

Thermodynamic control and coordination-engineering of novel 2D cadmium thiolate coordination polymers

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Supporting Information

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Materials and methods

General

The chemicals and solvents were purchased from Wako Pure Chemicals Industries, Ltd. They were of reagent grade and used without further purification. Elemental analysis was carried out on a Flash EA 1112 series, Thermo Finnigan instrument. ^1H nuclear magnetic resonance (NMR) spectra were recorded on a Jeol 400MHz JNM-ECS400 with NR30 spectrometer. Solid state electronic absorption spectra were taken in Al_2O_3 matrices with a V670 JASCO spectrophotometer equipped with an integration sphere. Infrared absorption spectra were recorded under vacuum with a FT/IR-6100 JASCO spectrometer using KBr pellets. Thermogravimetric (TG) analysis was performed using a Rigaku Thermo plus TG- 8120 apparatus in the temperature range between 298 K and 773 K in a N_2 atmosphere at a heating rate of 10 K min^{-1} . Single crystal X-ray diffraction measurements were performed with a Rigaku AFC10 diffractometer with Rigaku Saturn Kappa CCD system equipped with a MicroMax-007 HF / VariMax rotating-anode X-ray generator with confocal monochromated $\text{MoK}\alpha$ radiation and data were processed using CrystalClearTM-SM (Version 1.4.0)¹ and the implemented d*TREK[®] program.²

Structure determination

Single crystals of compounds **1**, **2** and **3** were coated in an inert Paratone-N oil (Hampton Research), mounted on a polyimide-based (Kapton[®]) MicroMountTM (MiTeGen) tip then placed on the Rigaku diffractometer. Data were recorded at 93.15 K (Rigaku cryostream) using confocal monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.710747 \text{ \AA}$) with the CCD detector placed at a minimum distance of 45 mm from the sample. Complete hemispheres of data were collected using ω -scans. All structures were solved by direct methods using SIR92³ and were refined by full-matrix least squares refinement on F^2 using the SHELXL-97⁴ embedded in the WinGX program system.⁵ All non-hydrogen atoms were refined with anisotropic displacement parameters, with one exception concerning the lone ethylenediamine molecule of compound **1** which is disordered over two sites and the atoms of these sites were refined isotropically: the presence of only one neutral ethylenediamine molecule has been confirmed by elemental analysis, and the s.o.f. of this neutral molecule has been fixed to 1; the molecule is disordered over two positions, the s.o.f. having been refined as 0.37139 and 0.62861 for each position; interatomic distances have been restrained to be similar to interatomic distances of one of the coordinated ethylenediamine ligand, in order to get a correct geometry thanks to the SADI command, which leads to the presence of 27 restraints. All hydrogen atoms were placed geometrically and refined with a riding model with U_{iso} constrained to be 1.2 times U_{eq} of the carrier atom (except for **3** where all hydrogen atoms have been located by Fourier-difference). The produced *.cif files were checked, edited and visualised with the program enCIFer⁶ from the CCDC.

Synthesis and characterization of 4,4'-biphenyldithiol (H_2 bpdt)

Synthesis conditions of H_2 bpdt ($HS-C_6H_4-C_6H_4-SH$)

We synthesized H_2 bpdt by following a published protocol.¹¹ Nevertheless, we adapted its purification process. In a typical procedure, biphenyl-4,4'-disulfonyl chloride (2.5 g, 7.1 mmol) is dissolved in a hot toluene-water mixture (30 and 20 mL, respectively). Then, at 70 °C and with vigorous stirring, 6.77 g of tin powder is added, followed by a dropwise addition of concentrated hydrochloric acid (10.1 mL, 0.114 mol) within 10-15 min while increasing the temperature to 90 °C. After the addition of acid, the mixture is kept at 90 °C for 2 hrs. Then, more toluene is added to improve phase separation. After cooling to room temperature, the toluene layer containing the dithiol is separated and dried with sodium sulfate. The toluene is distilled off *in vacuo*, and the product is obtained as a pale yellow solid.^{11, 12} Further purification is achieved in a two-step process.¹³ First the crude product is taken into 100 mL of a 1M NaOH aqueous solution, then well shaken and filtered through a sintered-glass funnel directly onto 30 mL of 35% hydrochloric acid. The precipitate present in the acidic phase is isolated by filtration and washed with cold distilled water. Once dried, the light yellow powder is sublimed at 170 °C at 10^{-3} mbar (1g, 68%).

NMR characterization

1H NMR($CDCl_3$): δ 7.42 (d, $J = 8.4$ Hz, 4 H), 7.32 (d, $J = 8.4$ Hz, 4 H), 3.47 (s, 2 H) ppm.

IR spectrum (KBr)

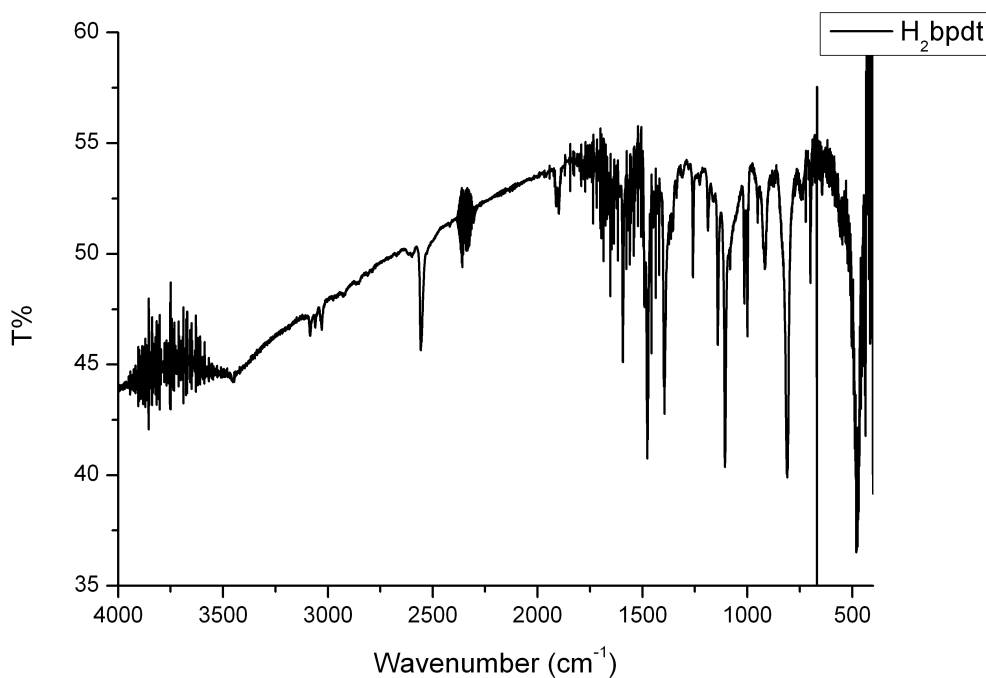


Figure S1 IR spectrum of H_2 bpdt

Synthesis of and characterization 1, 2 and 3

General synthetic conditions of cadmium thiolate coordination polymers

In an argon-filled glove box, cadmium acetate dihydrate and freshly prepared H_2bpd are placed in a borosilicate glass tube (dim. 200 x 7.92 mm, wall thickness 1.12 mm) and then 1 mL of alkyldiamine solvent is added. The tube is capped with a plastic stopper, secured with parafilm and taken out of the glove box. They are then placed standing in an oil bath at 105 °C. Single crystals are growing at 105 °C at the bottom of the tube (and not in the cold upper part of the tube). After one day of heating, the tube are removed from the bath and let to cool down to room temperature, then the cap is further wrapped in parafilm and the tube is introduced into the glove box. For single crystal measurement, the crystals are taken directly from the mother liquor to mineral oil on a watch glass and then mounted on a tip. For other measurements, the crystals are filtered through a glass sinter, and washed with methanol and diethyl ether.

[Cd(en)₃][Cd(bpdt)₂](en) (1)

Synthesis

Cd(OAc)₂·2H₂O (7.996 mg, 0.03 mmol) and H₂bpdt (7.862 mg, 0.036 mmol) are combined in 1 mL of ethylenediamine, and after usual sample preparation, the mixture is heated at 105 °C for 1 day. After usual workup, colorless plate-like crystals of **1** can be isolated. Yield of colorless [Cd(en)₃][Cd(bpdt)₂](en): 0.008-0.011 g, 61-84%. Anal. calc. for C₃₂H₄₄N₈S₄Cd₂: C, 42.8; H, 5.4; N, 12.5. Found: C, 42.7; H, 5.5; N, 12.5.

Infrared spectroscopy

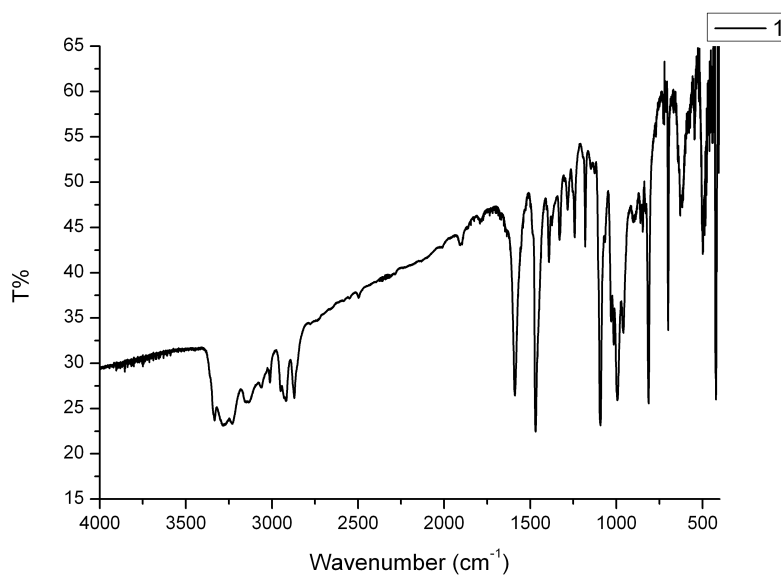


Figure S2 IR spectrum of **1**

Thermogravimetric analysis

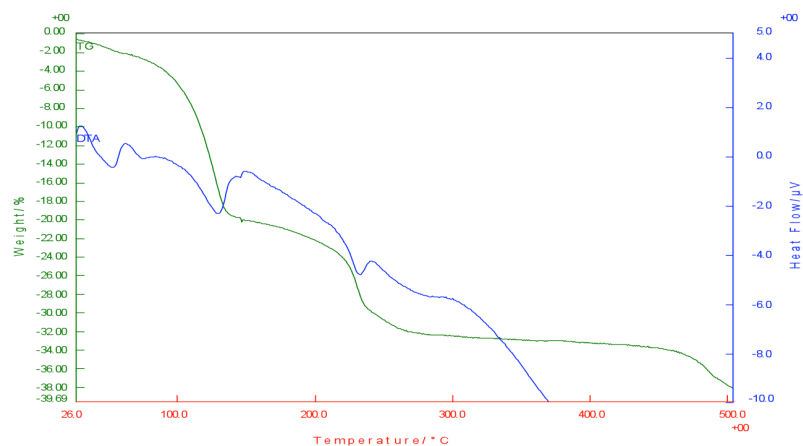


Figure S3 DT-TGA diagram of **1**

Additional crystal structure figure

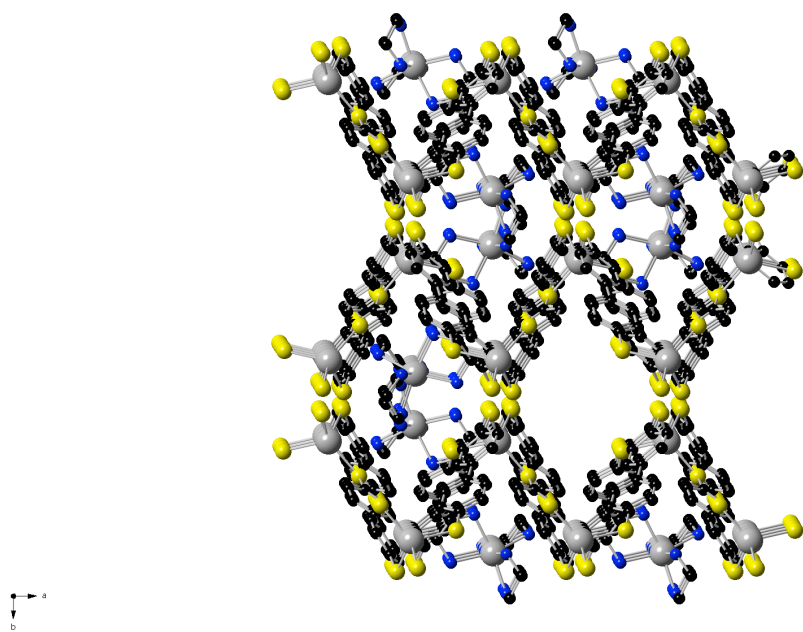


Figure S4 Packing diagram of **1** as viewed from the *c* axis; the one dimensional channels, created by the stacking of the anionic cadmium thiolates wave-like layers, are parallel to the *c* axis and have been emphasized by omitting [Cd(en)₃]²⁺ in one channel (bottom right).

[Cd₂(bpd_t)₂(tn)₃] (2)

Synthesis

Cd(OAc)₂·2H₂O (7.996 mg, 0.03 mmol) and H₂bpd_t (7.862 mg, 0.036 mmol) are combined in 1mL of 1,3-propanediamine, and after usual sample preparation, the mixture is heated at 105 °C for 1 day. After usual workup, colorless oblong plate-like crystals of **2** can be isolated. Yield of colorless [Cd₂(bpd_t)₂(tn)₃]: 0.005-0.09 g, 38-69%. Anal. calc. for C₃₃H₄₁N₆S₄Cd₂: C, 45.0; H, 5.2; N, 9.5. Found: C, 43.1; H, 5.1; N, 8.9.

Infrared spectroscopy

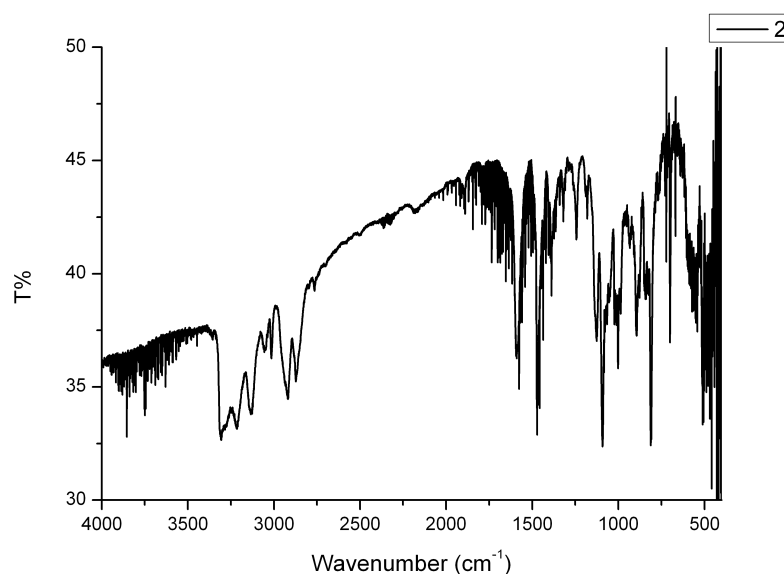


Figure S5 IR spectrum of **2**

Thermogravimetric analysis

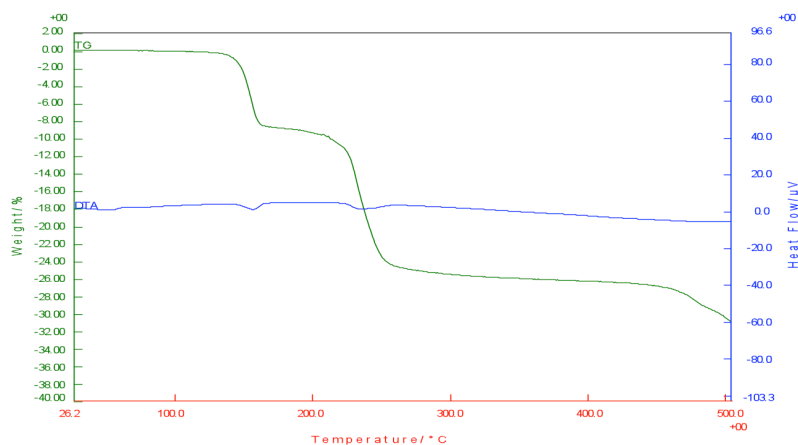


Figure S6 DT-TGA diagram of **2**

Additional crystal structure figure

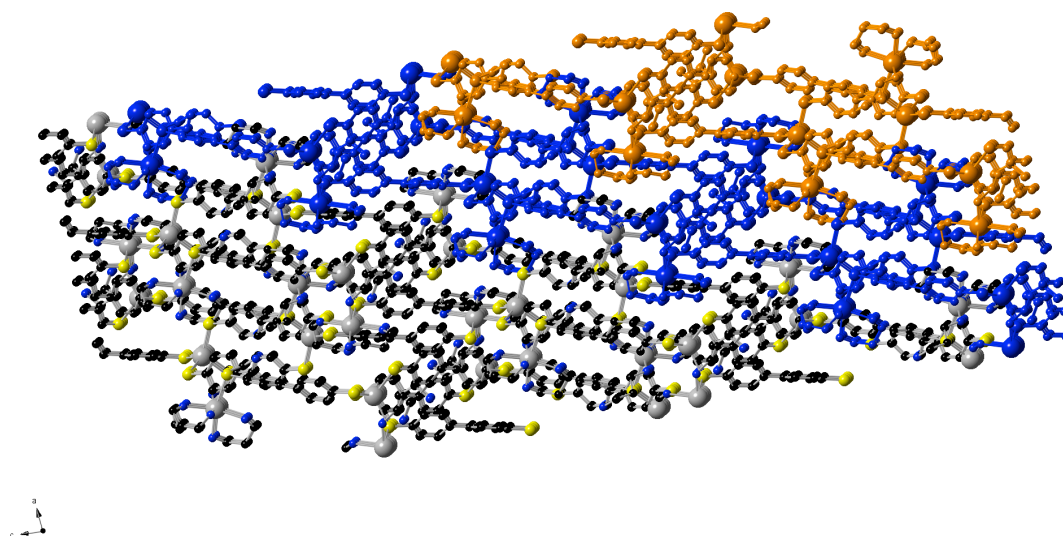


Figure S7 Packing diagram of **2** viewed along the *b* axis; the stacking of neutral slabs in the (10-1) lattice planes have been emphasized by colouring two adjacent layers in orange and blue, showing their wave-like nature

[Cd(bpdt)(*NN*-diethyl-tn)] (**3**)

Synthesis

Cd(OAc)₂·2H₂O (7.996 mg, 0.03 mmol) and H₂bpdt (7.862 mg, 0.036 mmol) are combined in 1mL of *N,N*-diethyl-1,3-propanediamine, and after usual sample preparation, the mixture is heated at 105 °C for 1 day. After usual workup, light yellow needle-like crystals of **3** can be isolated. Yield of light yellow [Cd(bpdt)(*NN*-diethyl-tn)]: 0.010-0.12 g, 77-92%. Anal. calc. for C₃₃H₄₁N₆S₄Cd₂: C, 49.7; H, 5.7; N, 6.1. Found: C, 49.9; H, 5.6; N, 6.2.

Infrared spectroscopy

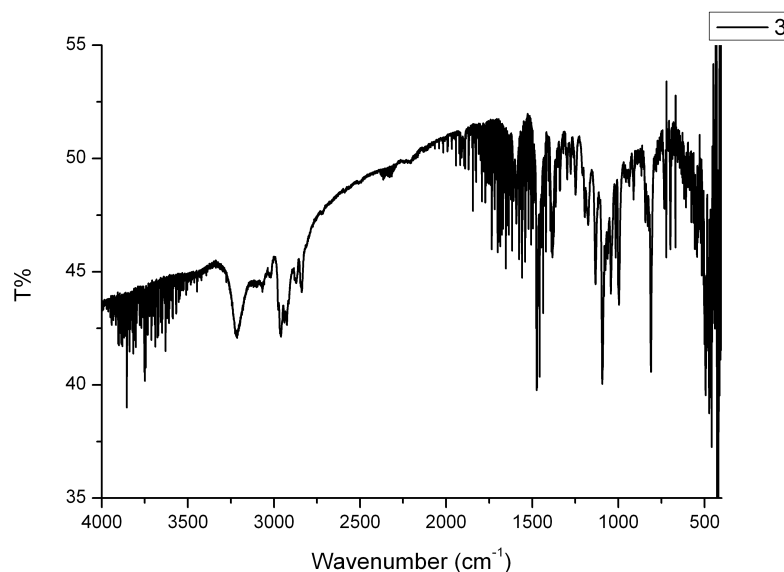


Figure S8 IR spectrum of **3**

Thermogravimetric analysis

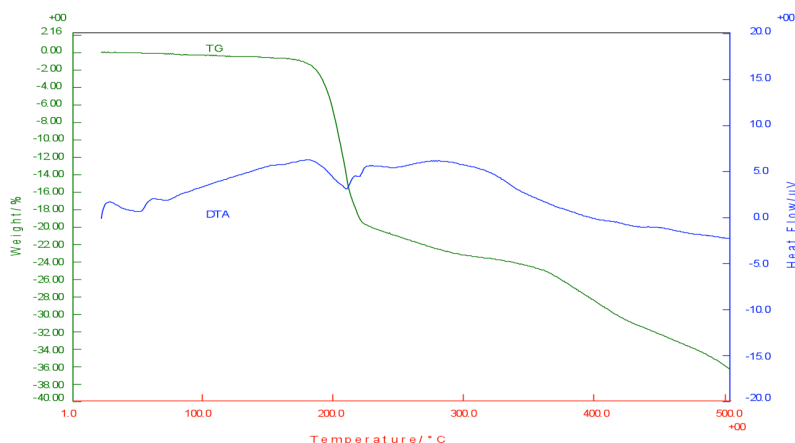


Figure S9 DT-TGA diagram of **3**

Additional crystal structure figure

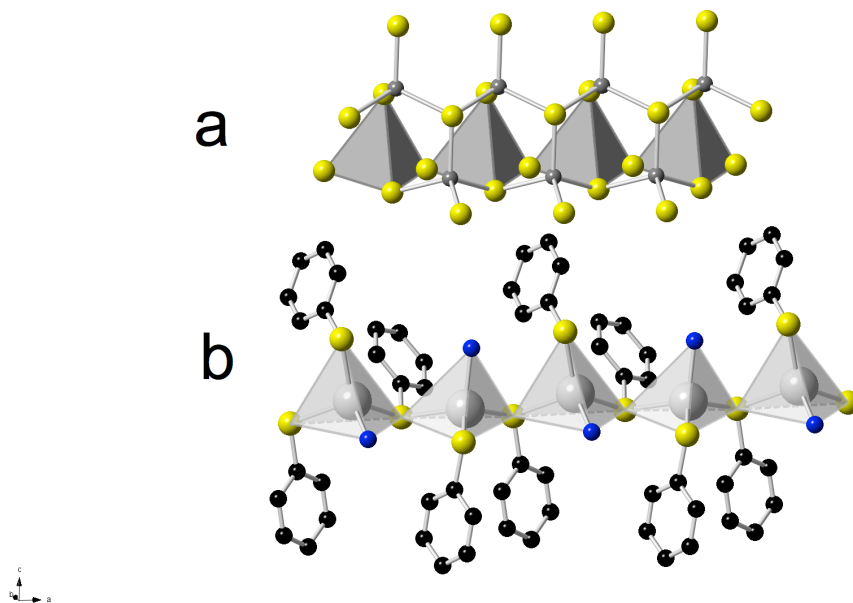


Figure S10 Comparison of **3** with ZnS wurtzite: (a) View of the wurtzite phase of bulk ZnS; a fragment of a ZnS chain substructure formed by corner-sharing ZnS_4 tetrahedra is highlighted in dark grey; tetrahedra are centred on Zn atoms; (b) tetrahedral representation of a CdS_3N chain as found in **3**; the N,N -diethyl-1,3-propanediamine are omitted; tetrahedra are centred on Cd atoms.

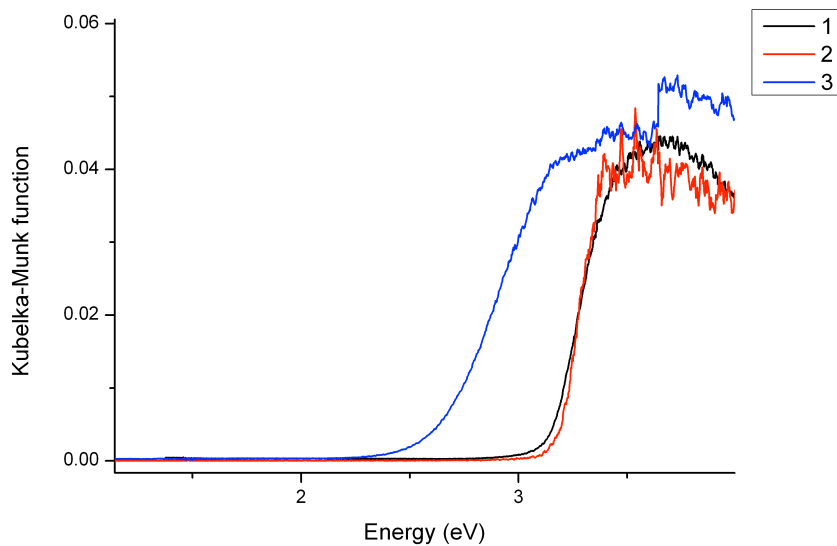


Figure S11 Optical absorption spectra of **1** (black), **2** (blue) and **3** (red); plot of the Kubelka-Munk function as a function of the energy

References and notes

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