**Electronic Supporting Information (ESI)**

# Syntheses, XRD- and DFT studies on Pb[*Ch*CN]$_2$ (*Ch*=O, S, Se) and Pb[SeCN][OH]

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# 1. Further details on quantum mechanical calculations

**Table S1:** Calculated and experimental Raman frequencies and intensities of $Pb[SeCN]_2$, Pb[SeCN][OH], and $Pb[OCN]_2$.

| **$Pb[SeCN]_2$** | | | | **Pb[SeCN][OH]** | | | | **$Pb[OCN]_2$** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Symm** | **Calc. ν** | **Calc. I** | **Exp** | **Symm** | **Calc. ν** | **Calc. I** | **Exp** | **Symm** | **Calc. ν** | **Calc. I** | **Exp** |
| **B2g** | 27 | 84 | | Ag | 46 | 202 | | B1g | 31 | 280 | |
| **B1g** | 29 | 1 | | B3g | 48 | 125 | | B2g | 37 | 7 | |
| **Ag** | 34 | 630 | | B1g | 50 | 183 | | Ag | 59 | 143 | |
| **Ag** | 49 | 136 | | B2g | 59 | 983 | | Ag | 72 | 105 | |
| **B3g** | 54 | 1 | | B1g | 70 | 236 | | B3g | 77 | 48 | |
| **B3g** | 74 | 47 | | B2g | 74 | 357 | | B1g | 108 | 62 | |
| **Ag** | 81 | 198 | | Ag | 82 | 199 | | B3g | 109 | 29 | |
| **B1g** | 85 | 152 | | B3g | 83 | 0 | | Ag | 116 | 686 | |
| **B2g** | 86 | 421 | | Ag | 94 | 787 | 74 | B2g | 126 | 29 | |
| **B3g** | 89 | 93 | | B3g | 107 | 44 | | B1g | 139 | 10 | |
| **B1g** | 89 | 6 | | Ag | 113 | 1000 | 99 | B3g | 139 | 14 | |
| **B2g** | 95 | 5 | | B3g | 120 | 64 | | B2g | 141 | 14 | |
| **Ag** | 105 | 925 | 89 | B2g | 122 | 605 | | Ag | 144 | 1000 | 100 |
| **B3g** | 112 | 383 | | B1g | 122 | 330 | | B3g | 149 | 27 | |
| **Ag** | 116 | 679 | 132 | Ag | 149 | 856 | 129 | B3g | 154 | 67 | |
| **B3g** | 127 | 11 | | B3g | 158 | 48 | | B2g | 169 | 228 | 125 |
| **B1g** | 127 | 154 | | B3g | 279 | 12 | | Ag | 173 | 25 | |
| **B3g** | 130 | 205 | | Ag | 280 | 128 | 255 | B1g | 178 | 15 | |
| **Ag** | 132 | 318 | | B2g | 295 | 13 | | B3g | 181 | 77 | |
| **B2g** | 134 | 39 | | B1g | 296 | 33 | | Ag | 186 | 137 | |
| **Ag** | 160 | 324 | | Ag | 331 | 291 | 331 | Ag | 206 | 266 | 149 |
| **B2g** | 169 | 30 | | B3g | 333 | 2 | | B2g | 206 | 159 | |
| **B1g** | 173 | 437 | | B2g | 406 | 1 | | B3g | 215 | 94 | |
| **B3g** | 181 | 2 | | B1g | 408 | 4 | | B1g | 216 | 368 | 207 |
| **B3g** | 195 | 149 | | B3g | 416 | 1 | | Ag | 236 | 109 | |
| **Ag** | 204 | 258 | | Ag | 417 | 12 | 401 | B3g | 316 | 15 | |
| **B1g** | 396 | 8 | | B3g | 585 | 6 | | Ag | 638 | 40 | 611 |
| **B2g** | 398 | 0 | | Ag | 593 | 89 | 563 | B3g | 643 | 1 | |
| **B3g** | 407 | 3 | | B1g | 616 | 3 | | B2g | 644 | 1 | |
| **Ag** | 409 | 3 | | B2g | 617 | 24 | | B1g | 646 | 4 | |
| **Ag** | 415 | 40 | 405 | Ag | 735 | 29 | | B1g | 651 | 3 | |
| **B2g** | 416 | 0 | | B3g | 757 | 83 | 794 | Ag | 653 | 11 | 630 |
| **B1g** | 420 | 9 | | Ag | 2181 | 464 | 2095 | B2g | 654 | 5 | |
| **B3g** | 421 | 0 | | B3g | 2184 | 539 | | B3g | 656 | 0 | |
| **B3g** | 567 | 13 | | Ag | 3712 | 147 | 3531 | Ag | 1309 | 19 | |
| **Ag** | 567 | 68 | 557 | B3g | 3713 | 8 | 3677 | B3g | 1312 | 0 | |
| **B3g** | 616 | 5 | | | | | | B3g | 1328 | 69 | |
| **Ag** | 618 | 16 | | | | | | Ag | 1340 | 399 | 1319 |
| **Ag** | 2159 | 1000 | 2105 | | | | | Ag | 2191 | 96 | 2090 |
| **B3g** | 2169 | 1 | | | | | | B3g | 2210 | 83 | 2113 |
| **Ag** | 2224 | 394 | 2149 | | | | | Ag | 2230 | 269 | 2131 |
| **B3g** | 2224 | 182 | | | | | | B3g | 2308 | 0 | |

**Table S2:** Calculated and experimental Raman properties of $Pb[SCN]_2$.

| | **$Pb[SCN]_2$** | | |
|---|---|---|---|
| **Symm** | **Calc. ν** | **Calc. I** | **Exp** |
| Bg | 31 | 195 | |
| Ag | 48 | 350 | |
| Bg | 87 | 291 | **76** |
| Ag | 93 | 265 | |
| Bg | 96 | 430 | |
| Bg | 114 | 500 | **104** |
| Ag | 126 | 180 | |
| Bg | 142 | 319 | |
| Ag | 158 | 712 | |
| Ag | 165 | 1000 | **156** |
| Bg | 167 | 26 | |
| Bg | 190 | 202 | |
| Ag | 209 | 410 | |
| Bg | 475 | 3 | |
| Ag | 489 | 4 | |
| Ag | 491 | 15 | **480** |
| Bg | 493 | 9 | |
| Ag | 783 | 97 | **759** |
| Bg | 785 | 9 | |
| Ag | 2107 | 730 | **2034** |
| Bg | 2109 | 600 | |

## 2. Collected Raman spectra

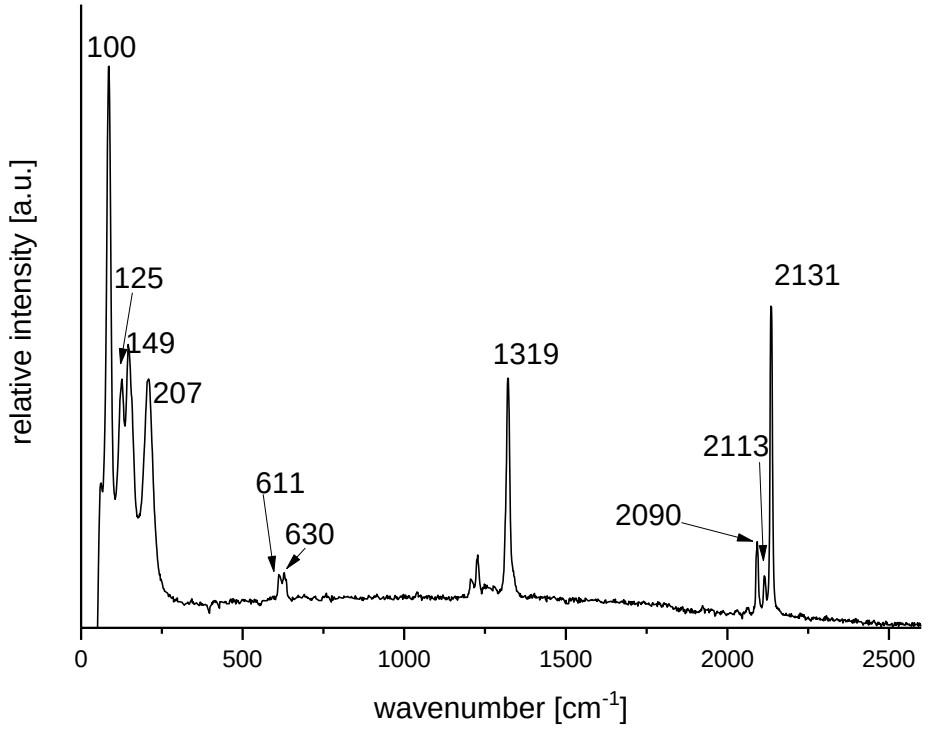


**Figure S1:** Raman spectrum of $Pb[OCN]_2$ collected on microcrystalline powder with 633 nm laser at room temperature.

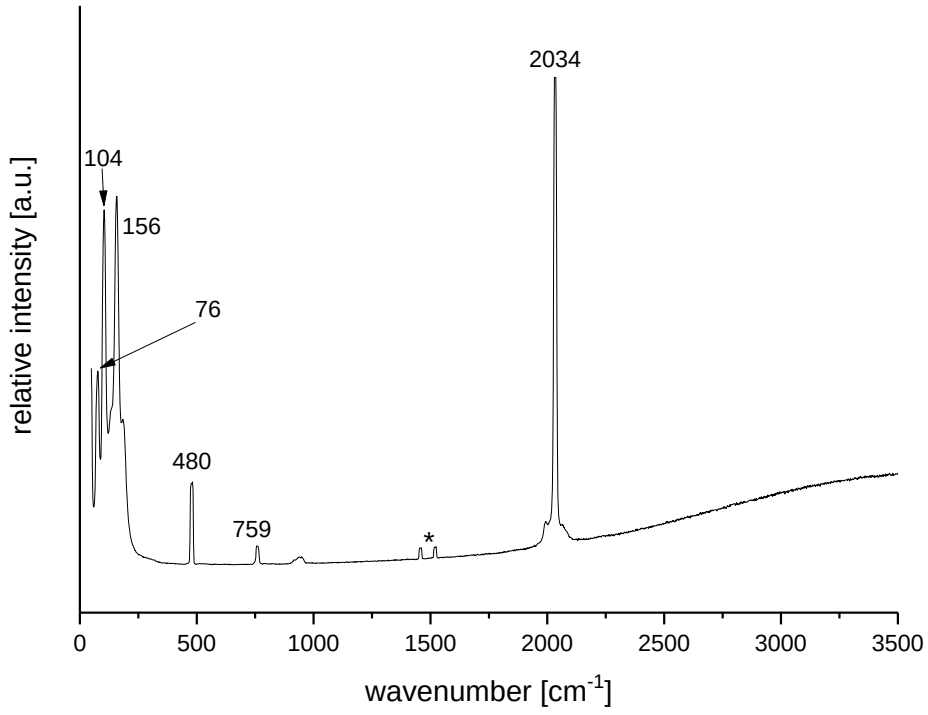


**Figure S2:** Raman spectrum of $Pb[SCN]_2$ collected on microcrystalline powder with 532 nm laser at room temperature. *: satellites caused by equipment construction.

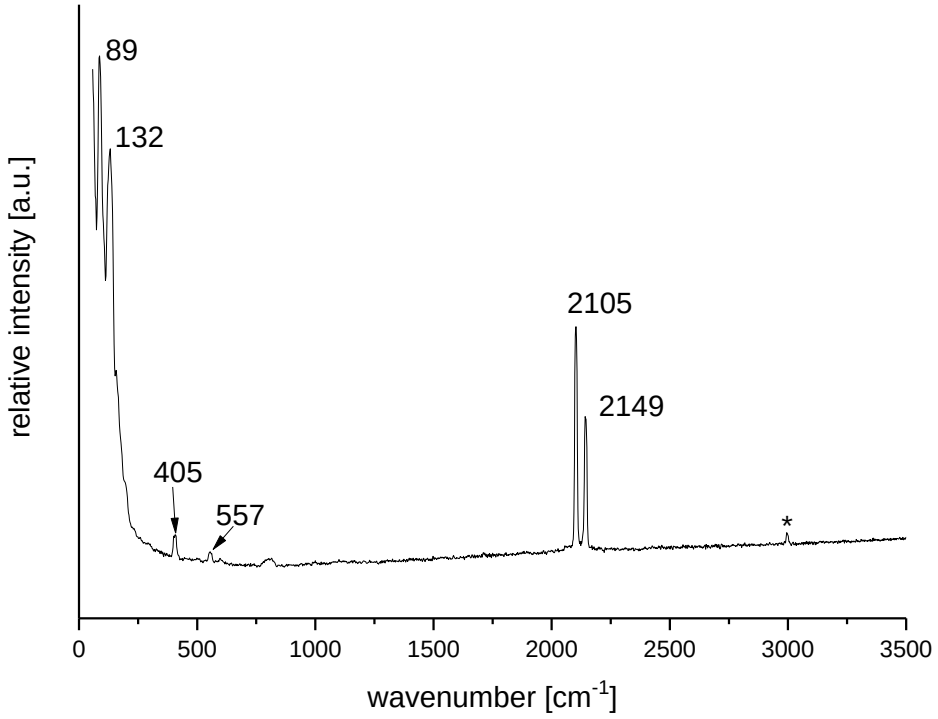


**Figure S3:** Raman spectrum of $Pb[SeCN]_2$ collected on single crystal with 532 nm laser at room temperature. *: impurity of Pb[SeCN][OH].

## 3. Additional crystallographic details

**Table S3:** Selected powder X-ray diffraction data collection and refinement parameters for Pb[*Ch*CN]$_2$ (*Ch*=O, Se), and Pb[SeCN][OH].

| | Pb[OCN]$_2$[a, b] | Pb[SeCN]$_2$[a, b] | Pb[SeCN][OH][a, c] |
|---|---|---|---|
| Formula | C2 N2 O2 Pb | C2 N2 Se2 Pb | C H N Se Pb |
| Fw / g mol$^{-1}$ | 123.02 | 212.85 | 335.87 |
| Crystal system | orthorhombic | orthorhombic | orthorhombic |
| Space group | *Pnma* (№ 62) | *Pnma* (№ 62) | *Pnma* (№ 62) |
| *a* / Å | 8.62373(15) | 12.6574(5) | 8.66931(11) |
| *b* / Å | 3.98198(6) | 4.30312(13) | 4.19306(2) |
| *c* / Å | 11.72148(18) | 10.8393(3) | 11.65257(8) |
| *V* / Å$^3$ | 402.509(11) | 90.38(3) | 423.582(6) |
| *Z* | 4 | 4 | 4 |
| Radiation, λ / Å | 1.54175 | 1.54175 | 1.54175 |
| T / K | 298(2) | 298(2) | 298(2) |
| $R_{wp}$ / % | 7.51684316 | 12.1849025 | 10.1929528 |
| $R_p$ / % | 5.53611169 | 8.92969863 | 7.6677716 |
| $R_{Bragg}$ / % | 5.09365506 | 4.4688295 | 5.9381605 |
| GoF | 1.35427749 | 1.02617433 | 1.09911186 |
| Starting angle measured / ° 2θ | 5 | 5 | 5 |
| Final angle measured / ° 2θ | 90 | 90 | 90 |
| Starting angle refined /° 2θ | 10 | 10 | 10 |
| Final angle refined / ° 2θ | 70 | 70 | 85 |
| Step width/ ° 2θ | 0.015 | 0.015 | 0.015 |
| Refined Parameters | 39 | 51 | 54 |
| Background Parameters | 12 | 23 | 18 |
| Profile Parameters | 14[b] | 10[b] | 24[c] |

**[a]:** The starting model derived from single crystal X-ray data was used as starting point. [OCN]$^-$, [SeCN]$^-$ and [OH]$^-$ anions were modelled as rigid bodies. Thermal expansion parameters for C and N were constrained to the same value. **[b]:** Profile parameters include preferred orientation refinement with spherical harmonics order 4. **[c]:** Profile parameters include preferred orientation refinement with spherical harmonics order 8.

**Table S4:** Selected single crystal X-ray data collection and refinement parameters for Pb[*Ch*CN]$_2$ (*Ch*=O, S, Se), and Pb[SeCN][OH].

| | Pb[OCN]$_2$ | Pb[SCN]$_2$ | Pb[SeCN]$_2$ | Pb[SeCN][OH] |
|---|---|---|---|---|
| Formula | $C_2N_2O_2Pb$ | $C_2N_2PbS_2$ | $C_2N_2PbSe_2$ | C H N O Pb Se |
| CCDC | 2383820 | 2383821 | 2383822 | 2383823 |
| Fw / g mol$^{-1}$ | 291.23 | 323.35 | 417.15 | 329.18 |
| Crystal system | orthorhombic | monoclinic | orthorhombic | orthorhombic |
| Space group | *Pnma* | *C*2/*c* | *Pnma* | *Pnma* |
| *a* / Å | 8.5689(18) | 9.6128(9) | 12.479(2) | 8.6244(2) |
| *b* / Å | 3.9410(9) | 6.5306(6) | 4.2277(9) | 4.1674(4) |
| *c* / Å | 16.660(3) | 8.1913(7) | 10.6523(17) | 11.5412(6) |
| *β* / ° | — | 92.734(7) | — | — |
| *V* / Å$^3$ | 393.74(17) | 513.64(8) | 562.00(17) | 414.81(5) |
| *Z* | 4 | 4 | 4 | 4 |
| Radiation, λ / Å | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Temp / K | 100 | 100 | 100 | 180.15 |
| $\rho_{calc}$ / g cm$^{-3}$ | 4.913 | 4.181 | 4.930 | 5.271 |
| μ / mm$^{-1}$ | 42.695 | 33.507 | 42.835 | 49.251 |
| Reflections collected | 6464 | 5951 | 12950 | 11581 |
| Ind. Reflns. / Ind. Reflns gt | 760 / 517 | 786 / 763 | 912/ 850 | 800 / 719 |
| Parameters | 43 | 34 | 43 | 35 |
| $R_{int}$ / $R_{(\sigma)}$ | 0.0993 / 0.0643 | 0.0165 / 0.0084 | 0.0855 / 0.0269 | 0.0473 / 0.0203 |
| *R*1/*wR*2,[a] $I \geq 2\sigma I$ (%) | 0.0415 / 0.0931 | 0.0124 / 0.0303 | 0.0377 / 0.0935 | 0.0232 / 0.0551 |
| *R*1/*wR*2,[a] all data (%) | 0.0641 / 0.0970 | 0.0130 / 0.0304 | 0.0397 / 0.0948 | 0.0268 / 0.0555 |
| GOF | 0.89980 | 1.16785 | 1.142 | 1.08358 |
| Twin law | — | — | — | — |
| BASF | — | — | — | — |
| Flack parameter | — | — | — | — |

[a] $R1 = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$; $wR2 = \{[\Sigma w[(F_o)^2 - (F_c)^2]^2]/[\Sigma w(F_o^2)^2\}^{1/2}$; $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.0610 and 0 for Pb[OCN]$_2$; 0.0219 and 0 for Pb[SCN]$_2$; 0.0387 and 0 for Pb[SeCN][OH]; 0.0684 and 0 Pb[SeCN]$_2$.

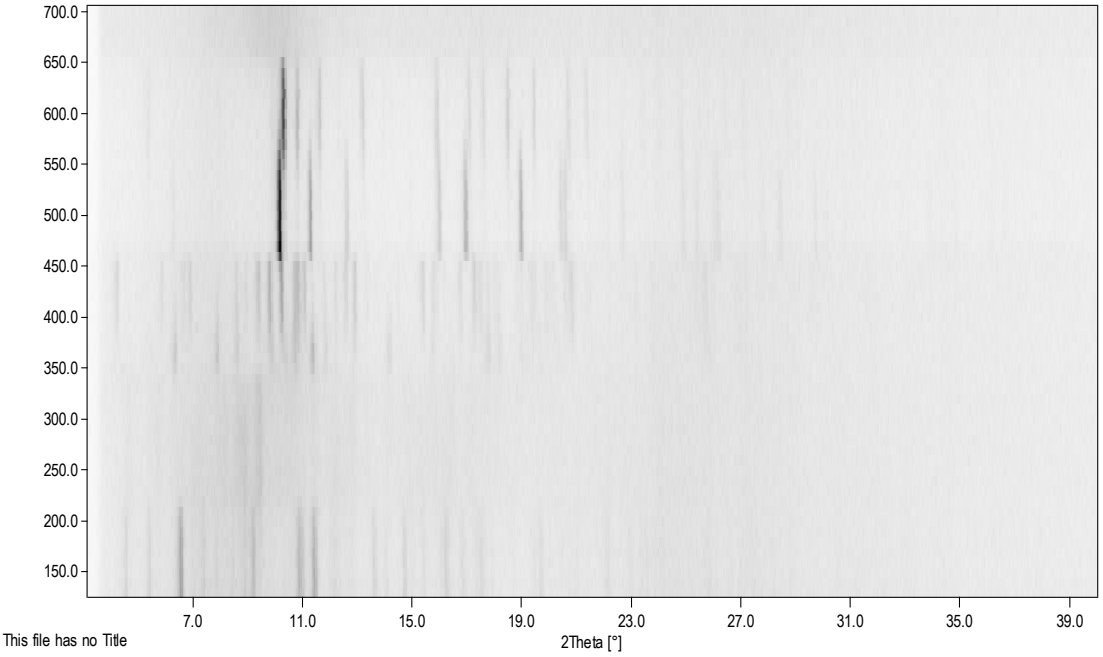


**Figure S4:** Temperature depended powder X-ray diffraction of $Pb[OCN]_2$.

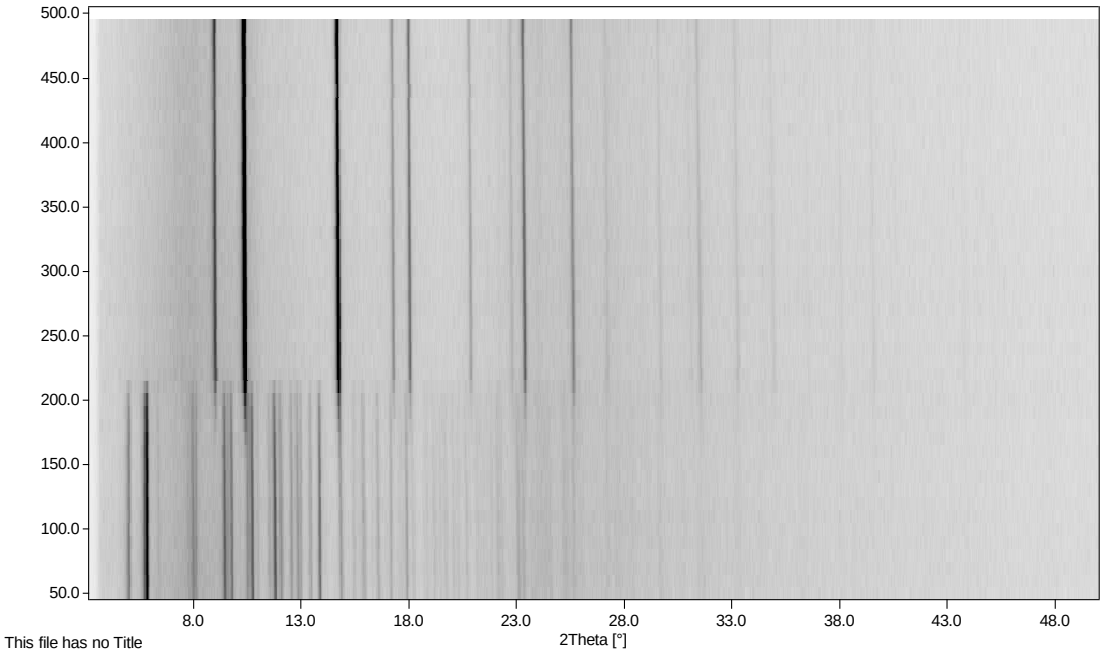


**Figure S5:** Temperature depended powder X-ray diffraction of $Pb[SeCN]_2$.

## 4. UV-Vis spectroscopic data

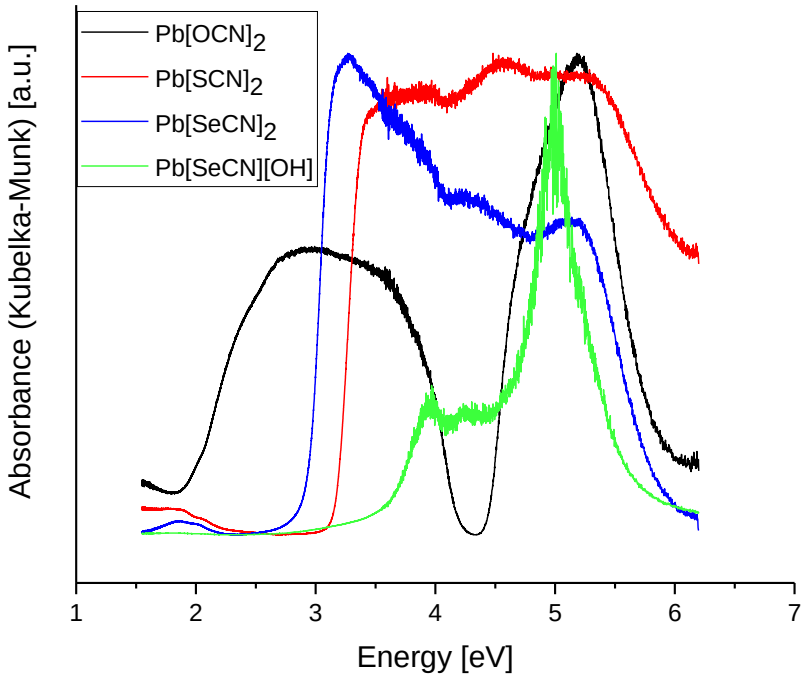


**Figure S6:** Kubelka-Munk plots of $Pb[OCN]_2$, $Pb[SCN]_2$, $Pb[SeCN]_2$ and Pb[SeCN][OH].