Supplementary material

Molecular Design of Luminescent Halogeno-thiocyano-d^{10} Metal Complexes with *in situ* Formation of Thiocyanate Ligand

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Lifetime of the luminescence

The decays of the emission intensities of the complex **3** accord with polytropic exponent relationship (see the fitting equations below).

Fitting equation for **3** (Em 442 nm): (Fit = Emission Intensity; t: time; Rel%: relative fluorescence intensity)

Fit = $A + B_1.\exp(-t/T_1) + B_2.\exp(-t/T_2)$

	Value	Std Dev		Value	Std Dev	Rel %
T_1	1.262E-9	1.487E-11	B_1	5.865E-2	4.018E-4	85.52
T_2	4.258E-9	1.210E-10	B_2	2.944E-3	2.393E-4	14.48
Chisq	1.108E + 0		A	1.840E-1		

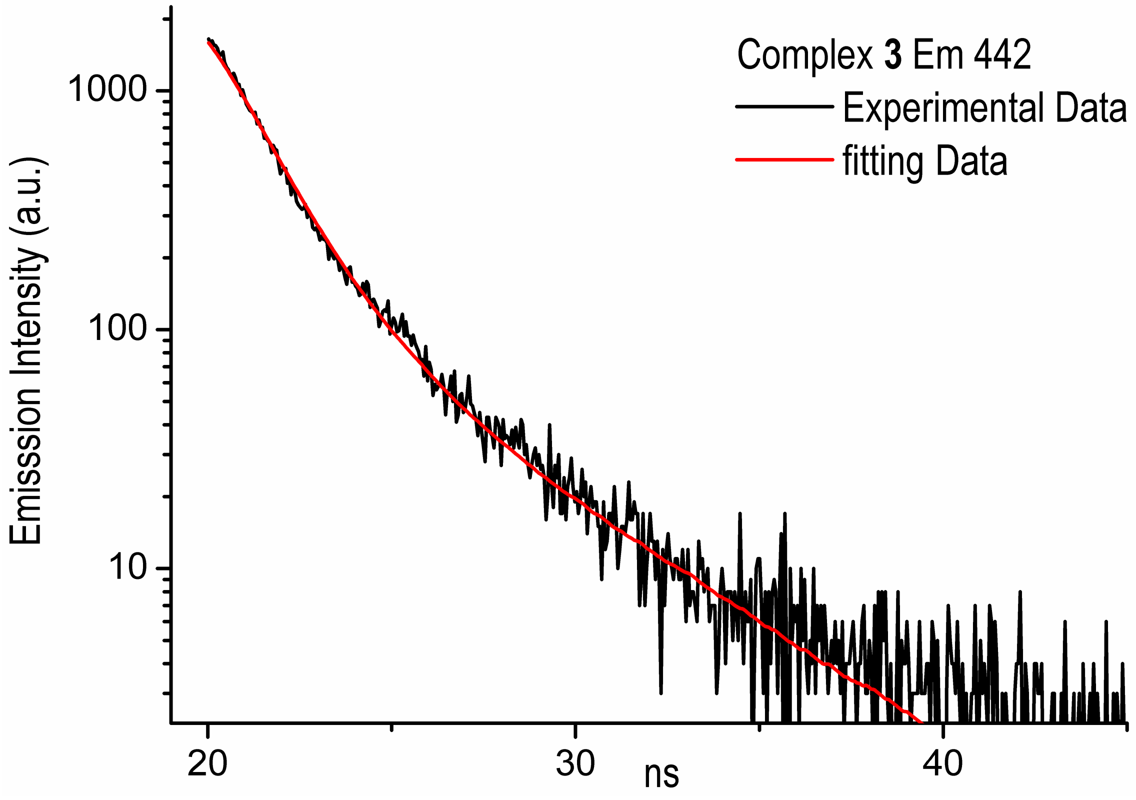
T = 1.7 ns

Em 496 nm

Fit = $A + B_1.\exp(-t/T1) + B_2.\exp(-t/T2)$

	Value	Std Dev		Value	Std Dev	Rel %
T_1	1.106E-9	1.805E-11	B_1	1.191E-1	1.457E-3	84.80
T_2	5.366E-9	1.586E-10	B_2	4.400E-3	3.112E-4	15.20
Chisq	7.365E-1		A	4.580E-1		

T = 1.8 ns



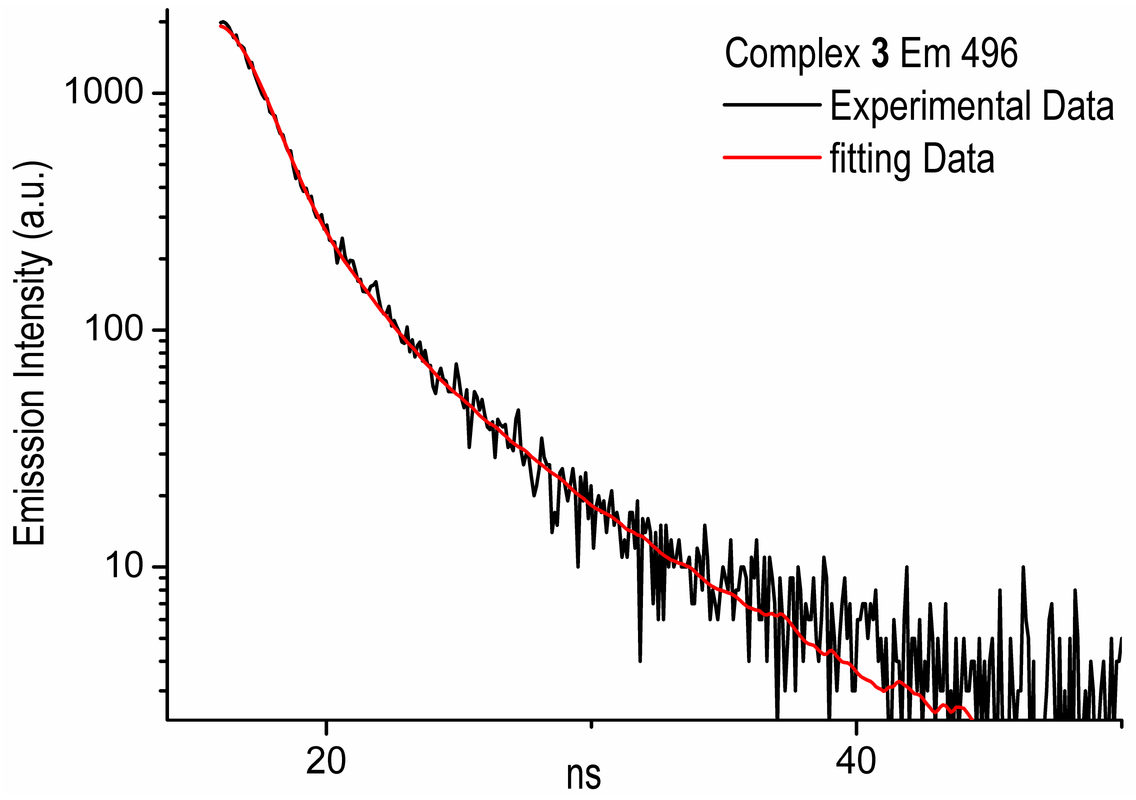


Figure S1. Lifetime spectra of **3** in which black lines represent experimental curves while the red lines represent the fitting curves.

DFT Calculation Approach Methodology

The crystallographic data of the present complexes determined by X-ray were used to calculate the electronic band structures. Calculations of the electronic band structures along with density of states (DOS) was carried out with density functional theory (DFT) using one of the three nonlocal gradientcorrected exchange-correlation functionals (GGA-PBE) and performed with the CASTEP code,[1] which uses a plane wave basis set for the valence electrons and norm-conserving pseudopotential[2] for the core electrons. The number of plane waves included in the basis was determined by a cutoff energy Ec of 550 eV. Pseudoatomic calculations were performed for H-1s^1, C-2s^{2}2p^2, N-2s^{2}2p^3, Cl-3s^{2}3p^5, Br-4s^{2}4p^5, I-5s^{2}5p^5, Cu-3d^{10}4s^1 and Ag-4d^{10}5s^1. The parameters used in the calculations and convergence criteria were set by the default values of the CASTEP code, e.g., reciprocal space pseudopotentials representations, eigen-energy convergence tolerance of 1×10^{-6} eV, Gaussian smearing scheme with the smearing width of 0.1 eV, and Fermi energy convergence tolerance of 1×10^{-7} eV.

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(1) (a) Segall, M.; Linda, P.; Probert, M.; Pickard, C.; Hasnip, P.; Clark, S.; Payne, M. *Materials Studio CASTEP*, version 2.2; Accelrys: San Diego, CA, **2002**. (b) Segall, M.; Linda, P.; Probert, M.; Pickard, C.; Hasnip, P.; Clark, S.; Payne, M. *J. Phys.: Condens. Matter* **2002**, *14*, 2717–2744.

(2) Hamann, D. R.; Schluter, M.; Chiang, C. *Phys. Rev. Lett.* **1979**, *43*, 1494–1497.

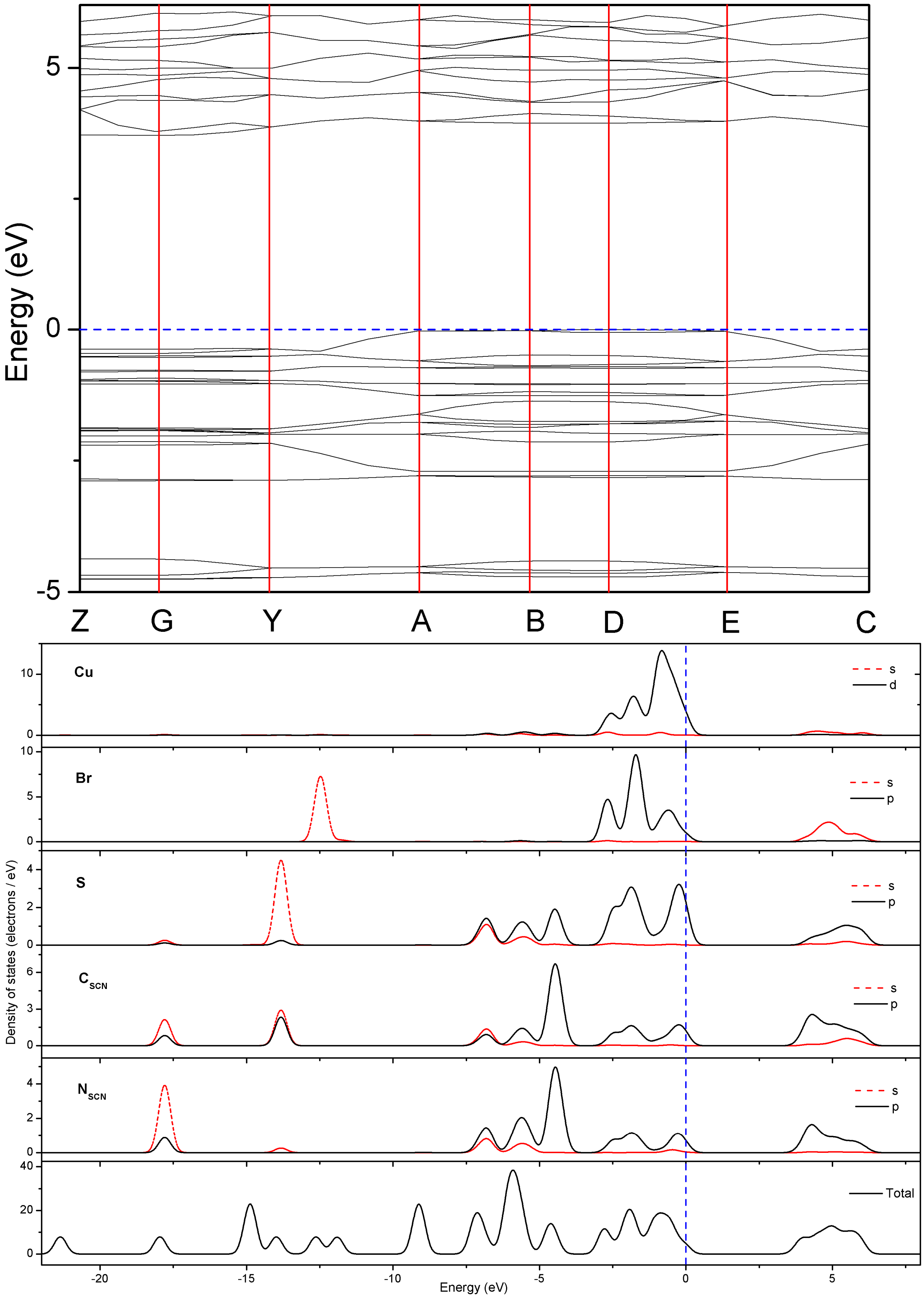

Figure S2. Energy band structures and density of states (total and partial) of **1**. Energy bands are shown only between -5 and 6.2 eV for clarity, and the Fermi level is set at 0 eV.

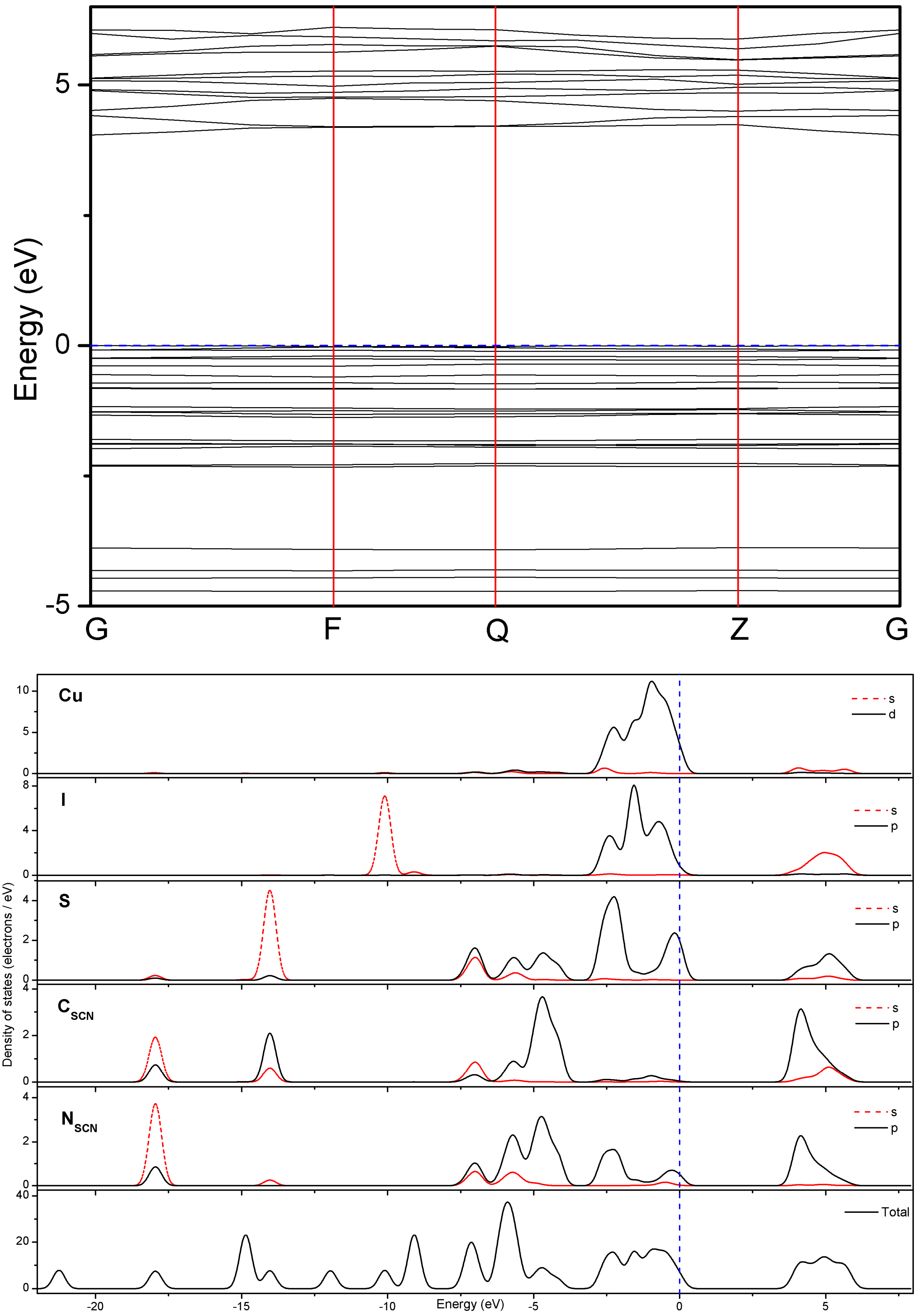

Figure S3. Energy band structures and density of states (total and partial) of **2**. Energy bands are shown only between -5 and 6.5 eV for clarity, and the Fermi level is set at 0 eV.

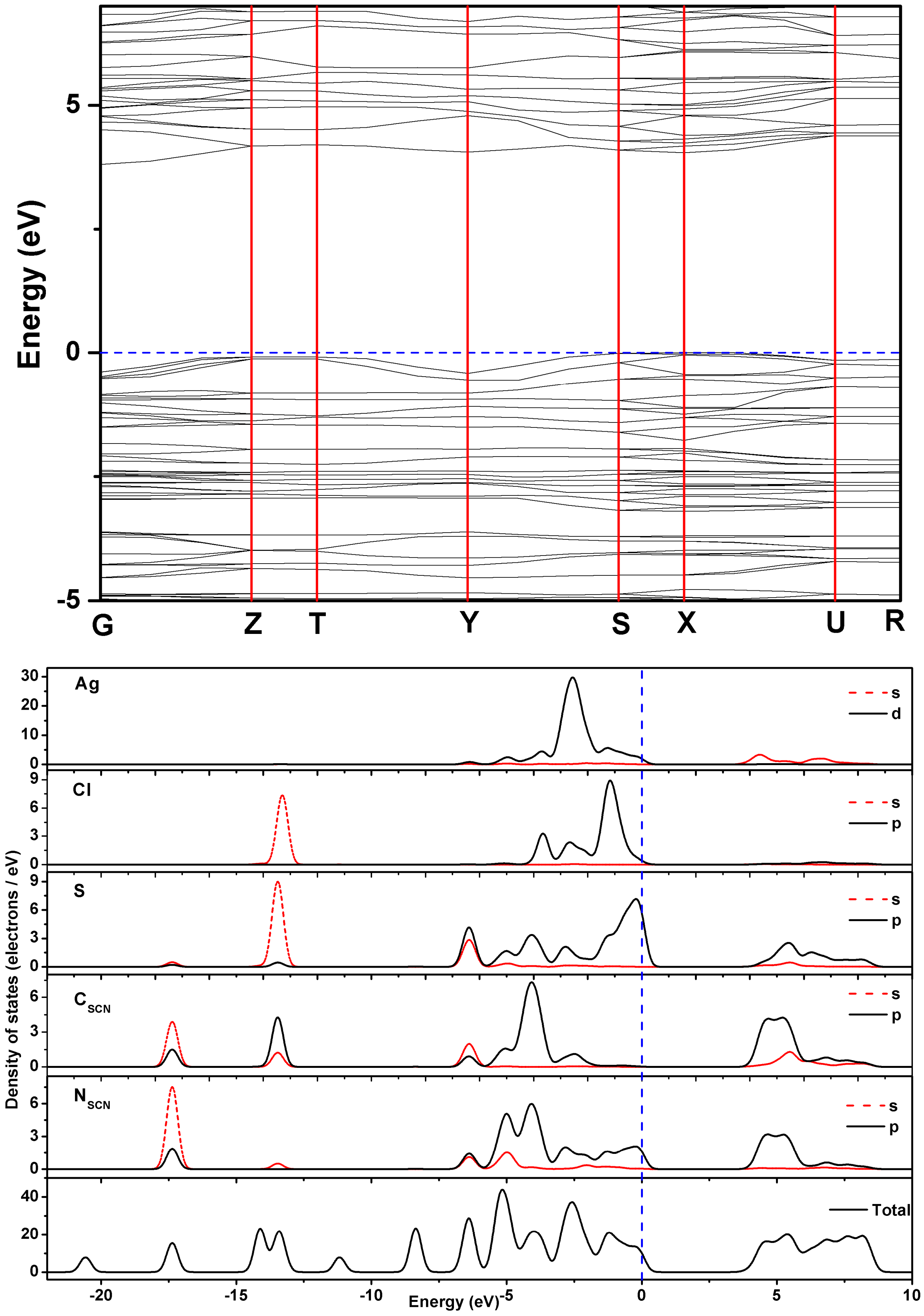

Figure S4. Energy band structures and density of states (total and partial) of **3**. Energy bands are shown only between -5 and 7.0 eV for clarity, and the Fermi level is set at 0 eV.

Computational Descriptions/Explanation

The calculated band structure of **1** along high symmetry points of the first Brillouin zone is plotted in Figure S1, where the labeled k-points are present as Z (0.0, 0.0, 0.5), G (0.0, 0.0, 0.0), Y (0.0, 0.5, 0.0), A (-0.5, 0.5, 0.0), B (-0.5, 0.0, 0.0), D (-0.5, 0.0, 0.5), E (-0.5, 0.5, 0.5), and C (0.0, 0.5, 0.5). It is observed that both the top of valence bands (VBs) and the bottom of conduction bands (CBs) have small dispersion. The lowest energy (3.71 eV) of conduction bands (CBs) is localized at the G point, and the highest energy (0.00 eV) of VBs is localized at the D point, indicating compound **1** shows a wide gap semiconductor character with an indirect band gap of 3.71 eV. The bands can be assigned according to total and partial densities of states (DOS). The S-3s, $C_{thiocyanate}$-2s, $N_{thiocyanate}$-2s, and Br-4S states, mixing with small S-3p, $C_{thiocyanate}$-2p, $N_{thiocyanate}$-2p states, create the VBs localized at about -19.0 and -11.0 eV. The VBs between energy -7.8 eV and the Fermi level (0.0 eV) are mostly formed by Cu-3d state mixing with a partial amount of Br-4p, S-3p, $C_{thiocyanate}$-2p, and $N_{thiocyanate}$-2p states, in which the top of VBs (-1.4 ~ 0.0 eV) mainly originates from Cu-3d (13.8 electrons/eV) state mixing with a small amount of Br-4p (3.5 electrons/eV) and S-3p (3.2 electrons/eV) states. The CBs between 3.3 and 6.5 eV are almost contribution from the hybridizations of S-3p, $C_{thiocyanate}$-2p and $N_{thiocyanate}$-2p states mixing with a small amount of Br-4s states. Accordingly, the origin of the emission band of **1** may be mainly ascribe to metal-to-ligand charge transfer (MLCT) where the electrons are transferred from the copper (Cu-3d state, VBs) to unoccupied π^* orbital of thiocyanate groups (S-3p, $C_{thiocyanate}$-2p and $N_{thiocyanate}$-2p states, CBs).

The calculated band structure of **2** along high symmetry points of the first Brillouin zone is plotted in Figure S2, where the labeled k-points are present as G (0.0, 0.0, 0.0), F (0.0, 0.5, 0.0), Q (0.0, 0.5, 0.5), and Z (0.0, 0.0, 0.5). The top of VBs appears to be relatively flat and the bottom of CBs have small dispersion. The lowest energy (4.04 eV) of conduction bands (CBs) is localized at the G point, and the highest energy (0.00 eV) of VBs is also localized at the G point, indicating compound **2** shows a wide gap semiconductor character with a direct band gap of 4.04 eV. The S-3s, $C_{thiocyanate}$-2s, $N_{thiocyanate}$-2s, and I-5s states, mixing with small S-3p, $C_{thiocyanate}$-2p, $N_{thiocyanate}$-2p states, create the VBs localized at about -19.0 and -9.6 eV. The VBs between energy -7.7 eV and the Fermi level (0.0 eV) are mostly formed by Cu-3d state mixing with a partial amount of I-5p, S-3p, $C_{thiocyanate}$-2p and $N_{thiocyanate}$-2p states, in which the top of VBs (-1.2 ~ 0.0 eV) mainly originates from Cu-3d (11.2 electrons/eV) state mixing with a small amount of I-5p (4.8 electrons/eV) and S-3p (2.4 electrons/eV) states. The CBs between 3.4 and 6.4 eV are almost contribution from the hybridizations of S-3p, $C_{thiocyanate}$-2p and $N_{thiocyanate}$-2p states mixing with a small amount of I-5s states. Accordingly, the origin of the emission band of **2** may be mainly ascribe to metal-to-ligand charge transfer (MLCT) where the electrons are transferred from the copper (Cu-3d states, VBs) to unoccupied π^* orbital of thiocyanate groups (S-3p, $C_{thiocyanate}$-2p and $N_{thiocyanate}$-2p states, CBs).

The calculated band structure of **3** along high symmetry points of the first Brillouin zone is plotted in Figure S3, where the labeled k-points are present as G (0.0, 0.0, 0.0), Z (-0.5, 0.0, 0.166667), T (-0.5, 0.166667, 0.0), Y (0.0, 0.5, 0.5), S (-0.5, 0.0, 0.333333), X (-0.5, 0.0, 0.0), U (0.0, 0.5, 0.333333), and R (-0.5, 0.5, 0.5). Both the top of VBs and the bottom of CBs have small dispersion. The lowest energy (3.80 eV) of CBs is localized at the G point, and the highest energy (0.00 eV) of VBs is localized at the X point, indicating compound **3** shows a wide gap semiconductor character with an indirect band gap of 3.80 eV. The bands can be assigned according to total and partial densities of states (DOS). The S-3s, $C_{thiocyanate}$-2s, $N_{thiocyanate}$-2s, and Cl-3s states, mixing with small S-3p, $C_{thiocyanate}$-2p, $N_{thiocyanate}$-2p states, create the VBs localized at about -18.0 and -12.0 eV. The VBs between energy -7.1 eV and the Fermi level (0.0 eV) are mostly formed by Ag-4d state mixing with partial Cl-3p, S-3p, $C_{thiocyanate}$-2p, and $N_{thiocyanate}$-2p states, in which the top of VBs (-3.3 ~ 0.0 eV) mainly originates from Ag-4d state (29.8 electrons/eV) mixing with a small amount of Cl-3p (8.9 electrons/eV) and S-3p (7.2 electrons/eV) states. The CBs between 3.7 and 8.9 eV are almost contribution from the hybridizations of S-3p, $C_{thiocyanate}$-2p and $N_{thiocyanate}$-2p states mixing with a small amount of Ag-5s states. Accordingly, the origin of the high-energy emission band at 442 nm of **3** may be mainly ascribe to metal-to-ligand charge transfer (MLCT) where the electrons are transferred from the silver (Ag-4d states, VBs) to unoccupied π^* orbital of thiocyanate groups (S-3p, $C_{thiocyanate}$-2p and $N_{thiocyanate}$-2p states, CBs), while the origin of the low-energy emission band at 496 nm of **3** may be mainly ascribe to ligand-to-ligand charge transfer (LLCT) where the electrons are transferred from the Cl and S (Cl-3p and S-3p states, VBs) to unoccupied π^* orbital of thiocyanate groups (S-3p, $C_{thiocyanate}$-2p and $N_{thiocyanate}$-2p states, CBs).

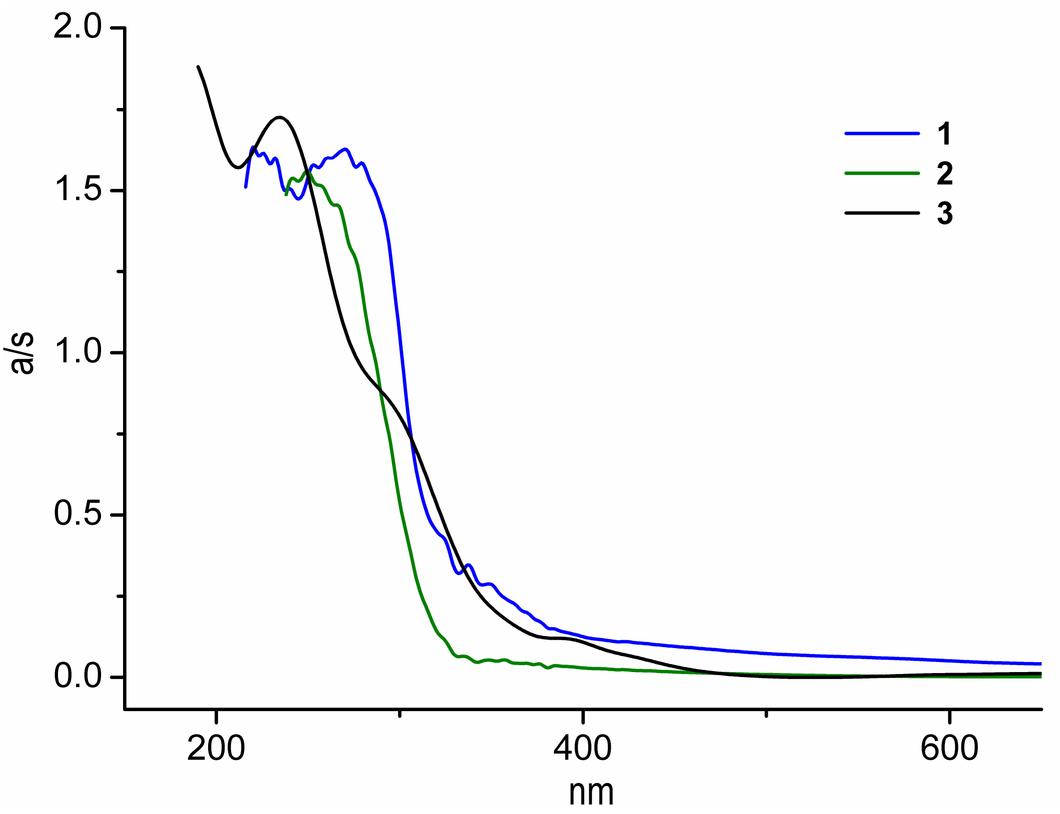

Figure S5. Optical absorption spectra of **1**, **2** and **3** at room temperature.

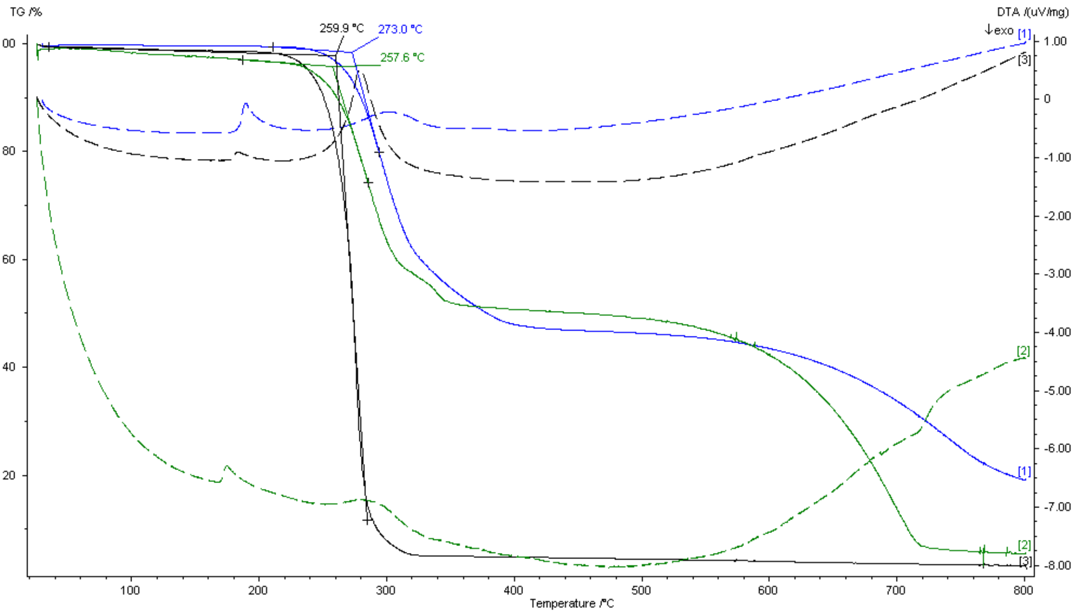

Figure S6. TGA spectra of **1** (blue), **2** (olive) and **3** (black) under N_2 atmosphere.