# Tunable bandgap in self-assembled transition metal-incorporated heterometallic $M_2Sb_4$ (M = V, Mn, Co, Ni, and Cu) oxo clusters

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## Contents:

**Table S1:** crystallographic information of compounds **1-5.**

| | **1** | **2** | **3** |
|---|---|---|---|
| Formula | $C_{44}H_{64}Cl_4O_{22}P_4Sb_4V_2$ | $C_{68}H_{110}Mn_2N_2O_{22}P_4Sb_4$ | $C_{67}Co_2H_{106}N_2O_{21}P_4Sb_4$ |
| Formula weight | 1799.51 | 2028.33 | 2004.27 |
| Temperature/K | 109(3) | 100(2) | 100(2) |
| Crystal system | monoclinic | monoclinic | monoclinic |
| Space group | *P2₁/n* | *C2/c* | *C2/c* |
| a/Å | 9.9319(2) | 25.252(3) | 25.233(8) |
| b/Å | 24.0942(5) | 20.379(3) | 20.100(8) |
| c/Å | 13.5380(2) | 16.0757(18) | 16.085(6) |
| α/° | 90 | 90 | 90 |
| β/° | 99.005(2) | 91.123(2) | 91.279(10) |
| γ/° | 90 | 90 | 90 |
| Volume/Å$^3$ | 3199.73(11) | 8271.1(16) | 8156(5) |
| Z | 2 | 4 | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.868 | 1.629 | 1.632 |
| μ/mm$^{-1}$ | 2.281 | 1.730 | 1.849 |
| F(000) | 1764.0 | 4088.0 | 4032.0 |
| Crystal size/mm$^3$ | 0.23 × 0.19 × 0.14 | 0.16 × 0.14 × 0.13 | 0.23 × 0.17 × 0.13 |
| Radiation | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) |
| 2θ range (°) | 4.484 to 50.698 | 2.568 to 52.838 | 2.59 to 53.728 |
| Index ranges | $-11 \le h \le 11$,<br>$-29 \le k \le 28$,<br>$-16 \le l \le 15$ | $-31 \le h \le 31$,<br>$-25 \le k \le 25$,<br>$-20 \le l \le 20$ | $-31 \le h \le 31$,<br>$-25 \le k \le 25$,<br>$-20 \le l \le 20$ |
| Reflections collected | 29157 | 43796 | 43123 |
| Independent reflections | 5855 | 8474 | 8521 |
| Goodness-of-fit on $F^2$ | 1.089 | 1.114 | 1.021 |
| $R_1(F)$ ($I > 2\sigma(I)$) | 0.0351 | 0.0356 | 0.0471 |
| $wR_2(F^2)$ (all data) | 0.0908 | 0.0837 | 0.1058 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.92/-0.87 | 1.17/-0.61 | 1.11/-0.69 |
| completeness to $\theta_{max}$, % | 100.0 | 99.5 | 96.8 |

| | **4** | 5 |
|---|---|---|
| Formula | $C_{68}H_{110}N_2Ni_2O_{22}P_4Sb_4$ | $C_{68}H_{110}Cu_2N_2O_{22}P_4Sb_4$ |
| Formula weight | 2035.87 | 2045.53 |
| Temperature/K | 100(2) | 100(2) |
| Crystal system | monoclinic | triclinic |
| Space group | *C2/c* | *P-1* |
| a/Å | 25.249(3) | 12.8207(14) |
| b/Å | 20.009(3) | 13.3637(15) |
| c/Å | 16.163(2) | 13.7013(15) |
| α/° | 90 | 99.588(2) |
| β/° | 91.427(2) | 93.106(2) |
| γ/° | 90 | 114.547(2) |
| Volume/Å$^3$ | 8163.4(18) | 2085.5(4) |
| Z | 4 | 1 |
| $\rho_{calc}$g/cm$^3$ | 1.657 | 1.629 |
| μ/mm$^{-1}$ | 1.904 | 1.922 |
| F(000) | 4112.0 | 1030.0 |
| Crystal size/mm$^3$ | 0.16 × 0.14 × 0.12 | 0.23 × 0.18 × 0.16 |
| Radiation | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) |
| 2θ range (°) | 2.598 to 52.776 | 3.044 to 52.866 |
| Index ranges | -31 ≤ h ≤ 31,<br>-24 ≤ k ≤ 24,<br>-20 ≤ l ≤ 20 | -15 ≤ h ≤ 16,<br>-16 ≤ k ≤ 16,<br>-17 ≤ l ≤ 16 |
| Reflections collected | 43172 | 16745 |
| Independent reflections | 8334 | 8416 |
| Goodness-of-fit on F$^2$ | 1.081 | 1.027 |
| $R_1$(F) (I > 2σ(I)) | 0.0365 | 0.0311 |
| $wR_2$(F$^2$) (all data) | 0.0873 | 0.0757 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.14/-0.64 | 0.84/-0.52 |
| completeness to $\theta_{max}$, % | 99.7 | 98.2 |

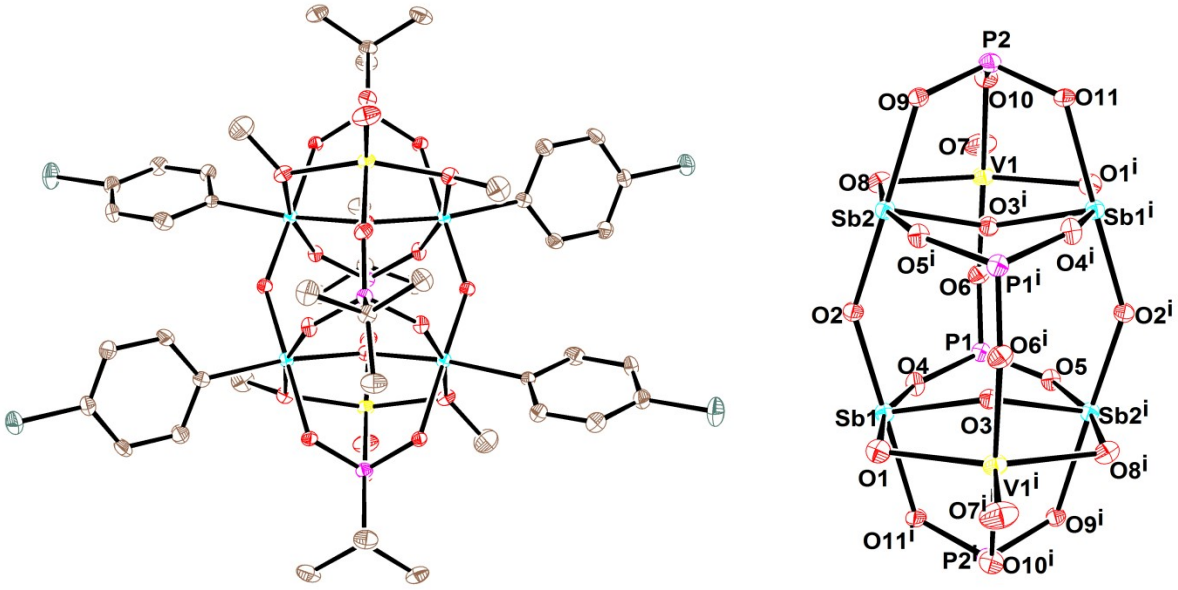



**Figure S1:** ORTEP view of **1** with thermal ellipsoids shown at 30% probability.

**Table S2:** Selected bond lengths (Å) and bond angles (deg) parameters of compound **1.**

| | | | | | |
|---|---|---|---|---|---|
| Sb1-O4 | 2.005(3) | O3-Sb1-O11[1] | 86.59(11) | O6-V1-O1[1] | 93.74(11) |
| Sb1-O3 | 1.967(3) | O3-Sb1-O1 | 76.46(11) | O7-V1-O3[1] | 178.88(13) |
| Sb1-O2 | 1.921(3) | O2-Sb1-O4 | 92.25(11) | O7-V1-O8 | 109.20(15) |
| Sb1-O11[1] | 2.052(3) | O2-Sb1-O3 | 94.59(11) | O7-V1-O10 | 93.31(14) |
| Sb1-O1 | 2.048(3) | O2-Sb1-O11[1] | 177.78(11) | O7-V1-O1[1] | 108.97(15) |
| Sb2-O3[1] | 1.965(3) | O1-Sb1-O11[1] | 88.20(11) | O7-V1-O6 | 92.61(14) |
| Sb2-O8 | 2.047(3) | O31-Sb2-O8 | 77.12(11) | O4-P1-O5 | 111.24(16) |
| Sb2-O9 | 2.060(3) | O31-Sb2-O9 | 86.38(10) | O6-P1-O4 | 112.36(16) |
| Sb2-O2 | 1.927(3) | O31-Sb2-O5[1] | 90.11(11) | O6-P1-O5 | 111.89(16) |
| Sb2-O5[1] | 2.004(3) | O8-Sb2-O9 | 87.73(11) | O11-P2-O9 | 109.51(16) |
| V1-O3[1] | 2.230(3) | O2-Sb2-O3[1] | 94.17(11) | O10-P2-O9 | 110.98(16) |
| V1-O8 | 2.051(3) | O2-Sb2-O8 | 91.46(11) | O10-P2-O11 | 110.59(16) |
| V1-O10 | 2.000(3) | O2-Sb2-O9 | 178.89(10) | P1-O4-Sb1 | 136.01(16) |
| V1-O11 | 2.065(3) | O2-Sb2-O5[1] | 93.72(11) | Sb1-O3-V11 | 103.55(12) |
| V1-O6 | 1.987(3) | O51-Sb2-O8 | 166.54(11) | Sb2[1]-O3-Sb1 | 138.61(14) |
| V1-O7 | 1.602(3) | O51-Sb2-O9 | 87.24(11) | Sb2[1]-O3-V1[1] | 102.89(10) |
| P1-O4 | 1.542(3) | O8-V1-O3[1] | 71.37(10) | Sb2-O8-V1 | 106.52(12) |
| P1-O5 | 1.543(3) | O8-V1-O1[1] | 141.02(11) | P2-O9-Sb2 | 122.87(15) |

| | | | | | |
|---|---|---|---|---|---|
| P1-O6 | 1.490(3) | O10-V1-O3$^1$ | 87.69(10) | Sb1-O2-Sb2 | 146.09(15) |
| P2-O9 | 1.554(3) | O10-V1-O8 | 84.97(11) | P2-O11-Sb1$^1$ | 123.16(16) |
| P2-O11 | 1.548(3) | O10-V1-O1$^1$ | 85.30(11) | P1-O5-Sb2$^1$ | 137.08(17) |
| P2-O10 | 1.510(3) | O1$^1$-V1-O3$^1$ | 70.60(10) | P2-O10-V1 | 123.13(16) |
| O4-Sb1-O11$^1$ | 85.85(11) | O6-V1-O3$^1$ | 86.40(11) | Sb1-O1-V1$^1$ | 106.77(13) |
| O4-Sb1-O1 | 166.00(11) | O6-V1-O8 | 92.12(12) | P1-O6-V1 | 153.53(18) |
| O3-Sb1-O4 | 90.54(11) | O6-V1-O10 | 173.99(12) | | |

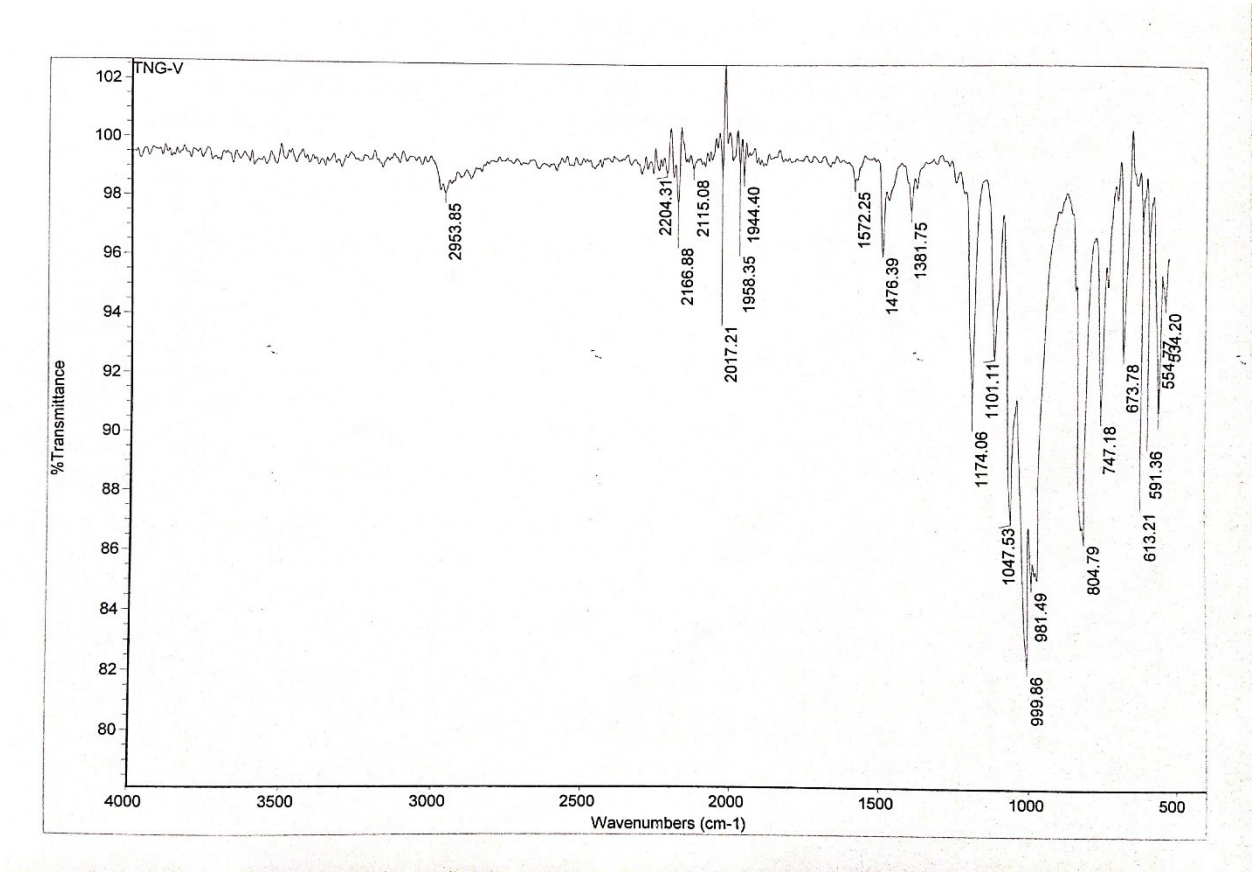



**Figure S2**: IR spectrum of compound **1**.

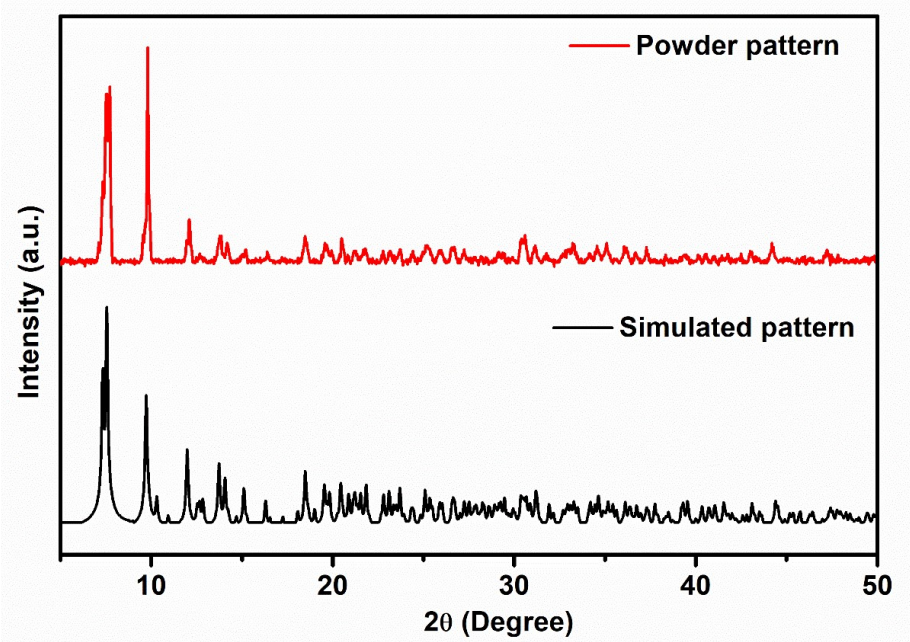



**Figure S3**: Powder X-ray diffraction pattern of a bulk sample of **1** compared to the simulated powder pattern extracted from single-crystal diffraction data.

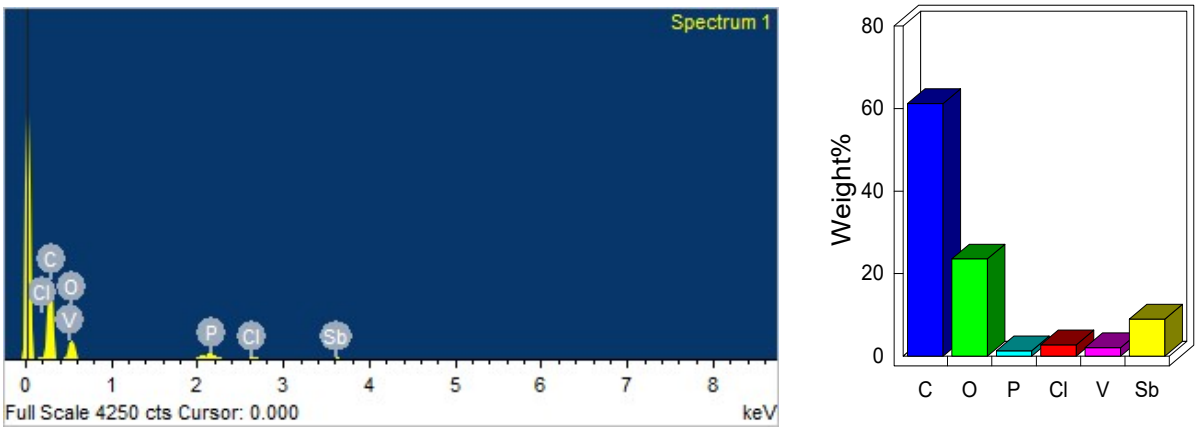


**Figure S4**: EDAX spectrum of compound **1**.

**Table S3:** EDAX analysis of **1**.

| Element | Calculated weight% | Measured weight% from EDAX analysis |
|---|---|---|
| C | 29.37 | 28.87 |
| Cl | 7.88 | 7.33 |
| O | 19.56 | 21.75 |
| P | 6.88 | 5.68 |
| V | 5.66 | 4.82 |
| Sb | 27.06 | 31.55 |
| H | 3.58 | Not detected |

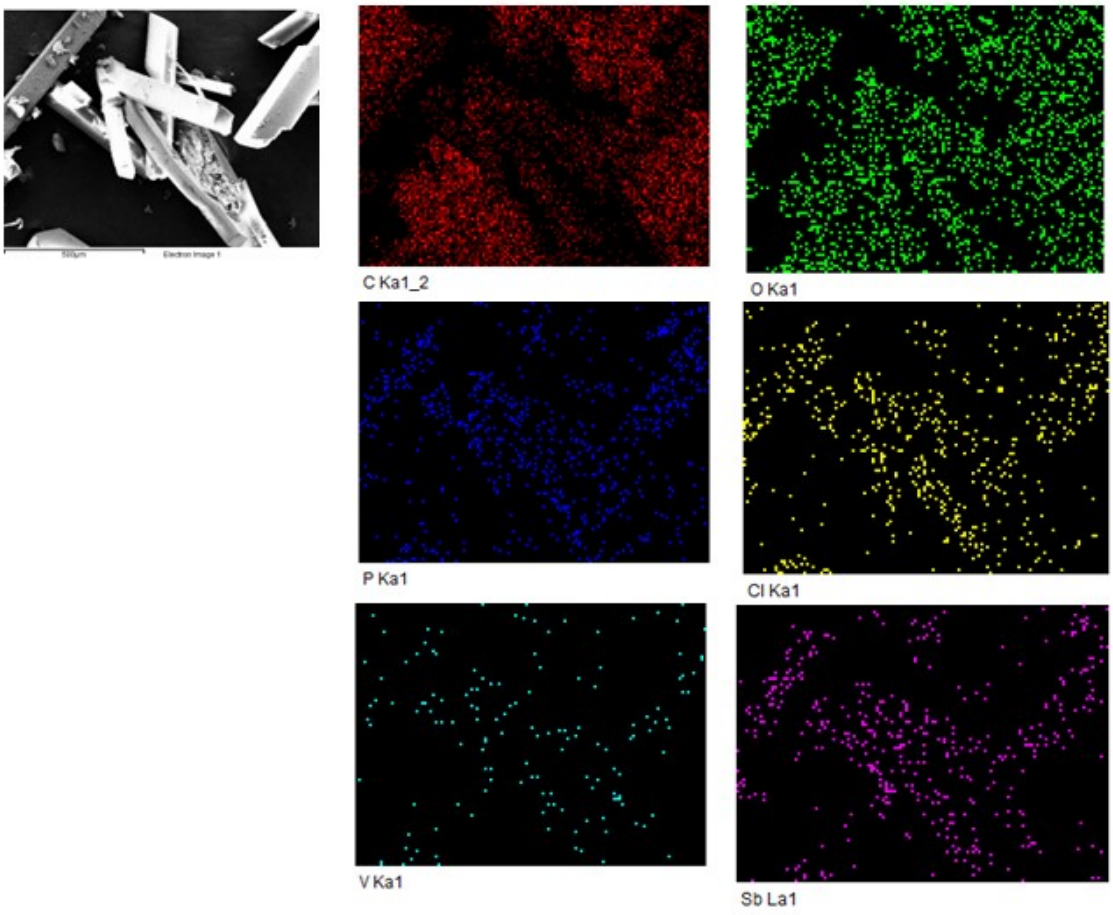



**Figure S5:** Elemental mapping of compound **1**.

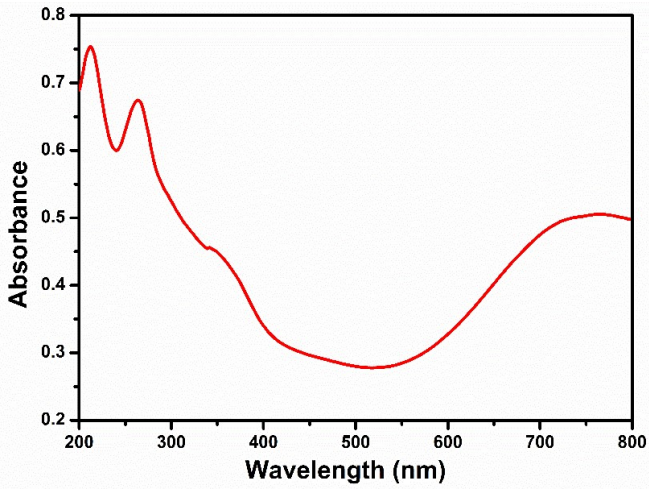
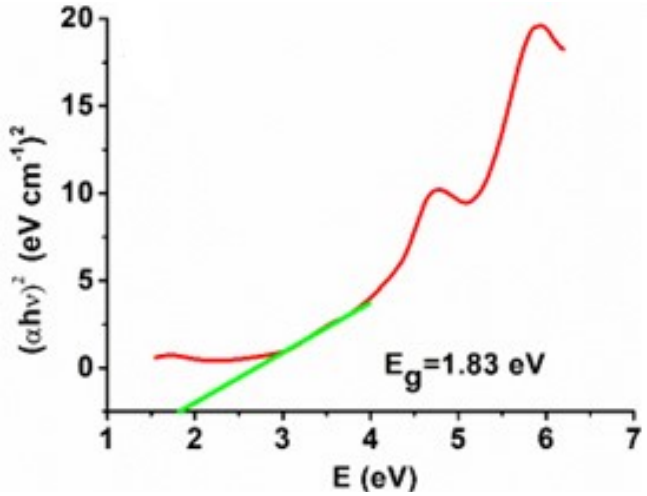
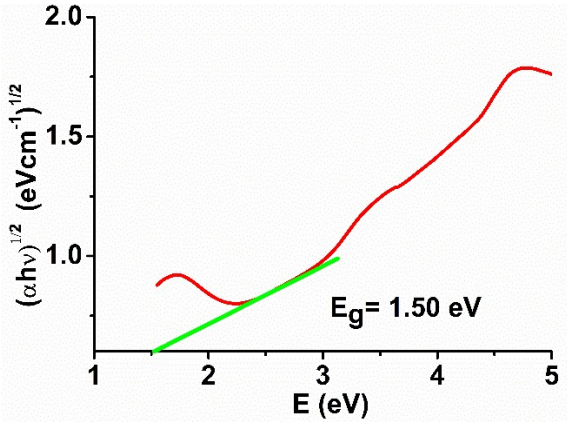



**Figure S6:** Solid-state UV-vis absorption spectrum of compound **1**.




**(a) Direct bandgap**




**(b) Indirect bandgap**

**Figure S7:** Tauc plot of compound **1**.

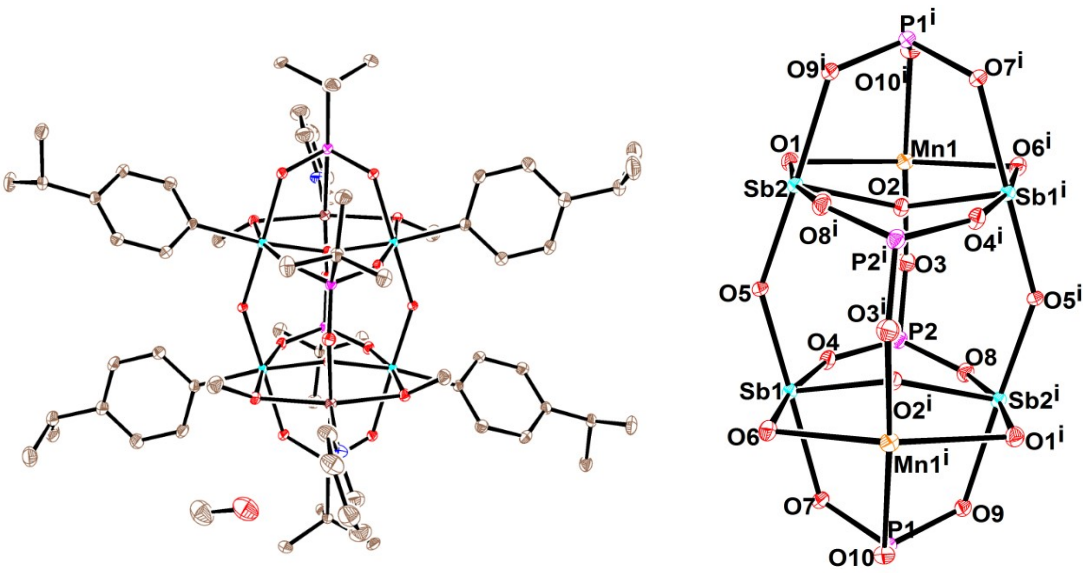



**Figure S8:** ORTEP view of **2** with thermal ellipsoids shown at 30% probability.

**Table S4:** Selected bond lengths (Å) and bond angles (deg) parameters of compound **2.**

| | | | | | |
|---|---|---|---|---|---|
| Sb2-O5 | 1.926(2) | O5-Sb2-O9[1] | 178.57(9) | O10[1]-Mn1-N1 | 88.81(11) |
| Sb2-O1 | 2.024(2) | O1-Sb2-O9[1] | 86.86(10) | O3-Mn1-O1 | 97.67(10) |
| Sb2-O8[1] | 2.017(2) | O8[1]-Sb2-O1 | 169.68(10) | O3-Mn1-O61 | 95.34(9) |
| Sb2-O2 | 1.962(2) | O8[1]-Sb2-O9[1] | 87.70(10) | O3-Mn1-O2 | 92.07(9) |
| Sb2-O9[1] | 2.053(2) | O2-Sb2-O1 | 80.63(10) | O3-Mn1-O10[1] | 176.85(10) |
| Sb1-O5 | 1.927(2) | O2-Sb2-O8[1] | 90.31(10) | O3-Mn1-N1 | 90.97(11) |
| Sb1-O7 | 2.056(2) | O2-Sb2-O9[1] | 86.71(9) | N1-Mn1-O2 | 175.65(11) |
| Sb1-O6 | 2.015(2) | O5-Sb1-O7 | 178.64(10) | O9-P1-O7 | 109.16(14) |
| Sb1-O4 | 2.010(2) | O5-Sb1-O6 | 91.74(10) | O10-P1-O7 | 112.01(14) |
| Sb1-O2[1] | 1.962(2) | O5-Sb1-O4 | 92.02(10) | O10-P1-O9 | 112.30(14) |
| Mn1-O1 | 2.204(2) | O5-Sb1-O2[1] | 93.90(10) | O8-P2-O4 | 110.58(13) |
| Mn1-O6[1] | 2.199(2) | O6-Sb1-O7 | 86.90(10) | O3-P2-O4 | 112.80(14) |
| Mn1-O2 | 2.264(2) | O4-Sb1-O7 | 89.33(10) | O3-P2-O8 | 113.10(14) |
| Mn1-O10[1] | 2.181(3) | O4-Sb1-O6 | 170.39(9) | Sb2-O5-Sb1 | 145.94(13) |
| Mn1-O3 | 2.069(3) | O2[1]-Sb1-O7 | 85.96(9) | Sb2-O1-Mn1 | 103.44(10) |
| Mn1-N1 | 2.219(3) | O2[1]-Sb1-O6 | 80.86(10) | P1-O7-Sb1 | 124.73(14) |
| P1-O7 | 1.558(2) | O2[1]-Sb1-O4 | 90.06(10) | Sb1-O6-Mn1[1] | 103.87(10) |
| P1-O9 | 1.550(3) | O1-Mn1-O2 | 70.50(8) | P2-O4-Sb1 | 138.57(14) |
| P1-O10 | 1.506(3) | O1-Mn1-N1 | 106.01(12) | P2-O8-Sb2[1] | 137.75(14) |
| P2-O4 | 1.554(2) | O6[1]-Mn1-O1 | 139.26(9) | Sb2-O2-Sb1[1] | 138.73(13) |
| P2-O8 | 1.549(2) | O6[1]-Mn1-O2 | 70.60(9) | Sb2-O2-Mn1 | 103.39(9) |

| | | | | | |
|---|---|---|---|---|---|
| P2-O3 | 1.497(3) | O6[1]-Mn1-N1 | 112.20(12) | Sb11-O2-Mn1 | 103.33(10) |
| O5-Sb2-O1 | 93.21(10) | O10[1]-Mn1-O1 | 85.41(9) | P1-O9-Sb2[1] | 124.81(14) |
| O5-Sb2-O8[1] | 92.44(10) | O10[1]-Mn1-O6[1] | 81.84(9) | P1-O10-Mn1[1] | 116.50(14) |
| O5-Sb2-O2 | 94.72(9) | O10[1]-Mn1-O2 | 88.32(9) | P2-O3-Mn1 | 142.66(16) |

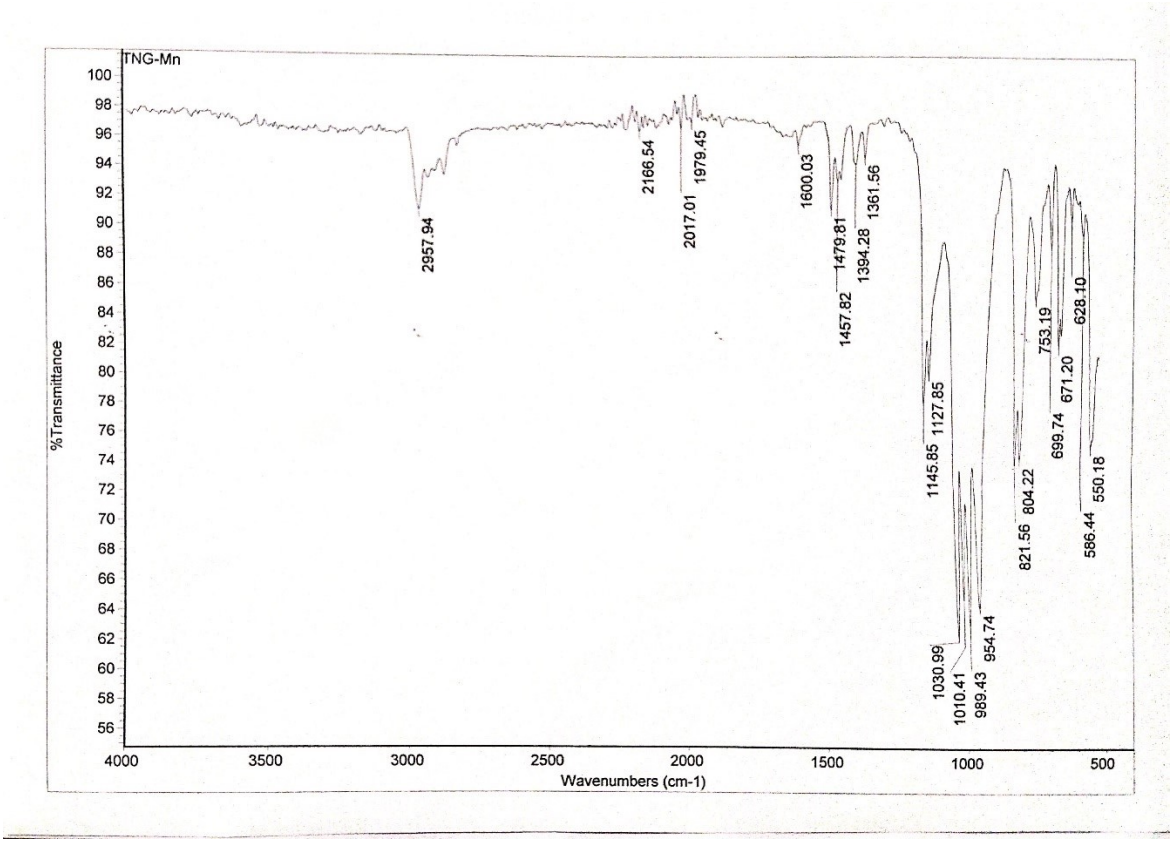



**Figure S9**: IR spectrum of compound **2**.

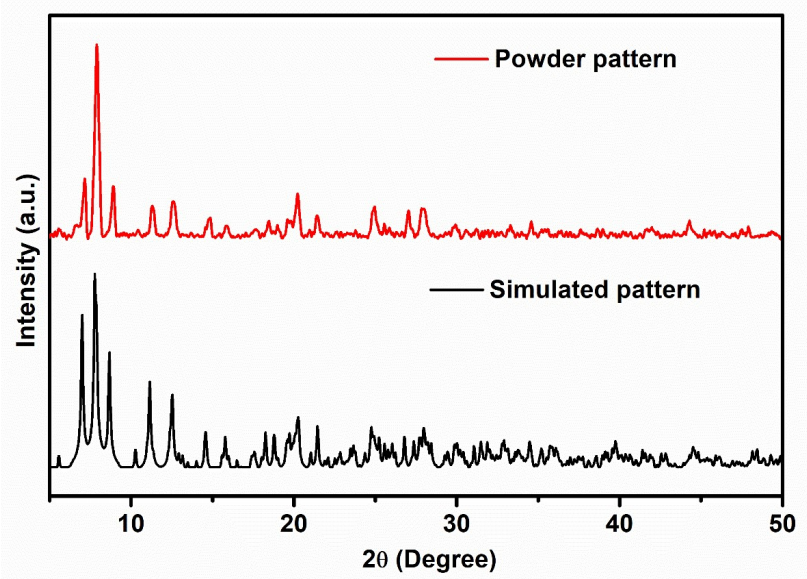



**Figure S10**: Powder X-ray diffraction pattern of a bulk sample of **2,** compared to the simulated powder pattern extracted from single-crystal diffraction data.

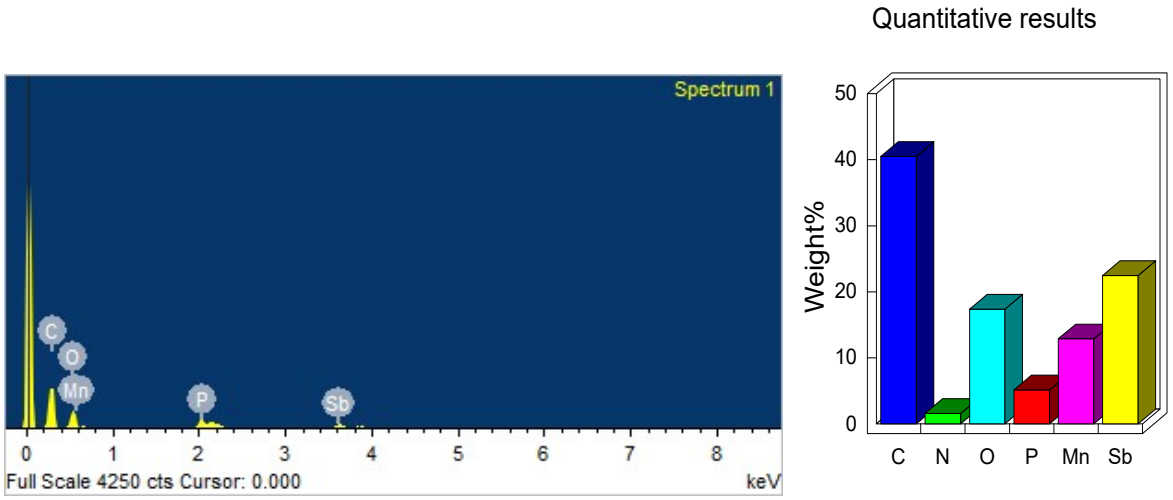



**Figure S11**: EDAX spectrum of compound **2**.

**Table S5:** EDAX analysis of **2**.

| Element | Calculated weight% | Measured weight% from EDAX analysis |
|---|---|---|
| C | 40.36 | 40.49 |
| N | 1.43 | 1.60 |
| O | 16.29 | 17.39 |
| P | 6.31 | 7.15 |
| Mn | 5.59 | 10.88 |
| Sb | 24.79 | 22.49 |
| H | 5.23 | Not detected |

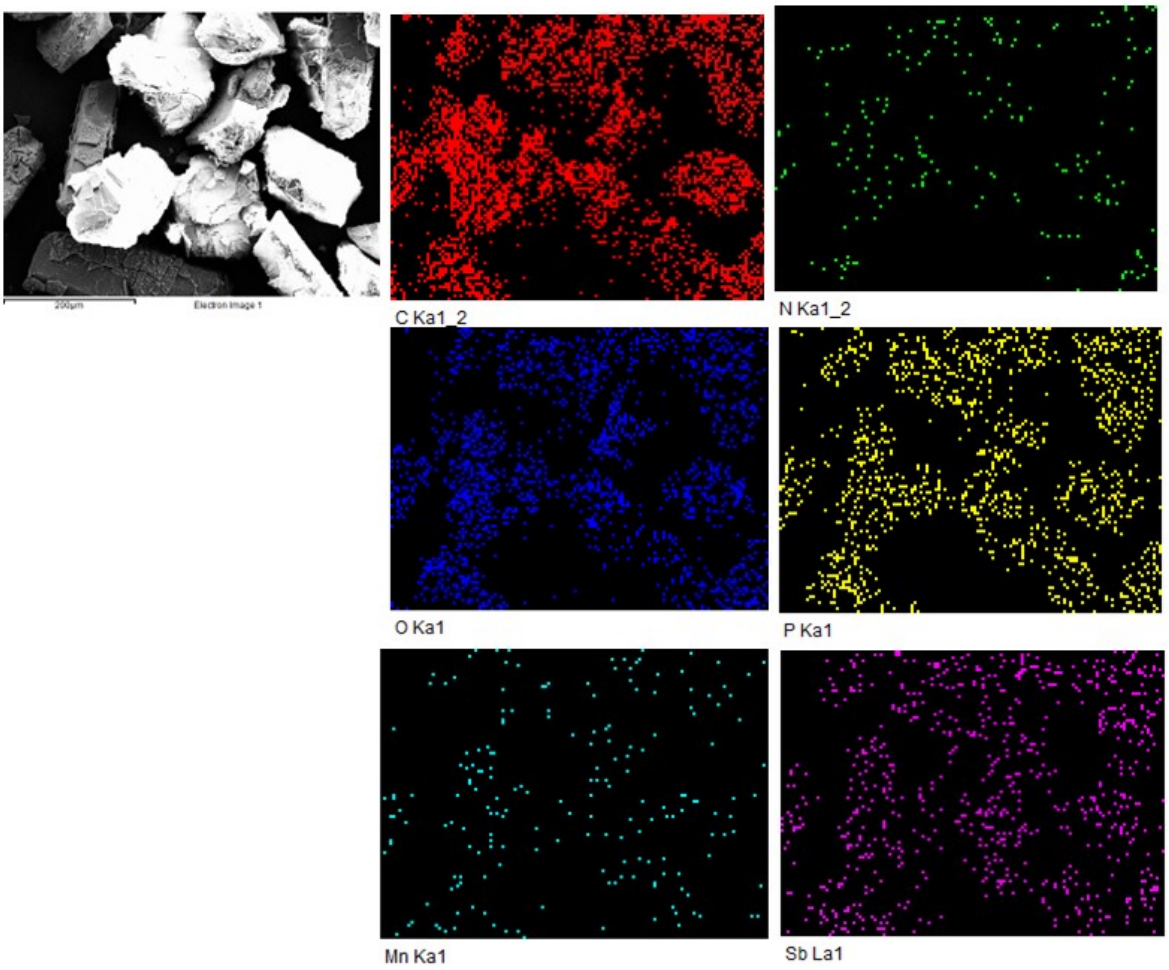



**Figure S12:** Elemental mapping of compound **2.**

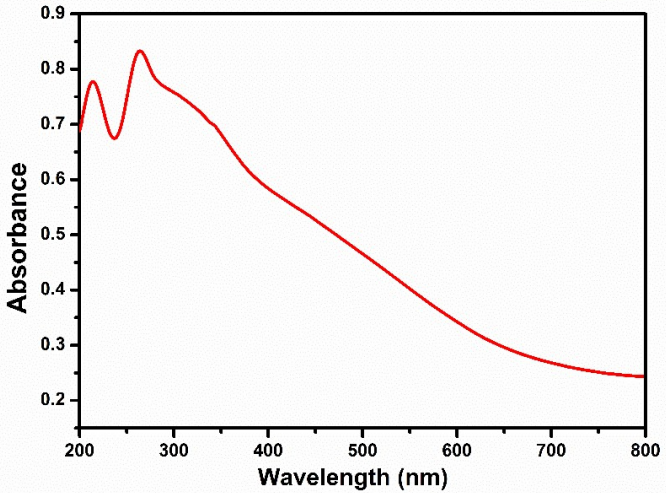
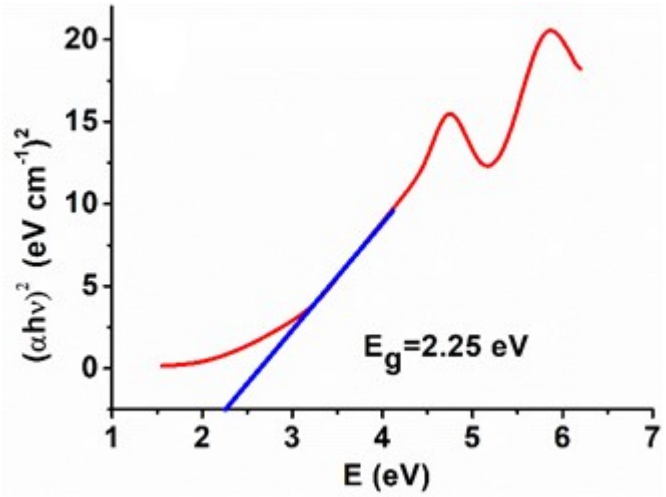
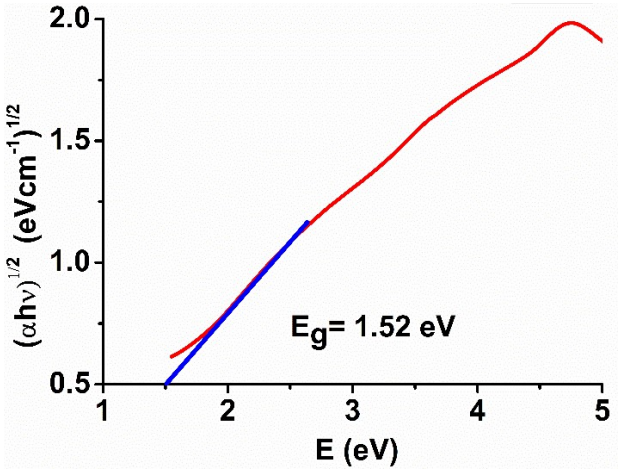



**Figure S13:** Solid-state UV-vis absorption spectrum of compound **2**.




**(a) Direct bandgap**




**(b) Indirect bandgap**

**Figure S14:** Tauc plot of compound **2**.

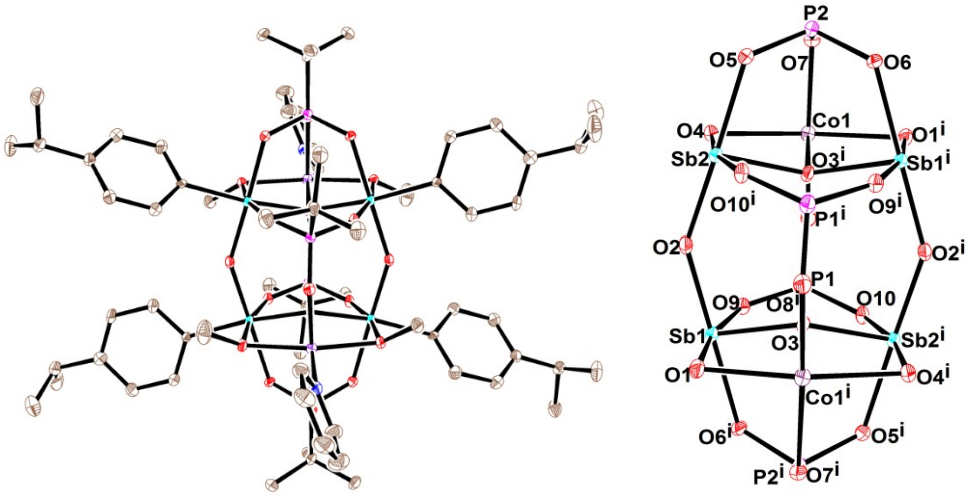



**Figure S15:** ORTEP view of **3** with thermal ellipsoids shown at 30% probability.

**Table S6**: Selected bond lengths (Å) and bond angles (deg) parameters of compound **3.**

| | | | | | |
|---|---|---|---|---|---|
| Sb2-O10[1] | 2.017(3) | O3[1]-Sb2-O4 | 79.74(13) | O8-Co1-O4 | 97.01(13) |
| Sb2-O3[1] | 1.967(3) | O3[1]-Sb2-O5 | 86.95(13) | O8-Co1-O1[1] | 94.72(13) |
| Sb2-O2 | 1.918(3) | O2-Sb2-O10[1] | 91.66(14) | O8-Co1-O7 | 176.28(13) |
| Sb2-O4 | 2.031(3) | O2-Sb2-O3[1] | 94.88(13) | O8-Co1-N1 | 89.32(16) |
| Sb2-O5 | 2.050(3) | O2-Sb2-O4 | 94.30(14) | N1-Co1-O3[1] | 177.95(14) |
| Sb1-O3 | 1.960(3) | O2-Sb2-O5 | 177.67(14) | N1-Co1-O4 | 104.32(15) |
| Sb1-O6[1] | 2.059(3) | O4-Sb2-O5 | 87.43(13) | N1-Co1-O1[1] | 108.30(14) |
| Sb1-O2 | 1.921(3) | O3-Sb1-O6[1] | 86.08(13) | O5-P2-O6 | 109.53(19) |
| Sb1-O1 | 2.016(3) | O3-Sb1-O1 | 79.81(13) | O7-P2-O6 | 112.03(19) |
| Sb1-O9 | 2.007(3) | O3-Sb1-O9 | 89.74(13) | O7-P2-O5 | 111.99(19) |
| Co1-O3[1] | 2.145(3) | O2-Sb1-O3 | 94.24(13) | O9-P1-O10 | 110.62(19) |
| Co1-O4 | 2.122(3) | O2-Sb1-O6[1] | 179.51(14) | O8-P1-O10 | 113.30(19) |
| Co1-O1[1] | 2.127(3) | O2-Sb1-O1 | 92.91(14) | O8-P1-O9 | 112.84(19) |
| Co1-O7 | 2.088(3) | O2-Sb1-O9 | 91.18(14) | P1-O10-Sb2[1] | 137.0(2) |
| Co1-O8 | 2.003(3) | O1-Sb1-O6[1] | 87.51(13) | Sb2[1]-O3-Co1[1] | 102.84(13) |
| Co1-N1 | 2.118(4) | O9-Sb1-O6[1] | 88.45(13) | Sb1-O3-Sb2[1] | 138.87(18) |
| P2-O6 | 1.550(3) | O9-Sb1-O1 | 169.02(12) | Sb1-O3-Co1[1] | 103.25(14) |
| P2-O5 | 1.549(3) | O4-Co1-O3[1] | 73.84(12) | P2-O6-Sb1[1] | 123.50(19) |
| P2-O7 | 1.501(4) | O4-Co1-O1[1] | 145.36(13) | Sb2-O2-Sb1 | 145.98(17) |
| P1-O10 | 1.548(3) | O1[1]-Co1-O3[1] | 73.33(12) | Sb2-O4-Co1 | 101.47(14) |
| P1-O9 | 1.545(3) | O7-Co1-O3[1] | 91.04(13) | Sb1-O1-Co1[1] | 101.95(14) |
| P1-O8 | 1.500(3) | O7-Co1-O4 | 86.10(13) | P1-O9-Sb1 | 138.5(2) |
| O10[1]-Sb2-O4 | 168.60(13) | O7-Co1-O1[1] | 83.78(13) | P2-O5-Sb2 | 123.25(19) |
| O10[1]-Sb2-O5 | 86.90(13) | O7-Co1-N1 | 87.93(16) | P2-O7-Co1 | 116.45(19) |

| | | | | | |
|---|---|---|---|---|---|
| $O3^1$-Sb2-$O10^1$ | 90.09(13) | O8-Co1-$O3^1$ | 91.79(13) | P1-O8-Co1 | 144.3(2) |

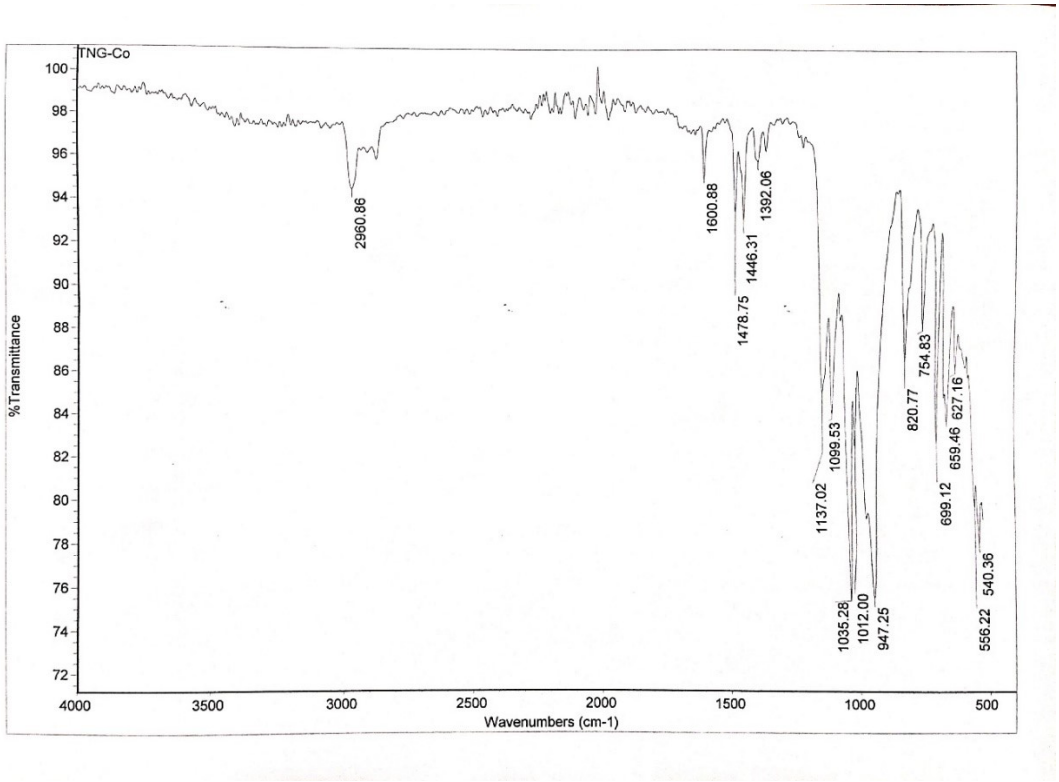



**Figure S16**: IR spectrum of compound **3**.

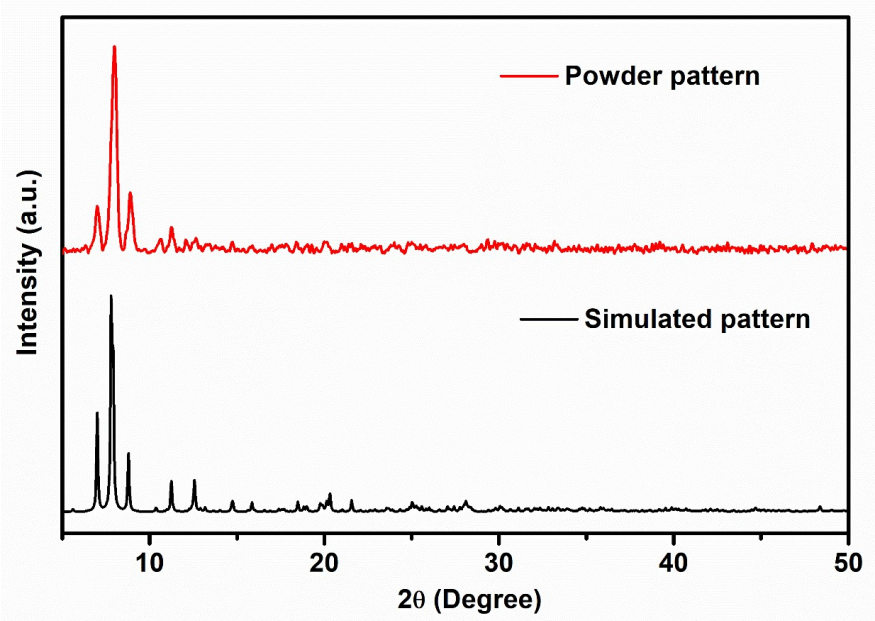



**Figure S17**: Powder X-ray diffraction pattern of a bulk sample of **3** compared to the simulated powder pattern extracted from single-crystal diffraction data.

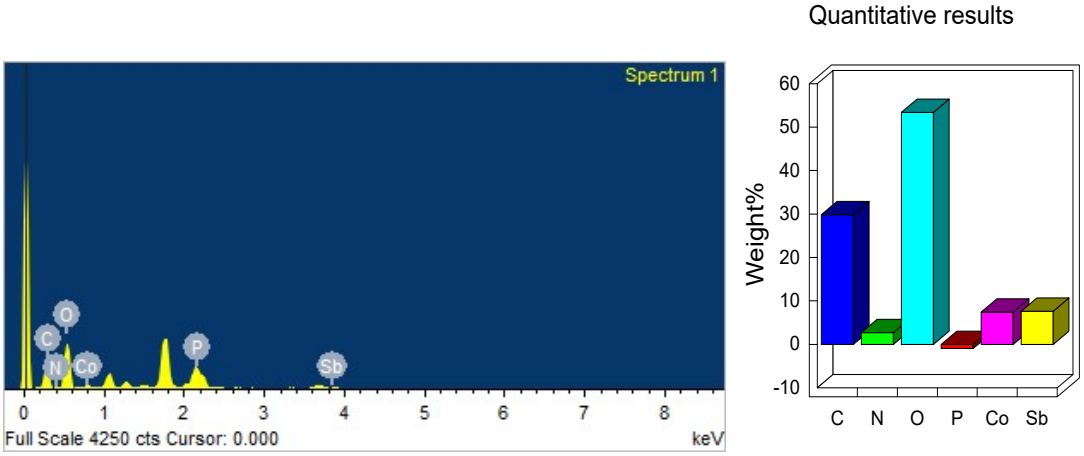



**Figure S18**: EDAX spectrum of compound **3**.

**Table S7:** EDAX analysis of **3**.

| Element | Calculated weight% | Measured weight% from EDAX analysis |
|---|---|---|
| C | 40.19 | 41.79 |
| N | 1.42 | 2.05 |
| O | 16.22 | 18.07 |
| P | 6.28 | 6.09 |
| Co | 5.98 | 8.11 |
| Sb | 24.69 | 23.89 |
| H | 5.21 | Not detected |

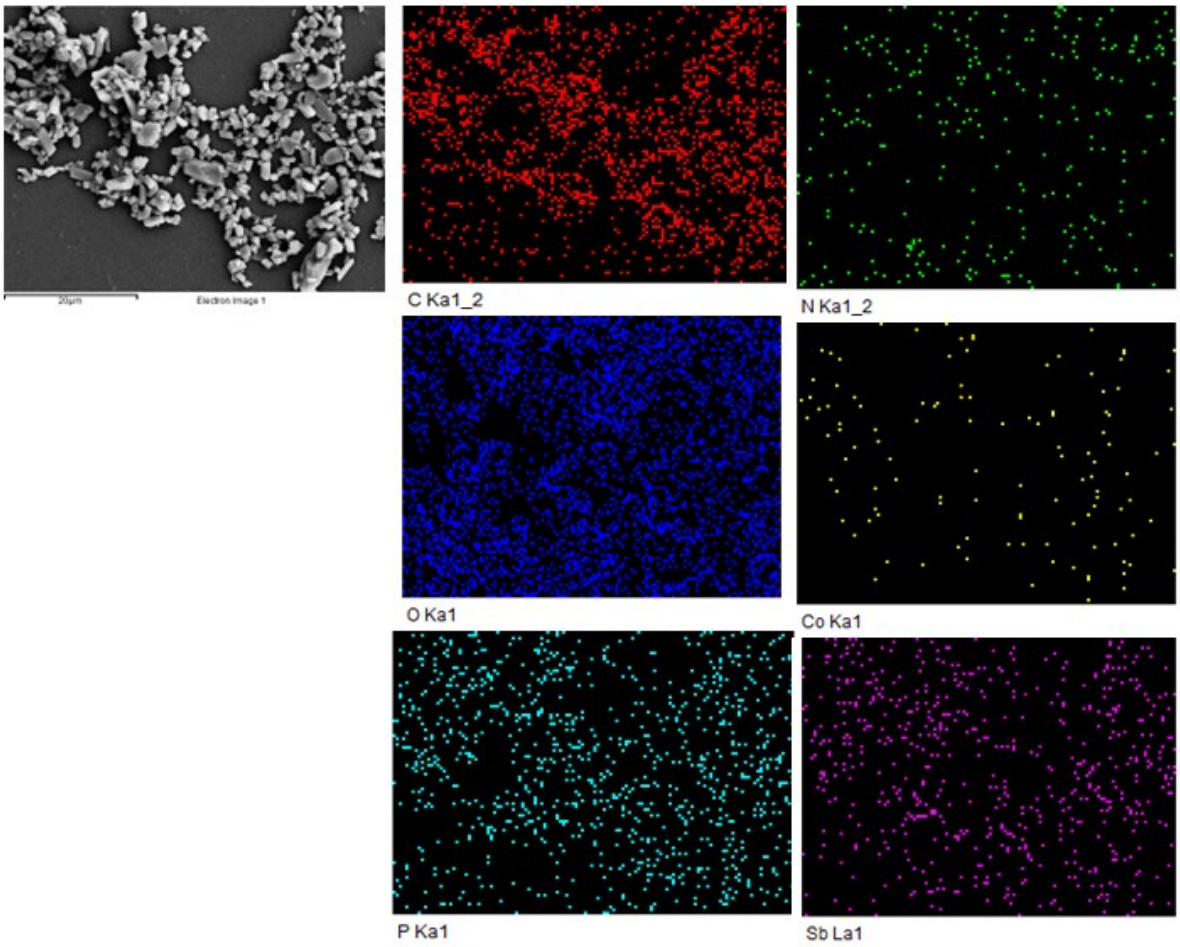



**Figure S19:** Elemental mapping of compound **3**.

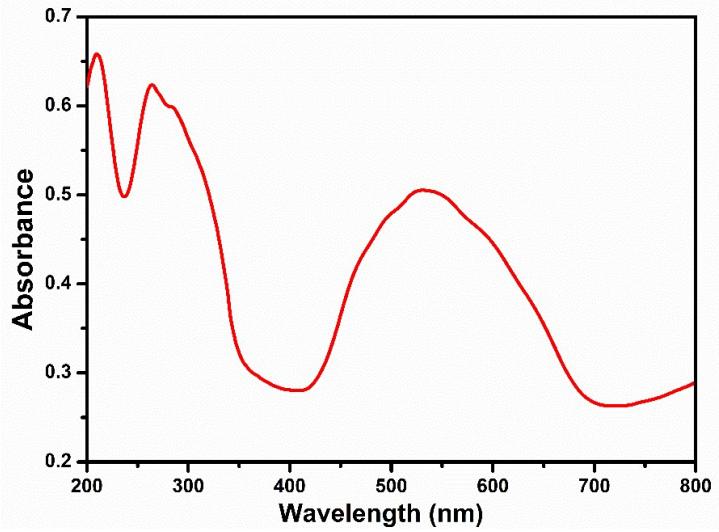
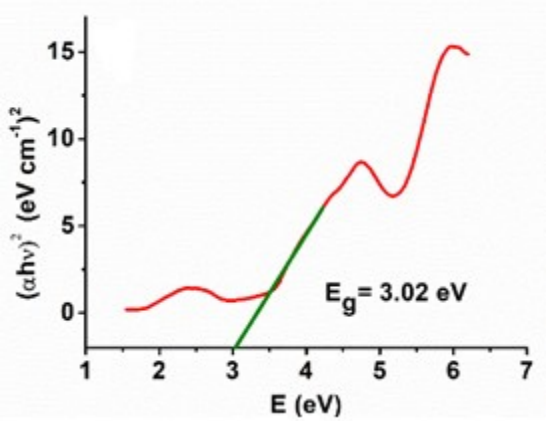
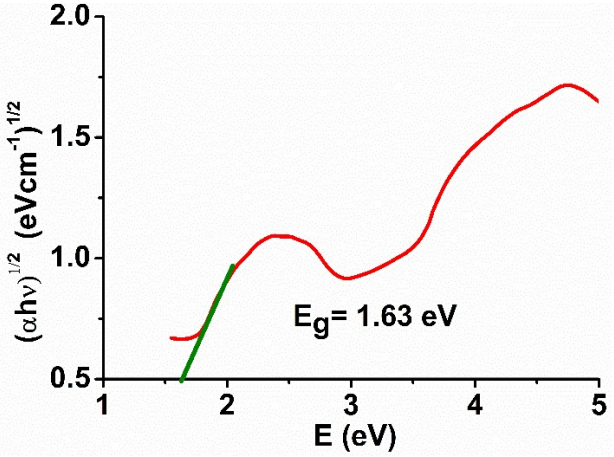



**Figure S20:** Solid-state UV-vis absorption spectrum of compound **3.**




**(a) Direct bandgap**




**(b) Indirect bandgap**

**Figure S21:** Tauc plot of compound **3**.

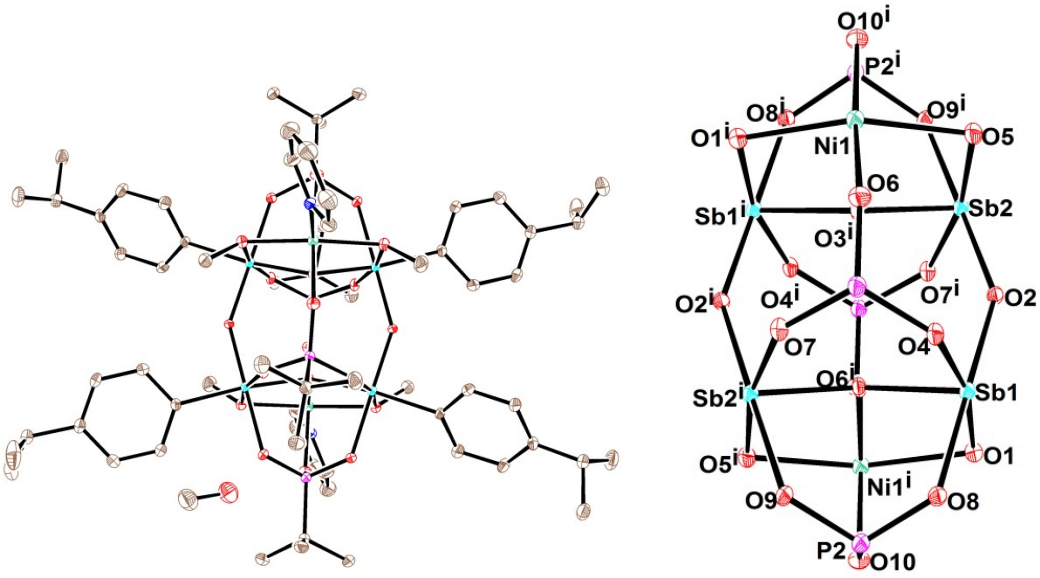



**Figure S22:** ORTEP view of **4** with thermal ellipsoids shown at 30% probability.

**Table S8:** Selected bond lengths (Å) and bond angles (deg) parameters of compound **4.**

| | | | | | |
|---|---|---|---|---|---|
| Sb2-O2 | 1.926(2) | O2-Sb2-O7[1] | 91.03(11) | O6-Ni1-O1[1] | 96.73(10) |
| Sb2-O9[1] | 2.053(2) | O31-Sb2-O91 | 86.24(9) | O6-Ni1-O10[1] | 174.90(10) |
| Sb2-O3[1] | 1.974(2) | O3[1]-Sb2-O5 | 79.18(10) | O6-Ni1-N1 | 89.03(11) |
| Sb2-O5 | 2.025(3) | O31-Sb2-O7[1] | 89.84(10) | N1-Ni1-O3[1] | 177.87(11) |
| Sb2-O7[1] | 2.003(2) | O5-Sb2-O9[1] | 87.87(10) | N1-Ni1-O5 | 106.82(11) |
| Sb1-O2 | 1.921(2) | O7[1]-Sb2-O9[1] | 87.65(10) | N1-Ni1-O1[1] | 102.33(11) |
| Sb1-O3 | 1.972(2) | O7[1]-Sb2-O5 | 168.39(10) | N1-Ni1-O10[1] | 87.08(12) |
| Sb1-O4 | 2.010(2) | O2-Sb1-O3 | 94.72(10) | O7-P1-O4 | 110.50(14) |
| Sb1-O1 | 2.039(3) | O2-Sb1-O4 | 91.57(10) | O6-P1-O4 | 113.70(14) |
| Sb1-O8 | 2.050(2) | O2-Sb1-O1 | 95.00(11) | O6-P1-O7 | 113.15(14) |
| Ni1-O3[1] | 2.076(3) | O2-Sb1-O8 | 177.23(11) | O8-P2-O9 | 109.56(14) |
| Ni1-O5 | 2.100(3) | O3-Sb1-O4 | 90.21(10) | O10-P2-O9 | 111.51(15) |
| Ni1-O1[1] | 2.090(2) | O3-Sb1-O1 | 78.98(10) | O10-P2-O8 | 112.00(15) |
| Ni1-O10[1] | 2.076(3) | O3-Sb1-O8 | 86.72(10) | Sb1-O2-Sb2 | 146.83(13) |
| Ni1-O6 | 2.002(2) | O4-Sb1-O1 | 167.76(10) | P2-O9-Sb2[1] | 123.17(14) |
| Ni1-N1 | 2.069(3) | O4-Sb1-O8 | 86.06(10) | Sb21-O3-Ni1[1] | 103.27(10) |
| P1-O4 | 1.555(3) | O1-Sb1-O8 | 87.59(10) | Sb1-O3-Sb2[1] | 138.56(13) |
| P1-O7 | 1.549(2) | O3[1]-Ni1-O5 | 75.24(9) | Sb1-O3-Ni1[1] | 103.00(10) |

| | | | | | |
|---|---|---|---|---|---|
| P1-O6 | 1.491(3) | $O3^{1}$-Ni1-$O1^{1}$ | 75.54(9) | P1-O4-Sb1 | 136.55(15) |
| P2-O9 | 1.558(2) | $O3^{1}$-Ni1-$O10^{1}$ | 92.63(10) | Sb2-O5-Ni1 | 100.64(10) |
| P2-O8 | 1.547(3) | $O1^{1}$-Ni1-O5 | 148.87(10) | Sb1-O1-$Ni1^{1}$ | 100.23(11) |
| P2-O10 | 1.505(3) | $O10^{1}$-Ni1-O5 | 83.52(10) | P2-O8-Sb1 | 123.60(14) |
| O2-Sb2-$O9^{1}$ | 178.68(11) | $O10^{1}$-Ni1-$O1^{1}$ | 87.32(10) | P1-O7-$Sb2^{1}$ | 138.10(15) |
| O2-Sb2-$O3^{1}$ | 93.78(10) | O6-Ni1-$O3^{1}$ | 91.39(10) | P2-O10-$Ni1^{1}$ | 115.46(15) |
| O2-Sb2-O5 | 93.44(10) | O6-Ni1-O5 | 94.47(10) | P1-O6-Ni1 | 145.11(17) |

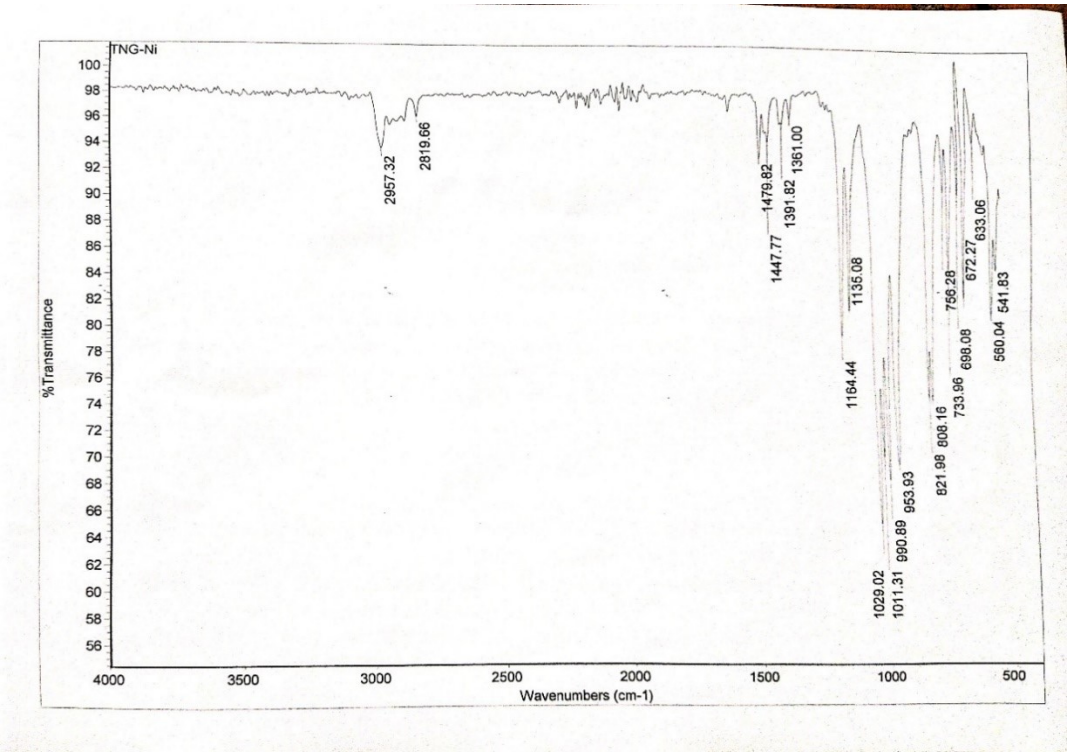



**Figure S23**: IR spectrum of compound **4**.

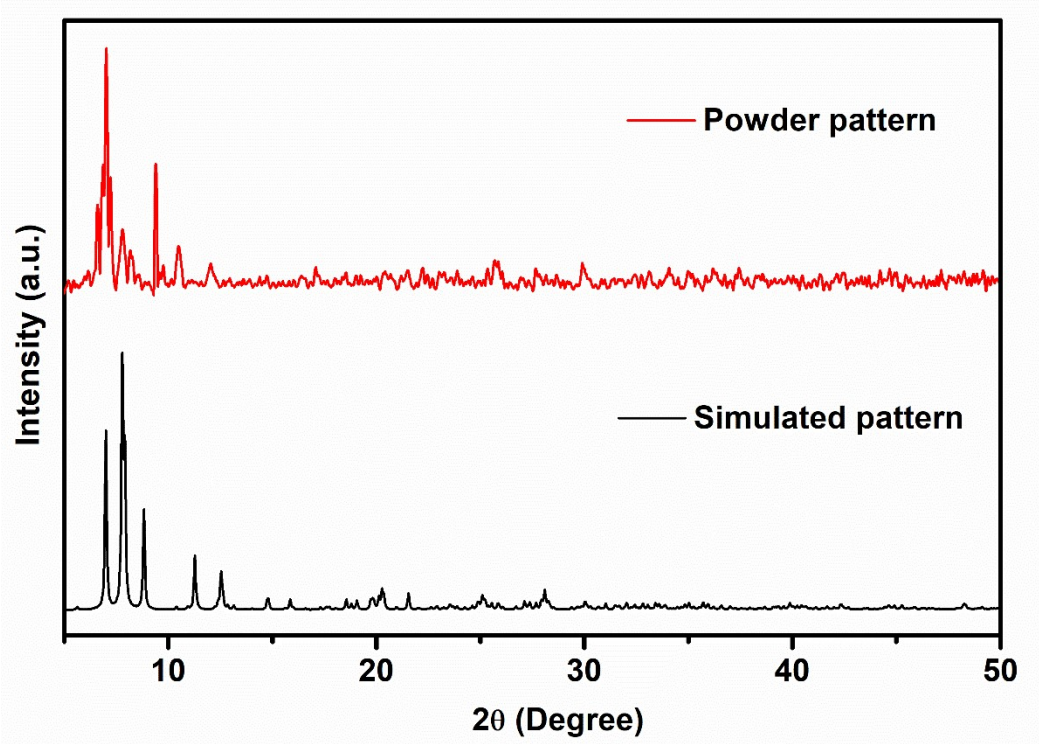



**Figure S24**: Powder X-ray diffraction pattern of a bulk sample of **4** compared to the simulated powder pattern extracted from single-crystal diffraction data.

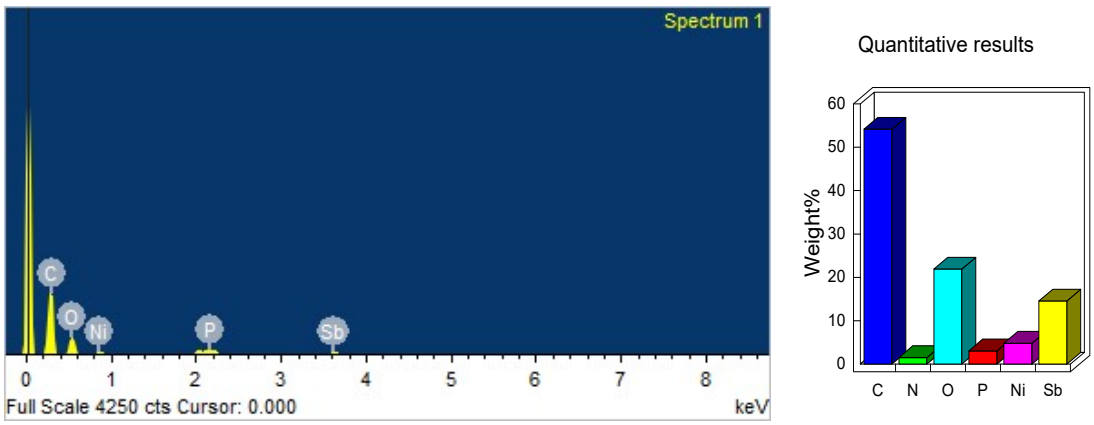



**Figure S25**: EDAX spectrum of compound **4**.

**Table S9:** EDAX analysis of **4**.

| Element | Calculated weight% | Measured weight% from EDAX analysis |
|---|---|---|
| C | 40.20 | 43.92 |
| N | 1.42 | 1.79 |
| O | 16.23 | 18.47 |
| P | 6.28 | 6.56 |
| Ni | 5.95 | 7.34 |
| Sb | 24.70 | 21.92 |
| H | 5.21 | Not detected |

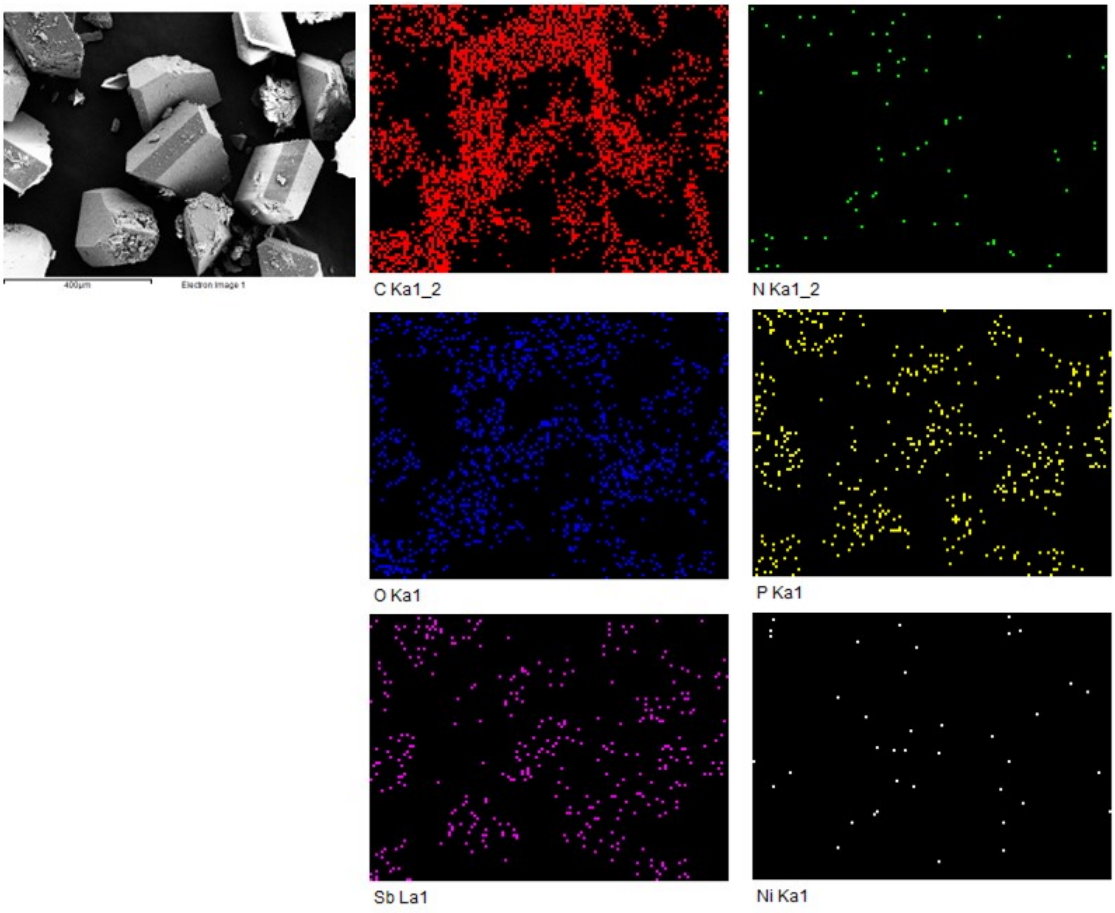



**Figure S26:** Elemental mapping of compound **4**.

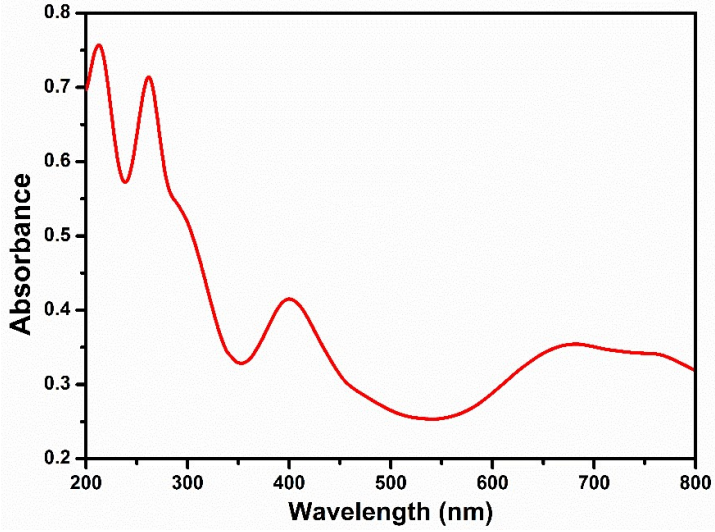
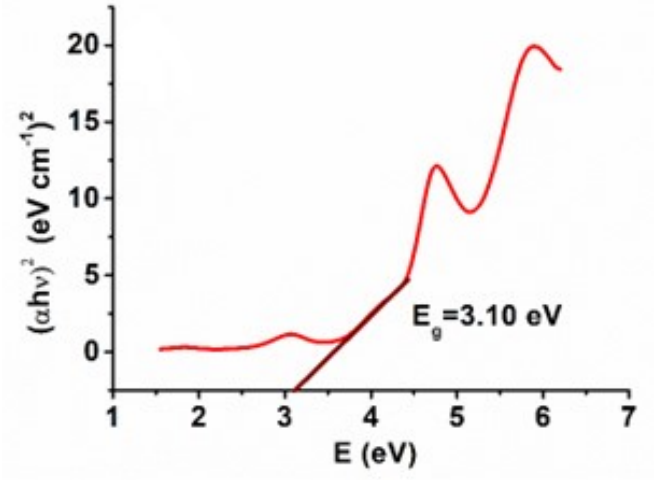
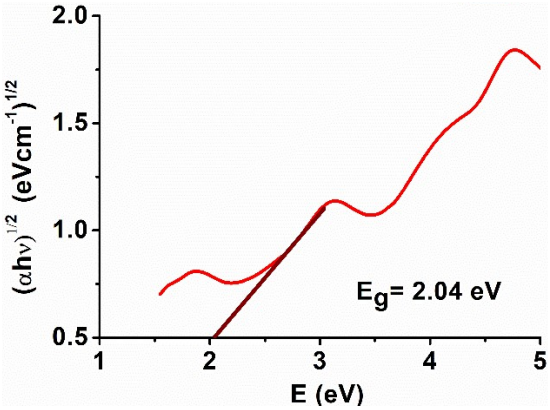



**Figure S27:** Solid-state UV-vis absorption spectrum of compound **4**.




**(a) Direct bandgap**




**(b) Indirect bandgap**

**Figure S28:** Tauc plot of compound **4**.

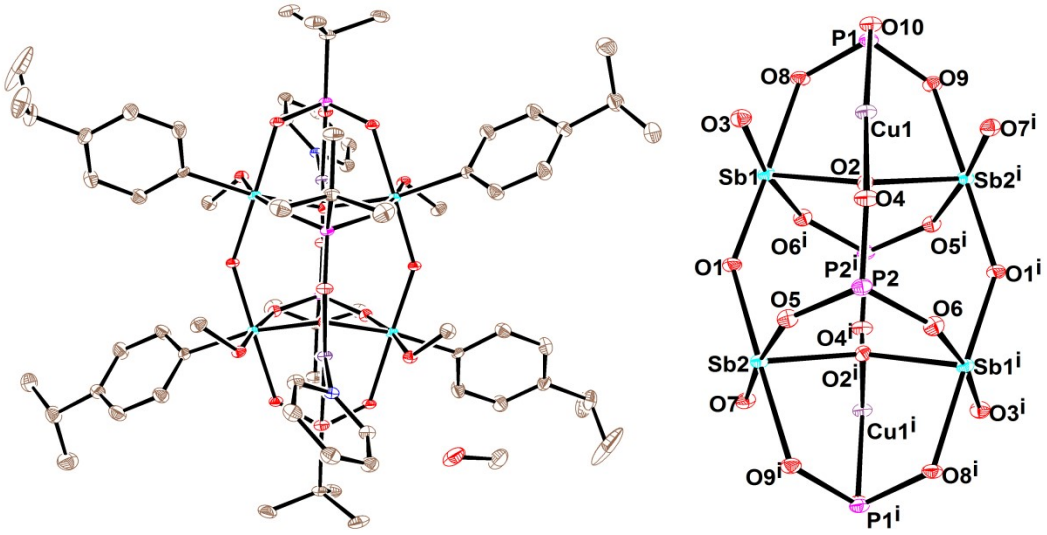



**Figure S29:** ORTEP view of **5** with thermal ellipsoids shown at 30% probability.

**Table S10:** Selected bond lengths (Å) and bond angles (deg) parameters of compound **5.**

| | | | | | |
|---|---|---|---|---|---|
| Sb1-O2 | 2.0074(19) | O3-Sb1-O8 | 84.55(8) | O4-Cu1-O3 | 99.63(8) |
| Sb1-O3 | 2.015(2) | O3-Sb1-O6$^{1}$ | 171.53(8) | O4-Cu1-O7$^{1}$ | 94.91(8) |
| Sb1-O1 | 1.915(2) | O1-Sb1-O2 | 94.80(8) | O4-Cu1-O10 | 175.12(8) |
| Sb1-O8 | 2.046(2) | O1-Sb1-O3 | 93.10(9) | O4-Cu1-N1 | 88.70(10) |
| Sb1-O6$^{1}$ | 2.016(2) | O1-Sb1-O8 | 177.63(9) | N1-Cu1-O2 | 176.02(9) |
| Sb2-O2$^{1}$ | 2.013(2) | O1-Sb1-O6$^{1}$ | 93.03(9) | N1-Cu1-O3 | 101.78(9) |
| Sb2-O9$^{1}$ | 2.043(2) | O6$^{1}$-Sb1-O8 | 89.34(9) | N1-Cu1-O7$^{1}$ | 109.94(9) |
| Sb2-O1 | 1.926(2) | O2$^{1}$-Sb2-O9$^{1}$ | 84.21(8) | O8-P1-O9 | 109.15(12) |
| Sb2-O7 | 1.998(2) | O1-Sb2-O2$^{1}$ | 95.64(8) | O10-P1-O9 | 112.38(12) |
| Sb2-O5 | 2.011(2) | O1-Sb2-O9$^{1}$ | 177.85(8) | O10-P1-O8 | 112.13(12) |
| Cu1-O2 | 2.076(2) | O1-Sb2-O7 | 92.71(8) | O5-P2-O6 | 110.10(12) |
| Cu1-O3 | 2.348(2) | O1-Sb2-O5 | 88.92(9) | O4-P2-O5 | 113.52(12) |
| Cu1-O7$^{1}$ | 2.326(2) | O7-Sb2-O2$^{1}$ | 82.51(8) | O4-P2-O6 | 113.14(13) |
| Cu1-O10 | 1.985(2) | O7-Sb2-O9$^{1}$ | 89.39(8) | Sb1-O2-Sb2$^{1}$ | 136.38(10) |
| Cu1-O4 | 1.940(2) | O7-Sb2-O5 | 173.52(8) | Sb1-O2-Cu1 | 105.12(9) |
| Cu1-N1 | 2.004(3) | O5-Sb2-O2$^{1}$ | 91.09(8) | Sb2$^{1}$-O2-Cu1 | 105.06(8) |
| P1-O9 | 1.549(2) | O5-Sb2-O9$^{1}$ | 88.94(8) | P1-O9-Sb2$^{1}$ | 123.54(12) |
| P1-O8 | 1.547(2) | O2-Cu1-O3 | 74.34(7) | Sb1-O3-Cu1 | 95.71(8) |
| P1-O10 | 1.509(2) | O2-Cu1-O7$^{1}$ | 73.60(7) | Sb1-O1-Sb2 | 145.46(12) |
| P2-O5 | 1.543(2) | O7$^{1}$-Cu1-O3 | 145.29(7) | P1-O8-Sb1 | 123.23(12) |
| P2-O4 | 1.506(2) | O10-Cu1-O2 | 91.20(8) | Sb2-O7-Cu1$^{1}$ | 96.99(8) |
| P2-O6 | 1.543(2) | O10-Cu1-O3 | 84.12(8) | P2-O5-Sb2 | 138.77(13) |

| | | | | | |
|---|---|---|---|---|---|
| O2-Sb1-O3 | 83.63(8) | O10-Cu1-O7[1] | 83.58(8) | P1-O10-Cu1 | 118.23(12) |
| O2-Sb1-O8 | 85.30(8) | O10-Cu1-N1 | 87.46(10) | P2-O4-Cu1 | 143.44(13) |
| O2-Sb1-O6[1] | 90.04(8) | O4-Cu1-O2 | 92.82(8) | P2-O6-Sb1[1] | 139.86(13) |

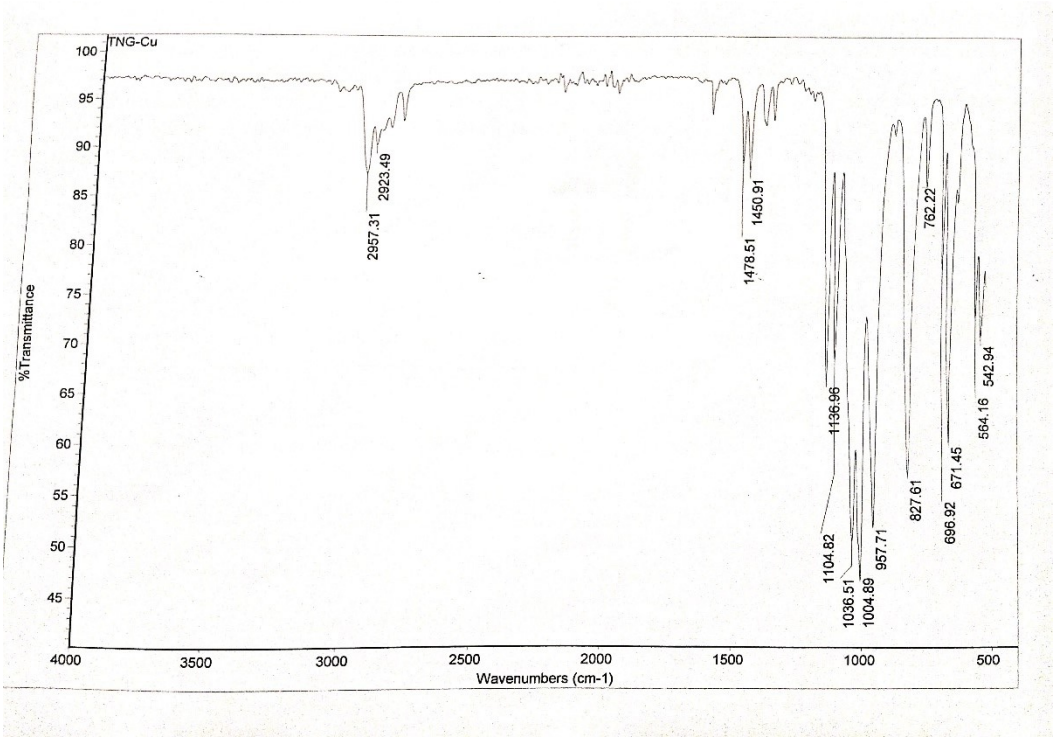



**Figure S30**: IR spectrum of compound **5**.

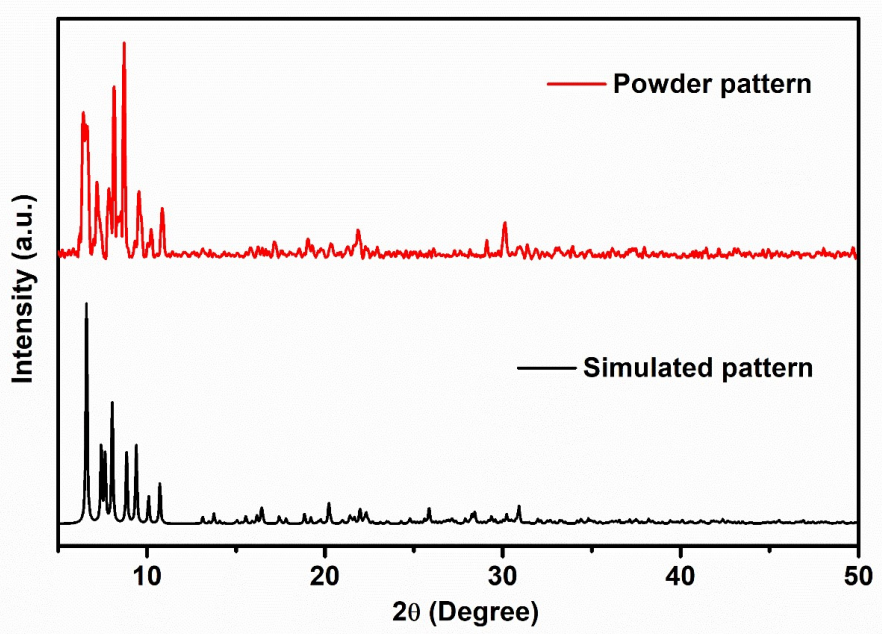



**Figure S31**: Powder X-ray diffraction pattern of a bulk sample of **5** compared to the simulated powder pattern extracted from single-crystal diffraction data.

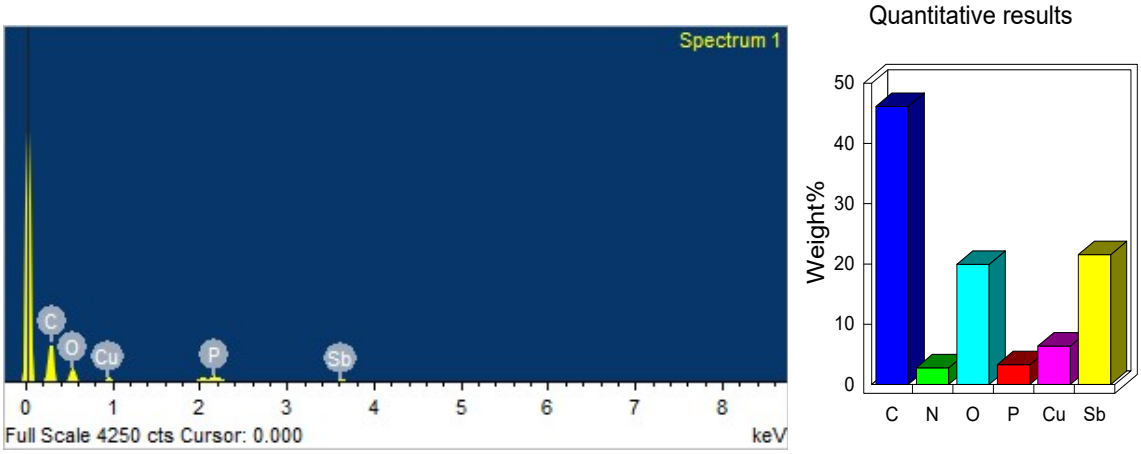



**Figure S32**: EDAX spectrum of compound **5**.

**Table S11:** EDAX analysis of **5**.

| Element | Calculated weight% | Measured weight% from EDAX analysis |
|---|---|---|
| C | 40.01 | 41.54 |
| N | 1.41 | 1.98 |
| O | 16.15 | 18.86 |
| P | 6.25 | 6.89 |
| Cu | 6.41 | 7.77 |
| Sb | 24.58 | 22.97 |
| H | 5.19 | Not detected |

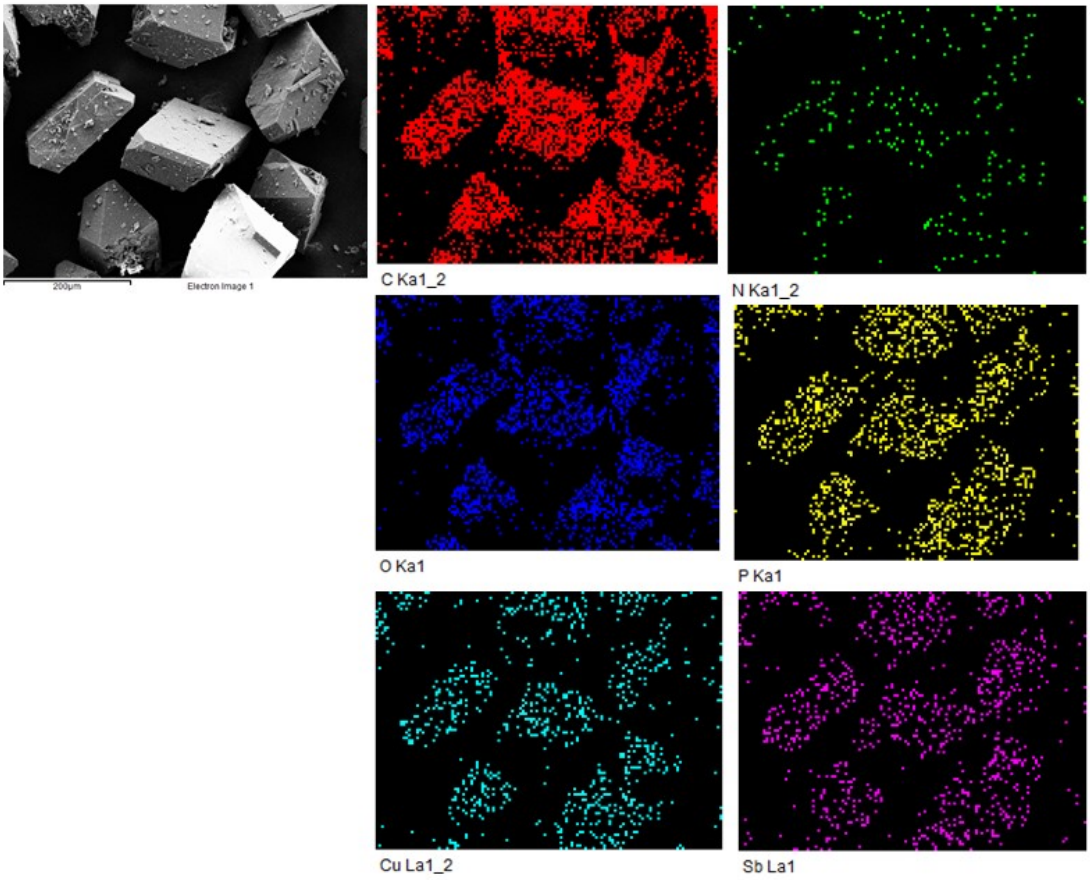



**Figure S33:** Elemental mapping of compound **5**.

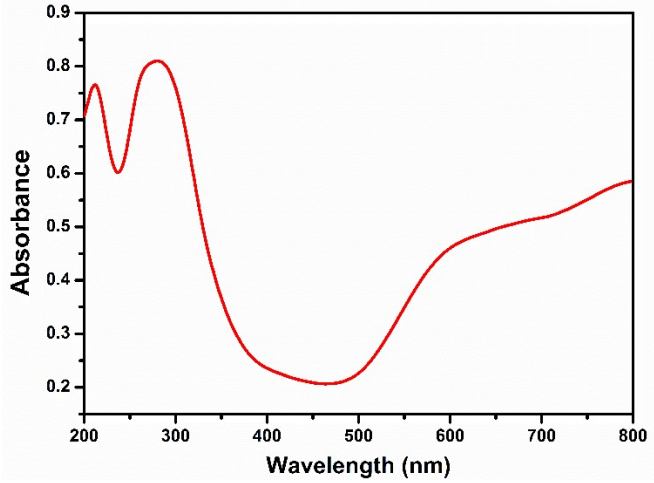
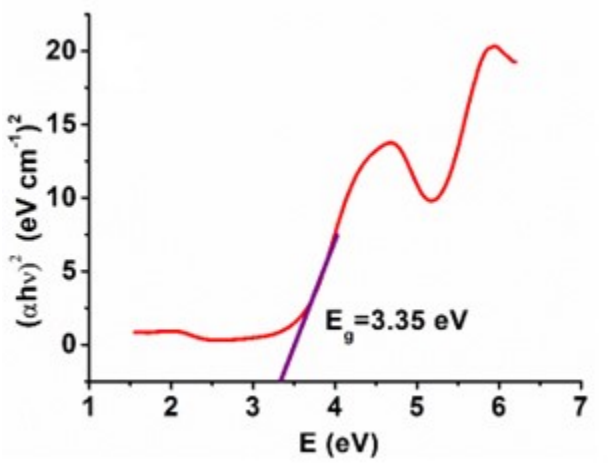
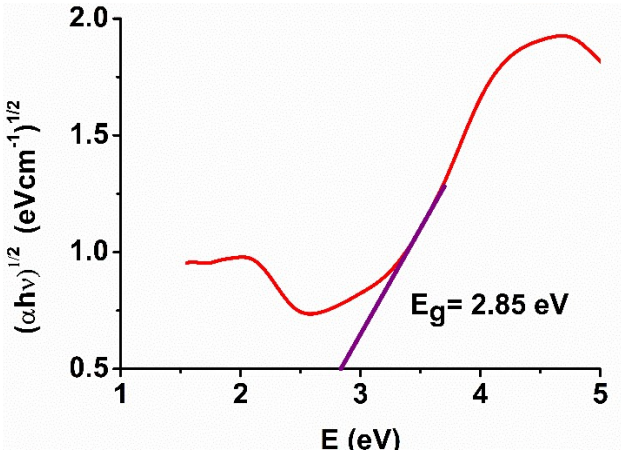



**Figure S34:** Solid-state UV-vis absorption spectrum of compound **5.**




**(a) Direct bandgap**




**(b) Indirect bandgap**

**Figure S35:** Tauc plot of compound **5**.

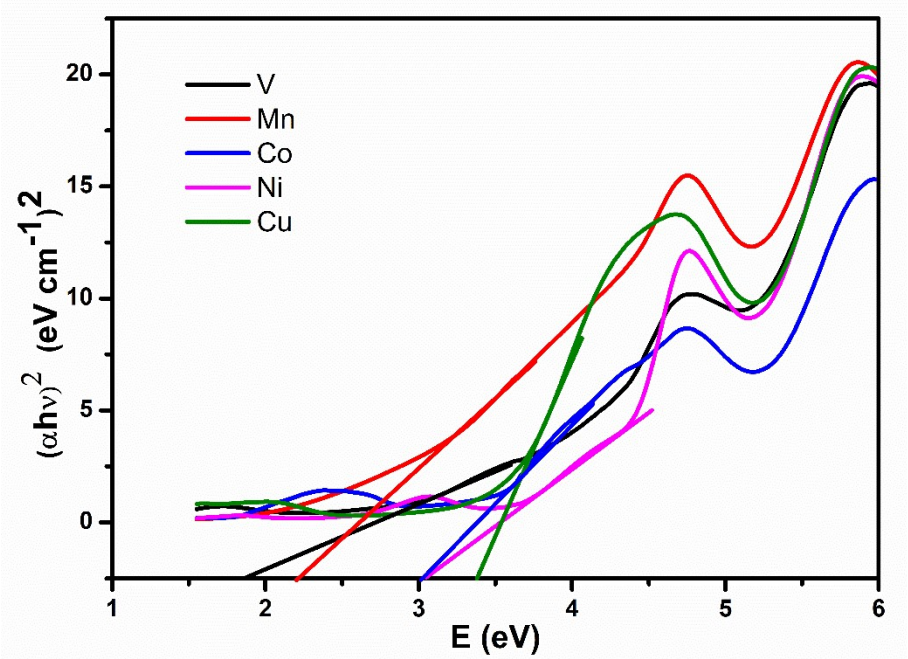



**Figure S36:** Tauc plots of compounds **1-5** (combined spectra). The direct bandgap ($E_g$) values are 1.83 eV for **1**, 2.25 eV for **2**, 3.02 eV for **3**, **3**.10 eV for **4**, and 3.35 eV for **5**.

**Table S12:** Shape calculation of compounds **1-5**.
**a)** Summary of SHAPE analysis for compounds **1-5** around metal ions:

| S.No | Geometry | CShM value for V1 | CShM value for Mn1 | CShM value for Co1 | CShM value for Ni1 | CShM value for Cu1 |
|---|---|---|---|---|---|---|
| **1** | Hexagon (D6h) | 34.395 | 34.710 | 34.342 | 33.692 | 34.010 |
| **2** | Pentagonal pyramid (C5v) | 23.097 | 21.247 | 21.876 | 22.046 | 22.472 |
| **3** | **Octahedron (Oh)** | **2.070** | **2.993** | **2.317** | **1.988** | **3.043** |
| **4** | Trigonal prism (D3h) | 12.110 | 11.258 | 11.348 | 11.167 | 10.521 |
| **5** | Johnson pentagonal pyramid J2 (C5v) | 27.043 | 25.050 | 25.80 | 25.994 | 26.240 |

**b)** Summary of **SHAPE** analysis for Sb1 in compound **1-5**:

| S.No | Geometry | CShM value for Sb1 in 1 | CShM value for Sb1 in 2 | CShM value for Sb1 in 3 | CShM value for Sb1 in 4 | CShM value for Sb1 in 4 |
|---|---|---|---|---|---|---|
| **1** | Hexagon (D6h) | 31.737 | 32.292 | 32.201 | 31.871 | 31.871 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **2** | Pentagonal pyramid (C5v) | 26.785 | 27.564 | 27.295 | 28.048 | 28.048 |
| **3** | **Octahedron (Oh)** | **0.636** | **0.332** | **0.396** | **0.284** | **0.284** |
| **4** | Trigonal prism (D3h) | 14.617 | 15.231 | 15.066 | 14.675 | 14.675 |
| **5** | Johnson pentagonal pyramid J2 (C5v) | 30.427 | 31.346 | 31.031 | 31.571 | 31.571 |

**Table S13:** Bond Valence Sum (BVS) calculations:

| Compound **1** | | | Compound **2** | | |
|---|---|---|---|---|---|
| **Metal Site** | **BVS** | **Assigned Oxidation state** | **Metal Site** | **BVS** | **Assigned Oxidation state** |
| V1 | 3.98 | 4 | Mn1 | 1.97 | 2 |

| Compound **3** | | | Compound **4** | | |
|---|---|---|---|---|---|
| **Metal Site** | **BVS** | **Assigned Oxidation state** | **Metal Site** | **BVS** | **Assigned Oxidation state** |
| Co1 | 2.03 | 2 | Ni1 | 2.05 | 2 |

| Compound **5** | | |
|---|---|---|
| **Metal Site** | **BVS** | **Assigned Oxidation state** |
| Cu1 | 1.99 | 2 |

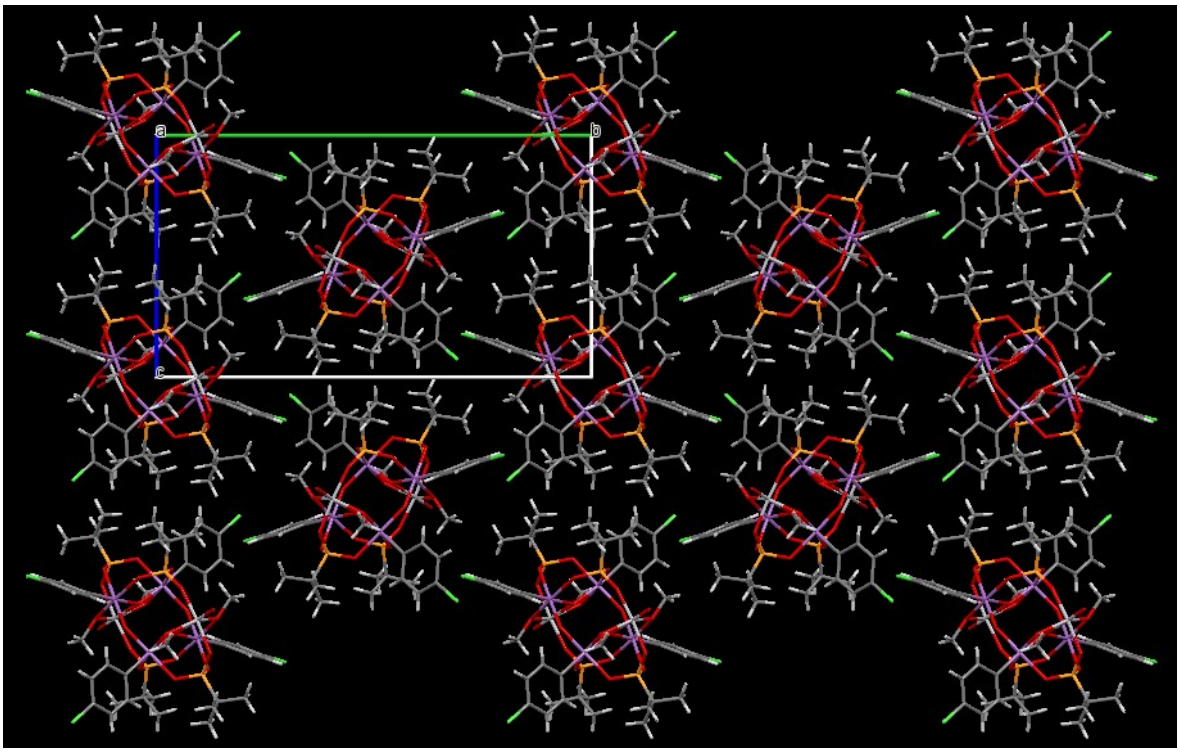


**Figure S37**: Packing diagram of compound **1** along a-axis

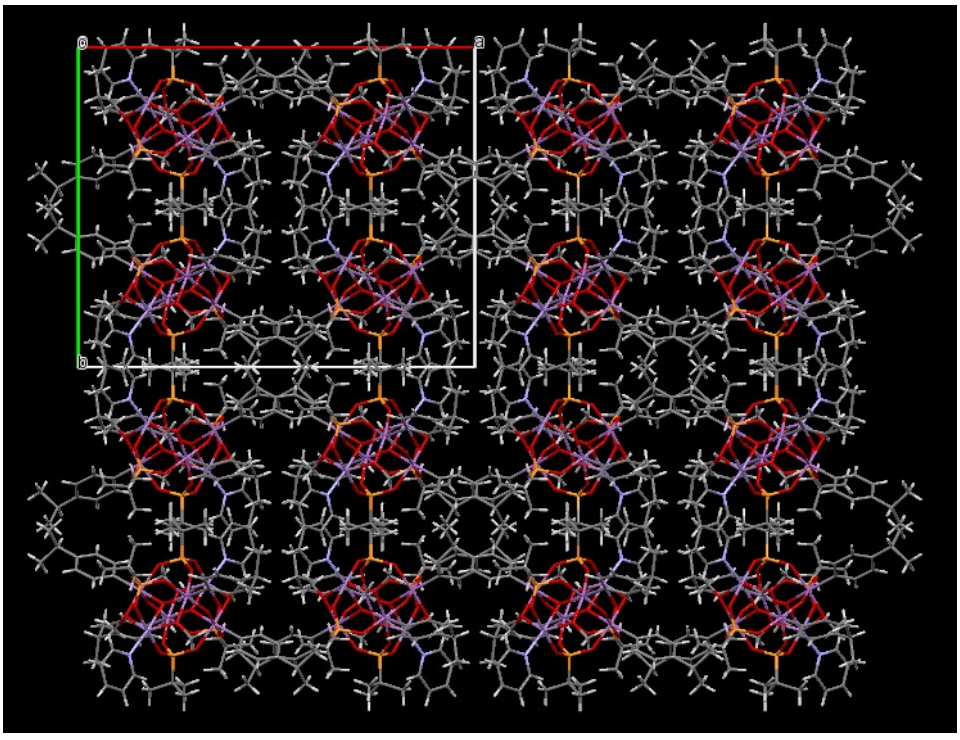


**Figure 38**: Packing diagram of compound **2** along the c-axis

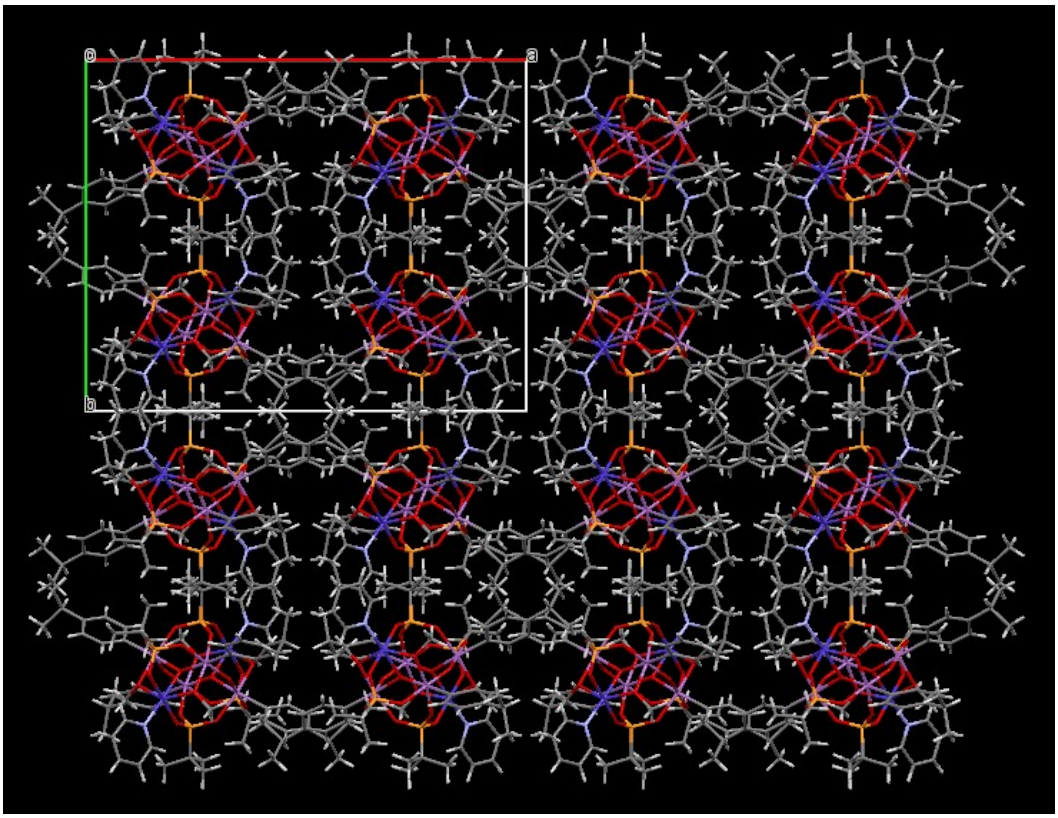


**Figure S39**: Packing diagram of compound **3** along the c-axis

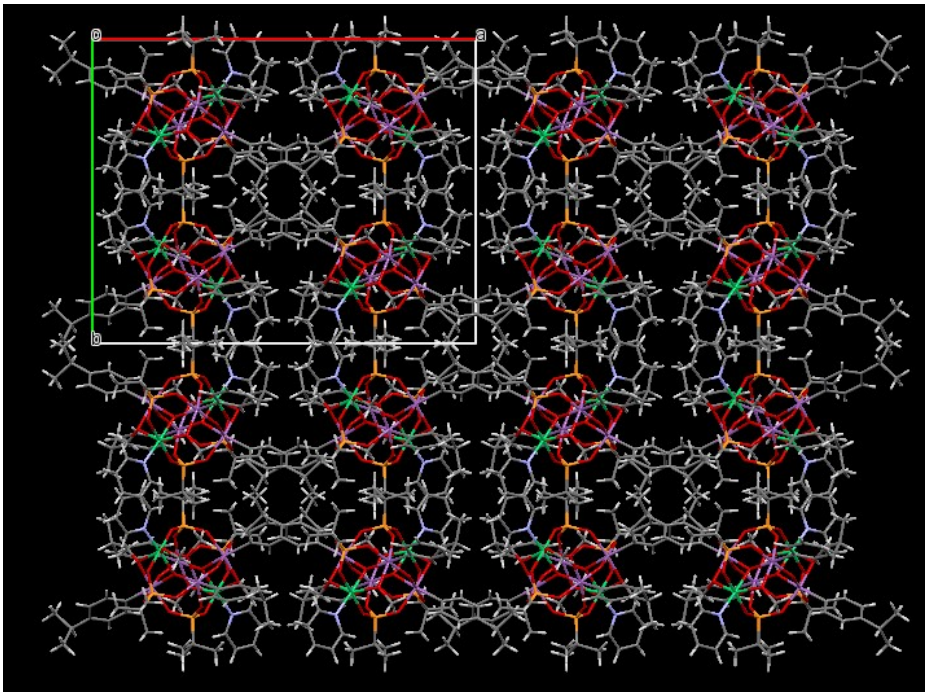


**Figure S40**: Packing diagram of compound **4** along the c-axis

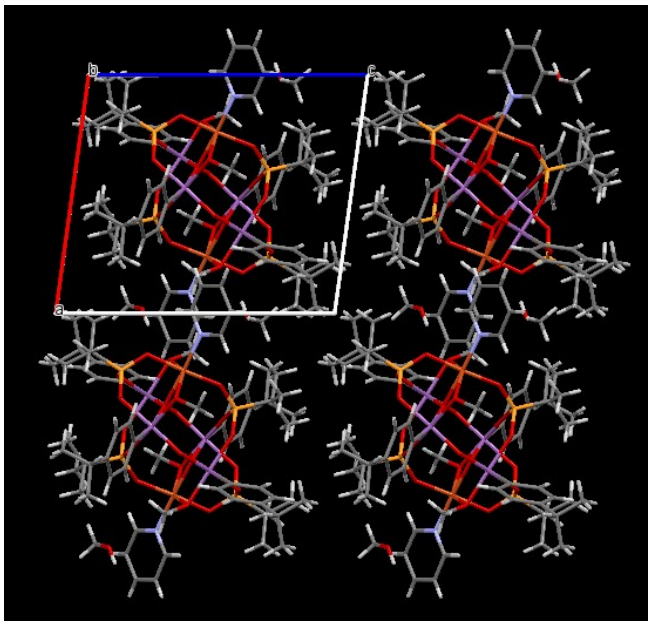


**Figure S41**: Packing diagram of compound **5** along b-axis

**Solvent treatment of compound 3:**
A solvent mask was calculated and 88 electrons were found in a volume of 740 $Å^3$ in 3 voids. This is consistent with the presence of 1[$CH_3OH$] per formula unit, which account for 72.0 electrons.