tables

Table S1. Crystal data and structure refinement for compound **1**

	Compound **1**
CCDC number	2380767
Empirical formula	$C_6H_{13}Ag_{2.5}NS_2$
Formula weight	432.97
Temperature (K)	200
Crystal system	monoclinic
Space group	I2/a
a (Å)	8.8251 (2)
b (Å)	15.4158 (3)
c (Å)	16.6158 (3)
β (°)	94.740 (2)
V (Å^3)	2552.78 (8)
Z	8
ρ_{calc} (g / cm^3)	2.553
μ (mm^{-1})	37.669
F (000)	1644.0
Crystal size (mm^3)	0.01 × 0.02 × 0.4
Radiation	CuKα (λ = 1.54184 Å)
2ϑ range for data collection (°)	10.686 to 148.136
Index ranges	-10 ≤ h ≤ 10, -18 ≤ k ≤ 19, -20 ≤ l ≤ 20

Reflections collected	7087
Independent reflections	2239 [R_{int} = 0.0381, R_{sigma} = 0.0335]
Data/restraints/ parameters	2239 / 78 / 179
Goodness-of-fit on F^2	1.122
Final R indexes [$I >= 2\sigma(I)$]	R_1 = 0.0494, wR_2 = 0.1142
Final R indexes [all data]	R_1 = 0.0551, wR_2 = 0.1176
Largest diff. peak/hole (e Å^{-3})	1.00/-1.37

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

Table S2. Refined lattice parameters and the unit-cell volumes of compound **1** at different pressure.

Space group	Pressure (GPa)	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)
	1 atm	8.83322	15.36488	16.60949	94.721	2246.613
	0.5	8.77316	15.22591	16.31379	95.714	2168.358
I2/a	1.0	8.73723	15.11045	16.11140	96.615	2112.923
	1.7	8.67822	14.98548	15.89973	97.483	2050.104
	2.4	8.64832	14.89062	15.73830	98.058	2006.752
	3.6	8.58844	14.76224	15.48983	98.420	1942.702
	4.8	8.51176	14.64990	15.29595	98.820	1884.798
	6.5	8.35633	14.56843	15.20552	99.146	1827.567
$P2_1/c$	8.3	8.27221	14.42626	15.14856	99.638	1782.267
	10.5	8.21607	14.33895	15.11040	100.189	1752.081
	13.1	8.11765	14.17760	15.10790	103.811	1688.485
	16.6	8.09958	14.13449	15.07487	104.027	1679.103
	D 1 atm	8.97046	15.32827	16.92922	94.841	2319.492

Supplemental Figures

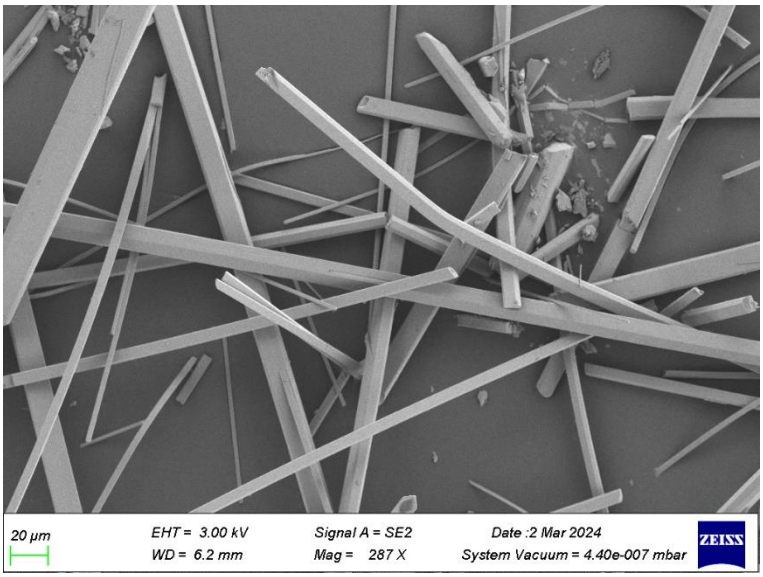

Figure S1. SEM micrographs of compound **1**.

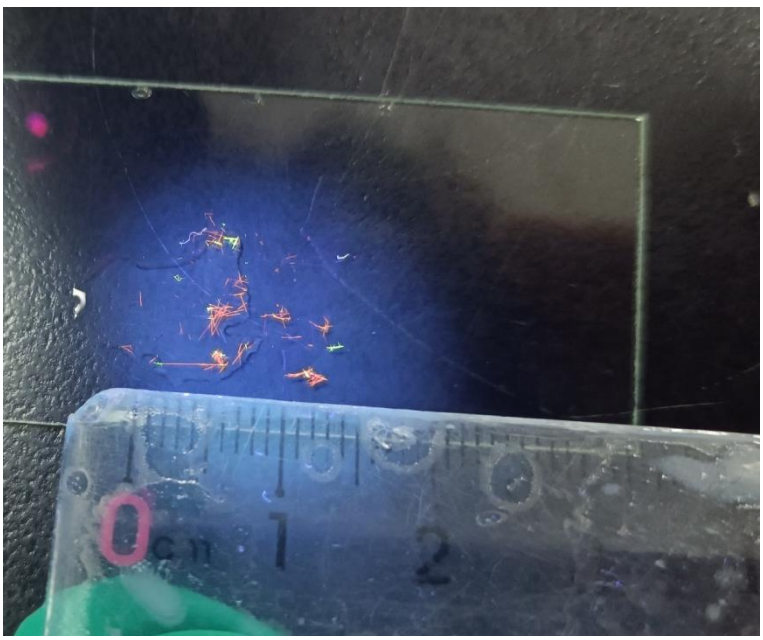

Figure S2. The length of macroscopically wire crystals under ultraviolet irradiation.

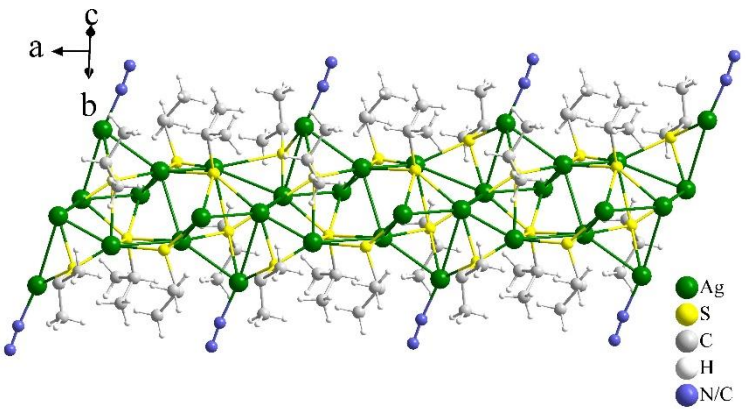

Figure S3. The 1D chains were protected by organic isopropyl sulfide ligands.

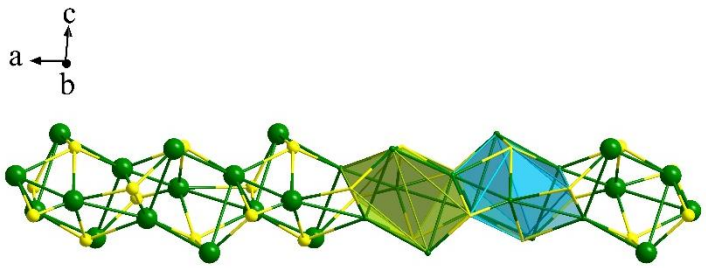

Figure S4. The core of the chain is composed of repeating irregular Ag_7S_6 tetrakaidecahedra.

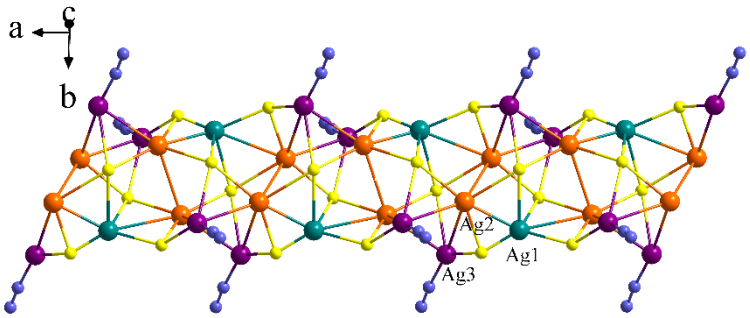

Figure S5. Different color indicates different coordination environment of silver atoms (indigo, orange, purple). Blue, C/N; yellow, S.

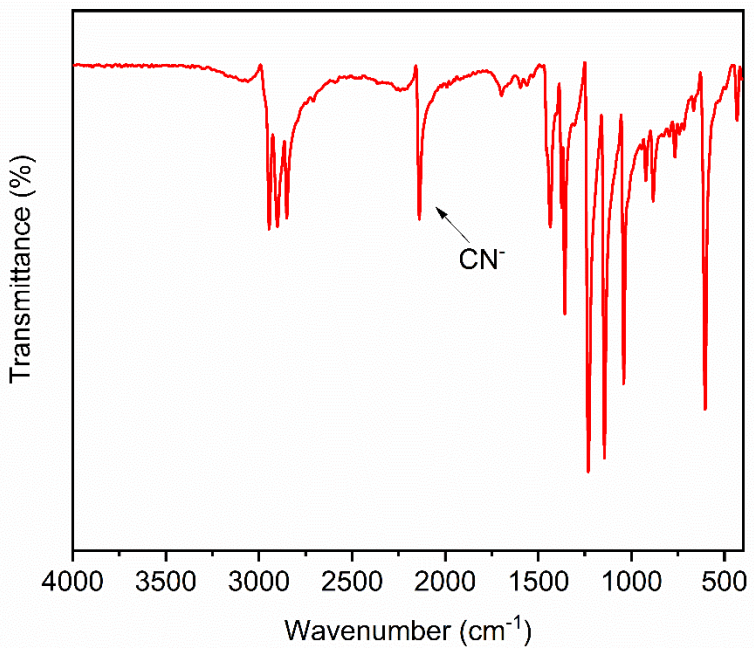

Figure S6. FT-IR spectra of compound **1**. The absorption peak at 2138 cm^{-1} is assigned to the nitrile group

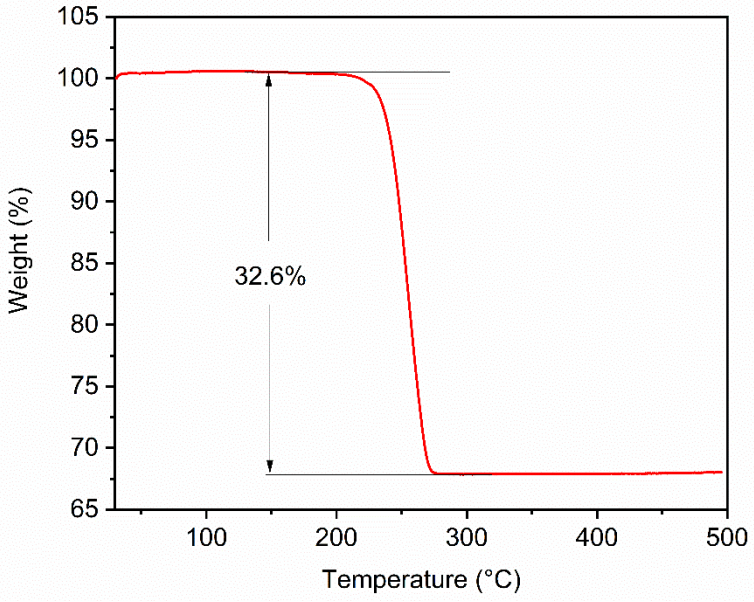

Figure S7. TGA of compound **1** under nitrogen atmosphere.

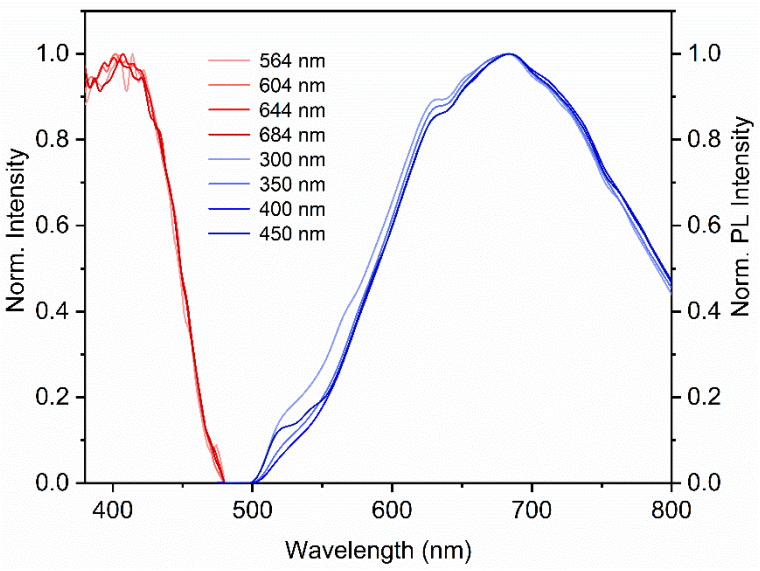

Figure S8. PL excitation (red, left) and emission (blue, right) spectra of compound **1**.

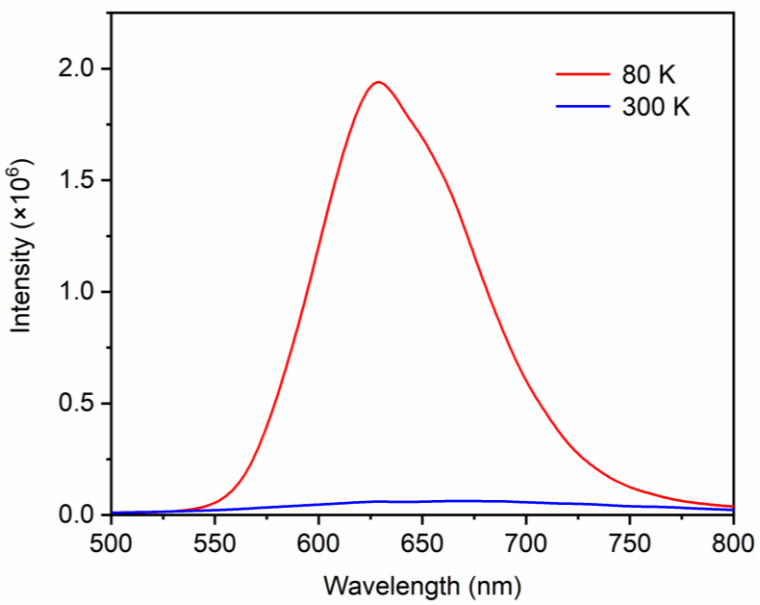

Figure S9. PL spectra of compound **1** at 80 K and 300 K.

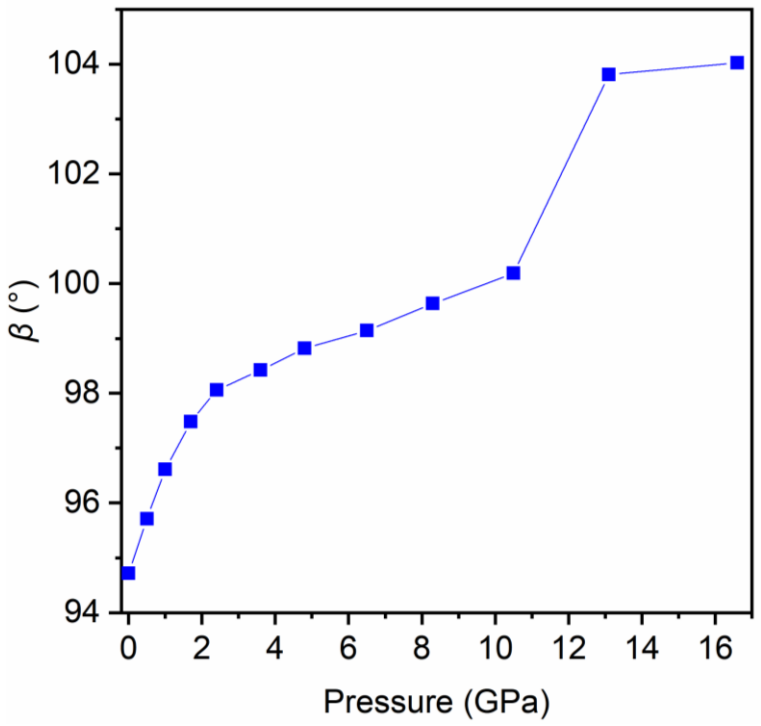

Figure S10. *β* of compound **1** under compression.

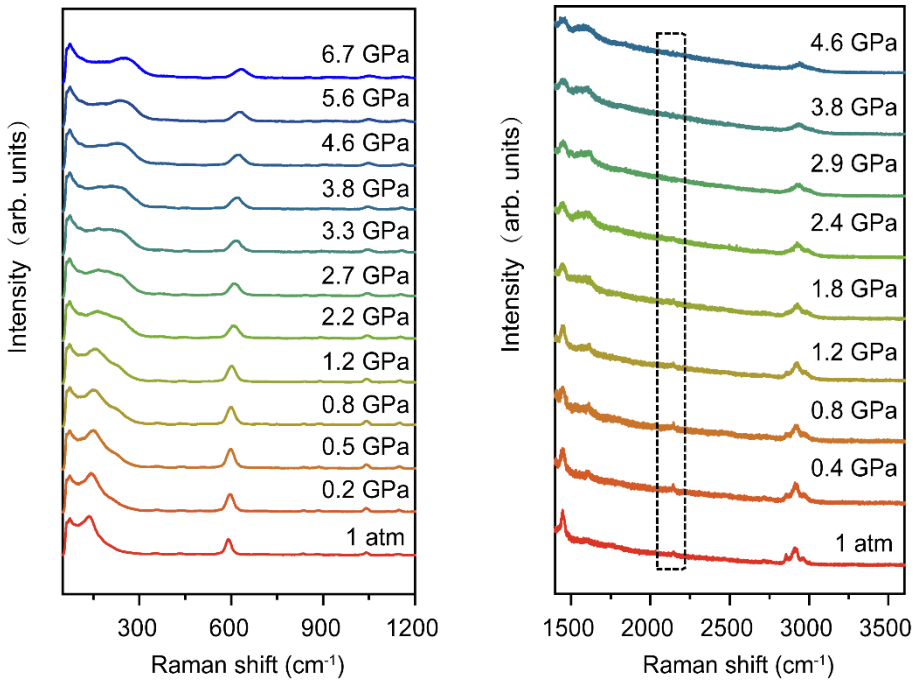

Figure S11. Raman spectra (a, b) of compound **1** at different pressure. It can be obviously seen from dotted box that the nitrile group disappears at 2.4 GPa.

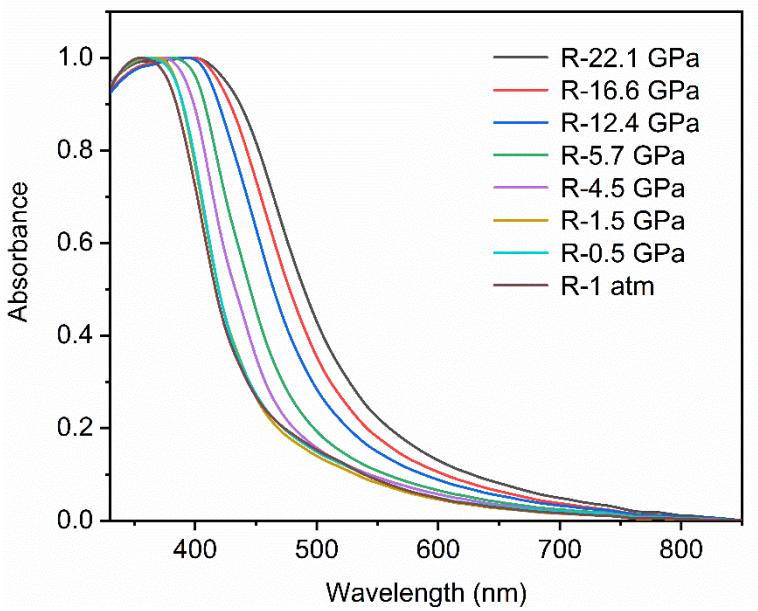

Figure S12. Absorption Spectrum of compound **1** under decompression.

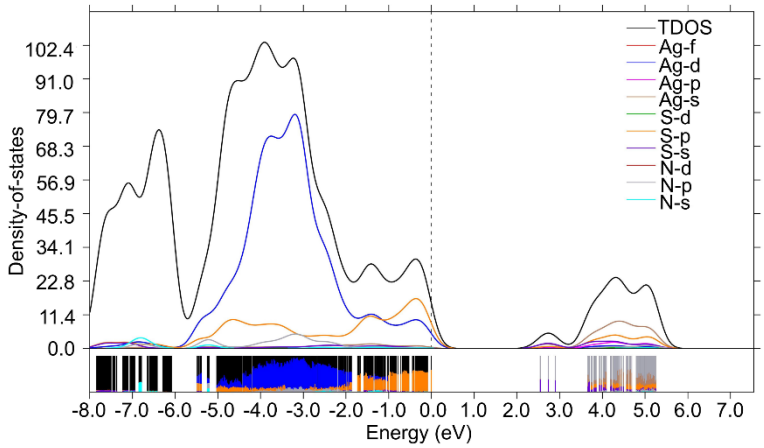

Figure S13. Calculated projected density of states (PDOS) for compound **1** under the normal pressure.

References

1. CrysAlisPro 2012, Agilent Technologies. Version 1.171.36.31.
2. G. M. Sheldrick, *Acta Cryst. A* 2015, **71**, 3-8.
3. G. M. Sheldrick, *Acta Cryst. A* 2008, **64**, 112-122.
4. K. Brandenburg, *Diamond*, 2010.