Electronic Supplementary Information

Stabilization of interpenetrating cluster-based frameworks promoted by N-H···X hydrogen bonds: synthesis, structures and properties of $\{[Cd(NH_3)_4]_3[Re_3Mo_3Se_8(CN)_6]\}X$ (X = Cl, Br and I).

Viktoria K. Muravieva,[a, b] Yakov M. Gayfulin,[a] Pierric Lemoine,[b]
Nikolay G. Naumov,* [a, c] Stéphane Cordier[b]

[a] Nikolaev Institute of Inorganic Chemistry SB RAS,

3, Acad. Lavrentiev ave., Novosibirsk, 630090, Russia;

E-mail: naumov@niic.nsc.ru ;

[b] Univ. Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) - UMR 6226, F-35000, France ;

[c] Novosibirsk State University, 2, Pirogova str., Novosibirsk, 630090, Russia.

Table of contents:

Table S1. Summary of single-crystal data collections and structure refinement conditions of **1-4**.

Compound	**1**	**2**	**3**	**4**
Chemical formula	$C_{12}Cd_5H_{76}Mo_6N_{34}O_5Re_6Se_{16}$	$C_6Cd_3Cl_1H_{36}Mo_3N_{18}Re_3Se_8$	$C_6Br_1Cd_3H_{36}Mo_3N_{18}Re_3Se_8$	$C_6Cd_3H_{36}I_1Mo_3N_{18}Re_3Se_8$
Space group	*P*-1	*R*-3	*R*-3	*R*-3
Temperature (K)	150	150	150	150
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Formula weight (g.mol^{-1})	4295.26	2211.28	2255.74	2302.73
Crystal system	triclinic	trigonal	trigonal	trigonal
a (Å)	10.2664(8)	15.0363(8)	15.2258(10)	15.3596(14)
b (Å)	17.7456(11)	-	-	-
c (Å)	22.3759(14)	15.3935(9)	15.3834(11)	15.3897(13)
α (°)	85.142(4)	90	90	90
β (°)	86.718(4)	90	90	90
γ (°)	88.258(4)	120	120	120
V (Å^3)	4053.9(5)	3014.0(4)	3088.5(5)	3144.3(6)
Z	2	3	3	3
Calculated density (g.cm^{-3})	3.519	3.655	3.638	3.648
Absorption coefficient (mm^{-1})	18.317	18.796	19.249	18.691
F(000)	3824	2946	3000	3054
Crystal size (mm)	0.16 × 0.06 × 0.04	0.06 × 0.05 × 0.04	0.18 × 0.10 × 0.09	0.20 × 0.17 × 0.14
Crystal color	dark purple	dark purple	dark purple	dark purple
Theta range (°)	2.949 - 27.510	3.074 – 27.479	3.066 – 27.484	3.058 – 27.483
h_min, h_max	-13, 13	-19, 19	-19, 19	-19, 19
k_min, k_max	-13, 22	-19, 19	-19, 19	-19, 19
l_min, l_max	-29, 29	-17, 19	-19, 19	-19, 19
R(int)	0.0662	0.0329	0.0422	0.0416
Reflections collected	31877	6288	14709	12940
Reflections unique [I > 2σ]	9447	1302	1440	1488
Completeness	0.962	0.997	0.999	0.999
Data/restraints/parameters	17950/42/650	1533/0/69	1571/0/69	1609/0/69
Goodness-of-fit	0.964	1.088	1.109	1.077
Final R1 [I > 2σ]	0.0620	0.0271	0.0148	0.0277
Final wR2 [I > 2σ]	0.1149	0.0672	0.0340	0.0724
Largest difference peak and hole (e.Å^{-3})	2.448 and -2.851	1.362 and -1.617	0.507 and -0.890	1.876 and -2.650

Table S2. Selected hydrogen bond geometries for **1**–**4**.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
Compound 1*				
N13-H13B···N11^{i}	0.890	2.305	3.009	136
N15-H15A···N6^{ii}	0.890	2.351	3.221	166
N15-H15B···O37^{iii}	0.890	2.432	3.213	147
N17-H17B···O37^{iv}	0.890	2.083	2.926	158
N17-H17C···N4^{v}	0.890	2.402	3.242	157
N20-H20B···N3^{vi}	0.890	2.451	3.105	131
N20-H20C···N11^{vii}	0.890	2.322	3.036	137
N21-H21B···N11^{i}	0.890	2.411	3.240	155
N22-H22C···N8^{viii}	0.890	2.527	3.269	141
N24-H24C···N7^{ix}	0.890	2.332	3.134	150
N26-H26A···O38^{x}	0.890	2.377	3.214	157
N28-H28A···N2^{xi}	0.890	2.467	3.272	150
N28-H28C···N2^{xii}	0.890	2.297	3.103	151
N29-H29A···O39^{xiii}	0.890	2.424	3.235	152
N29-H29C···O38^{x}	0.890	2.337	3.220	172

N30-H30C···N10[xiv]	0.890	2.231	3.049	153
N31-H31B···N10[xiv]	0.890	2.471	3.209	141
N32-H32A···O35[xv]	0.890	2.331	3.139	151
N34-H34B···N7[xvi]	0.890	2.217	3.102	173
Compound 2				
N2-H2···Cl[a]	0.890	2.543	3.334	148
N2-H2···N1[b]	0.890	2.371	3.246	168
Compound 3				
N2-H2···Br[a]	0.890	2.633	3.468	157
N2-H2···N1[c]	0.890	2.383	3.267	171
Compound 4				
N2-H2···I[a]	0.910	2.833	3.641	149
N2-H2···N1[b]	0.910	2.380	3.261	163

* Hydrogen atoms on lattice water were not located, hydrogen bonds for **1** were selected with criteria for M-NH_3 donor group D···A < 3.28 Å. [1]

Symmetry codes: (i) -x+2, -y+1, -z+2 (ii) -x+1, -y+1, -z+2 (iii) x+1, y, z+1 (iv) x, y, z+1 (v) -x+1, -y+1, -z+2 (vi) -x+1, -y+1, -z+1 (vii) -x+2, -y+1, -z+1 (viii) x, y, z (ix) -x+2, -y+1, -z+1 (x) x+1, y-1, z (xi) -x+1, -y, -z+2 (xii) x+1, y, z (xiii) -x+2, -y, -z+1 (xiv) -x+2, -y+2, -z+1 (xv) -x+1, -y+1, -z+1 (xvi) x-1, y, z.

(a) x, y, z; (b) -y+2/3, x-y+1/3, z+1/3; (c) -x+y-1/3, -x+1/3, z+1/3.

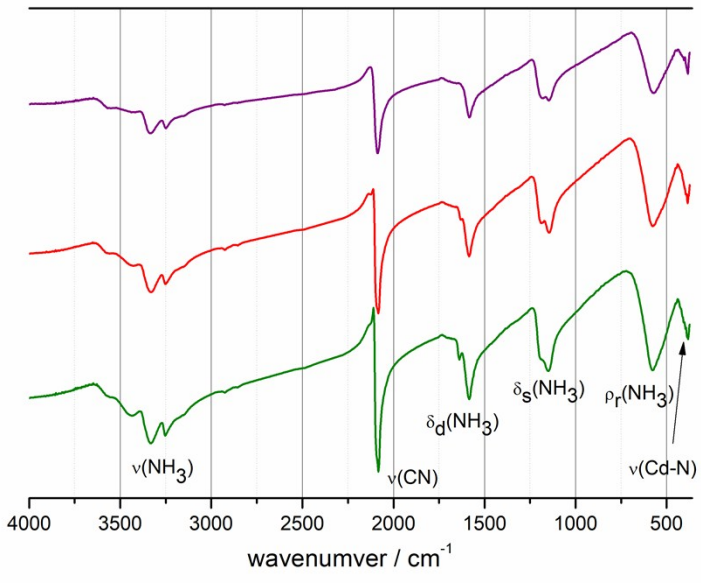


Figure S1. FT-IR spectra in KBr pellets for compounds: **2**(green line), **3** (red line) and **4** (purple line).

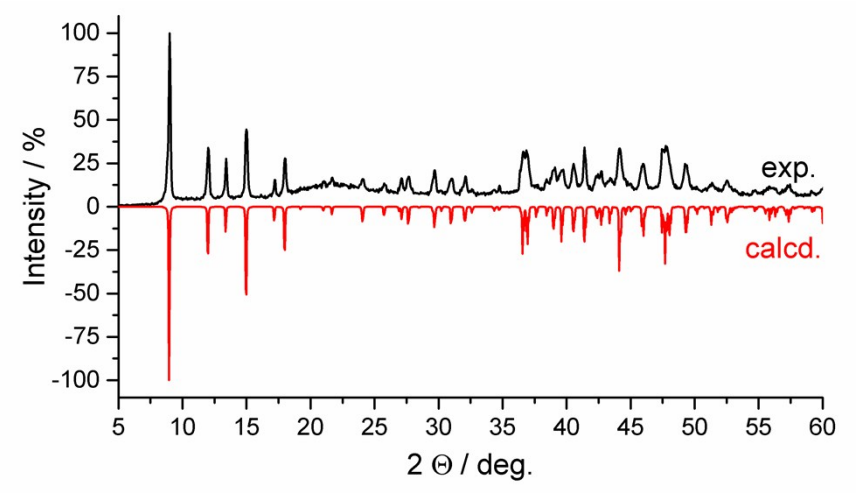


Figure S2. Powder XRD patterns (recorded, black *vs* calculated, red) for compound **2**. Refined parameters: a = 14.78(1) Å, c = 15.49(1) Å.

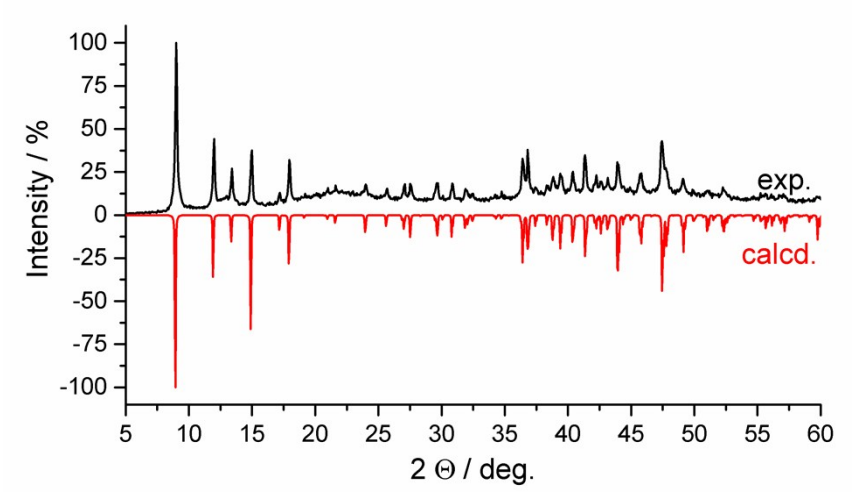


Figure S3. Powder XRD patterns (recorded, black *vs* calculated, red) for compound **3**. Refined parameters a = 14.86(1) Å, c = 15.49(1) Å.

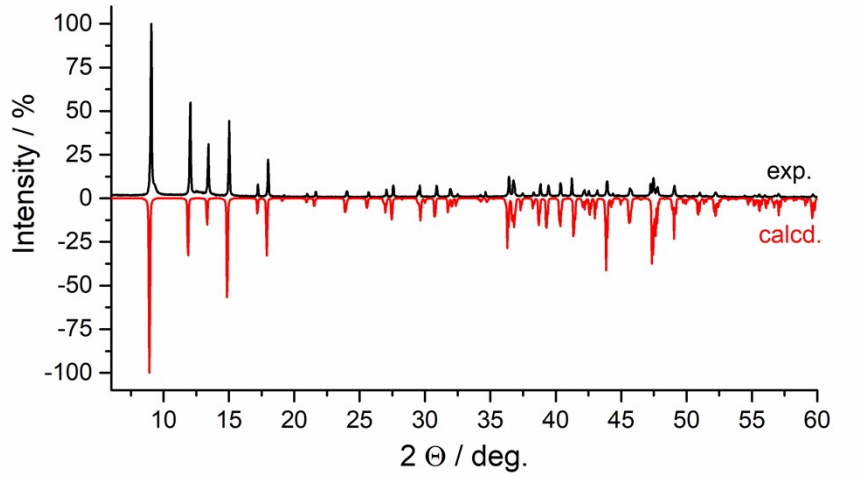


Figure S4. Powder XRD patterns (recorded, black *vs* calculated, red) for compound **4**. Refined parameters a = 14.90(1) Å, c = 15.49(1) Å.

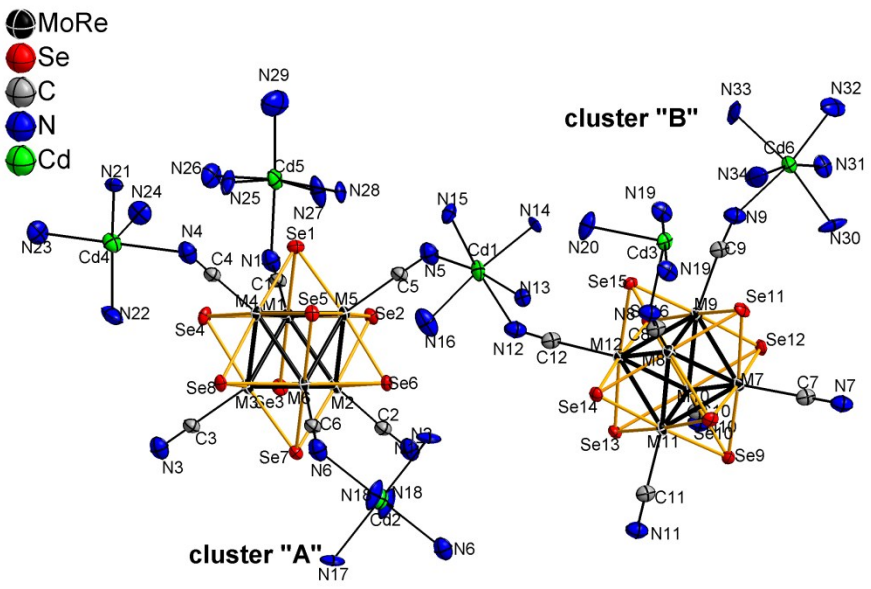


Figure S5. The structure of the asymmetric unit in **1**. Hydrogen atoms of ammonia molecules are omitted for clarity, ORTEP drawing of 75% probability level.

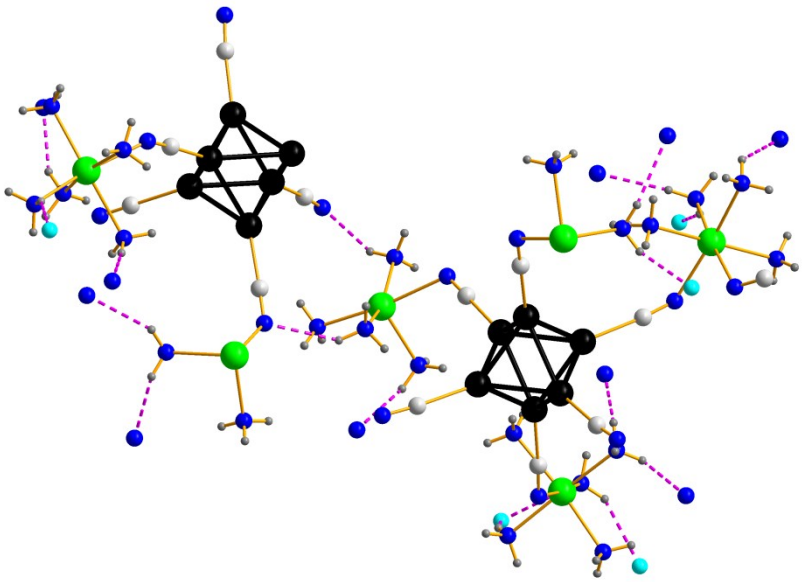
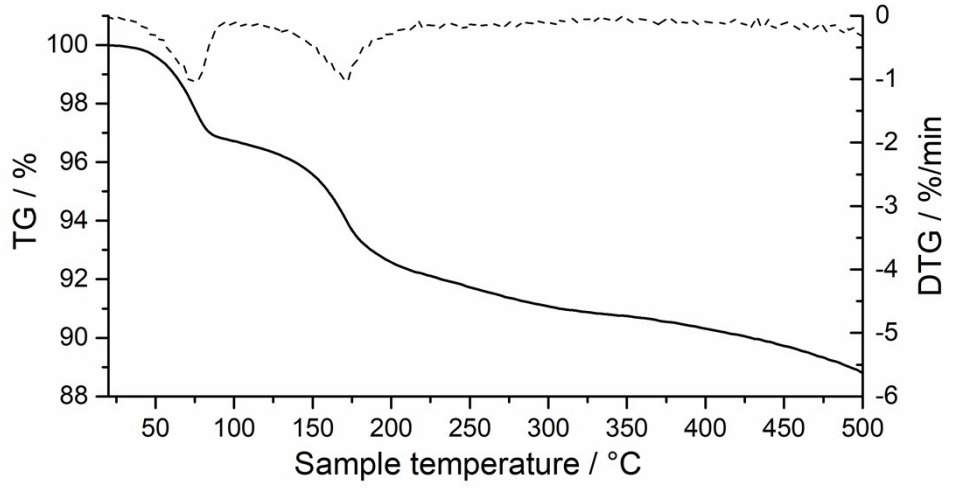
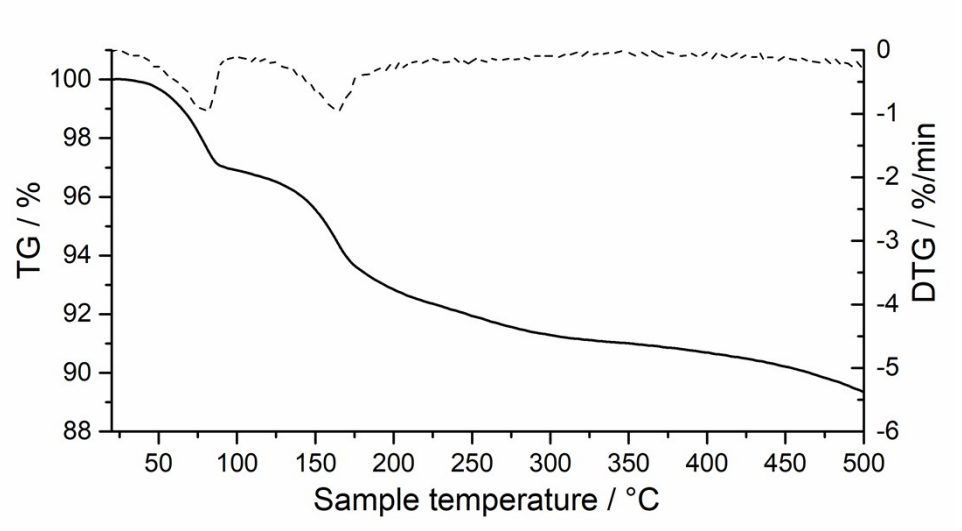


Figure S6. Selected hydrogen bonds (dash lines, magenta colored) location in structure **1**. Selenium atoms were omitted for clarity.

a)



b)



c)

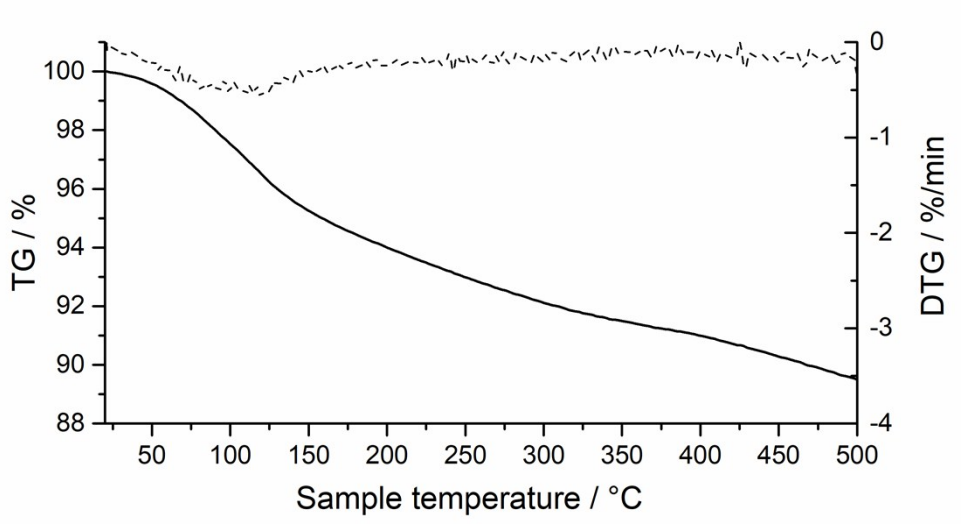
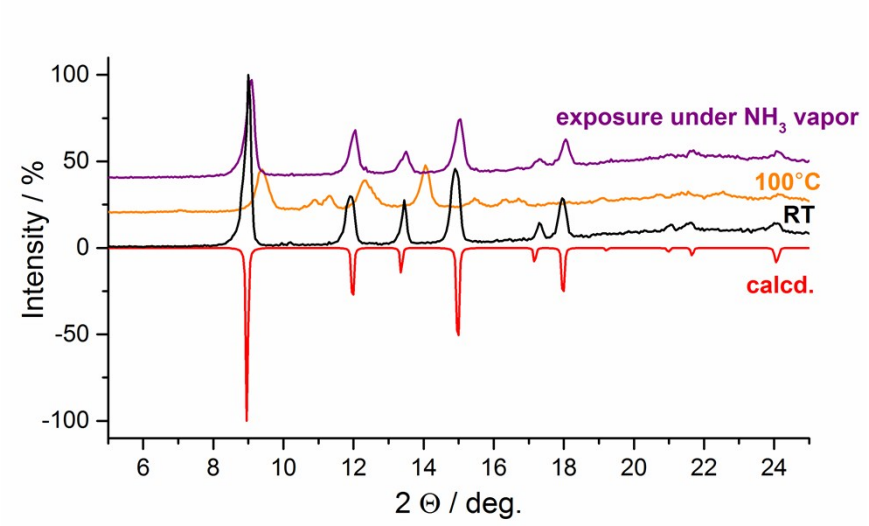


Figure S7. TG and DTG diagrams for **2** (a), **3** (b) and **4** (c)

a)



b)

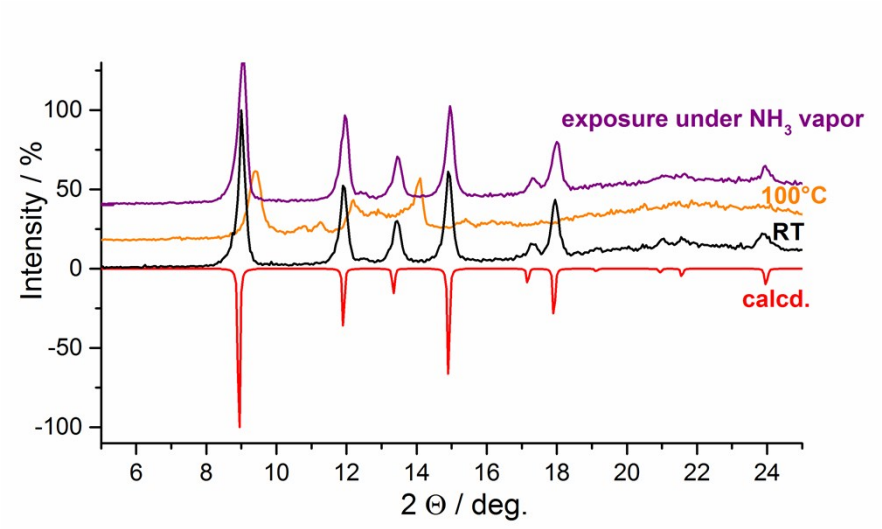


Figure S8. Powder XRD analysis for a) the sample of **2** and b) the sample of **3**. Red line represents the calculated pattern; black line was obtained for sample at room temperature; orange lines corresponds to samples heated for several minutes 100°C. Purple lines are for samples after exposure under dry NH_3 vapor.

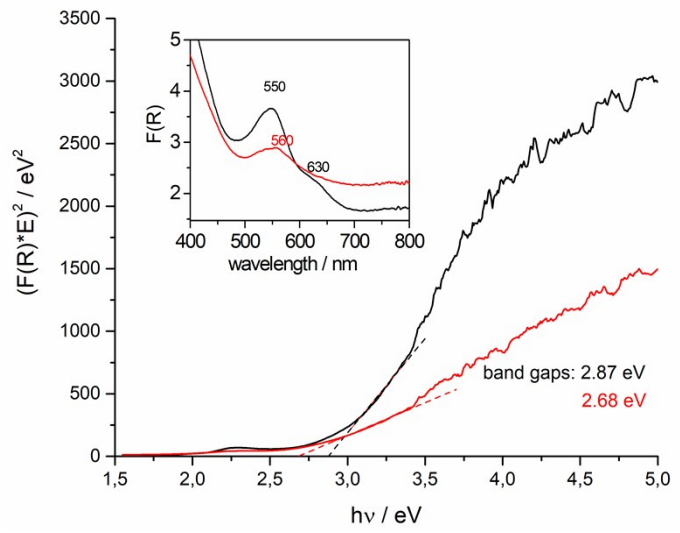


Figure S9. Tauc plot for **4** before heating (black line) and for sample heated in air at 100°C for several minutes (red line) calculated from diffuse reflectance spectra, on the onset there are initial diffuse reflectance spectra (DRS) with characteristic cluster bands.

References

1. T. Steiner, *Angew. Chem. Int. Ed.*, **2002**, 41, 48-76.