Supplementary Information for:

Structural complexity in indium selenides prepared using bicyclic amines as structure-directing agents

Sarah J. Ewing[a] *and Paz Vaqueiro*[a,b*]

[a]Institute of Chemical Sciences, Heriot Watt University, Edinburgh, EH14 4AS, UK.

[b]Present Address: Department of Chemistry, University of Reading, Whiteknights, Reading, RG6 6AD.

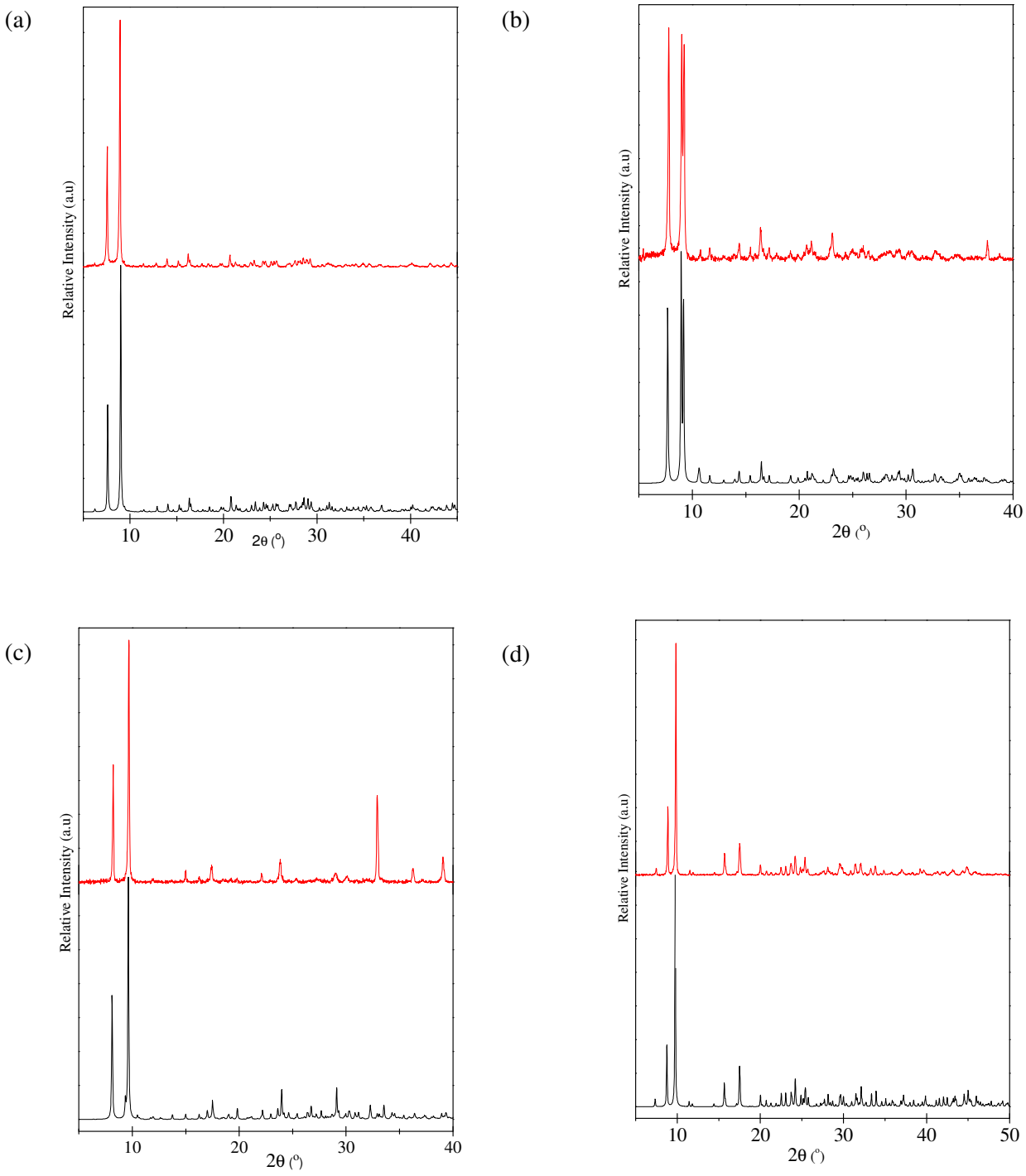

Figure S1. Experimental powder X-ray diffraction pattern (red) for the bulk product of the reaction producing (a) **1**, (b) **2**, (c) **3** and (d) **4.** The pattern calculated using the structure determined by single crystal X-ray diffraction is shown in black.

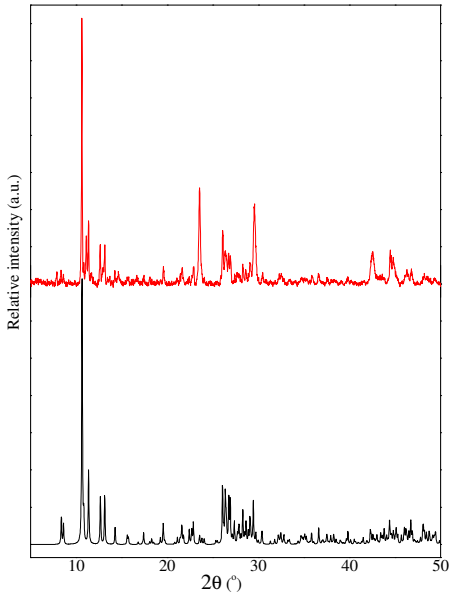

Figure S2. Experimental powder X-ray diffraction pattern (red) for the bulk product of the reaction producing **5**. The pattern calculated using the structure determined by single crystal X-ray diffraction is shown in black.

Table S1: Lattice parameters determined using powder X-ray diffraction data for compounds **1** to **5**.

Compound	**1**	**2**	**3**	**4**	**5**
a (Å)	11.115(8)	10.99(1)	34.60(8)	15.257(6)	10.279(3)
b (Å)	23.26(2)	12.98(2)	21.571(6)	20.352(6)	13.425(4)
c (Å)	18.23(1)	18.18(2)	10.70(8)	12.280(3)	10.590
α (°)	-	105.63(9)	-	-	
β (°)	101.60(3)	99.81(8)	91.45(2)	98.63(2)	96.08(2)
γ (°)	-	109.77(6)	-	-	

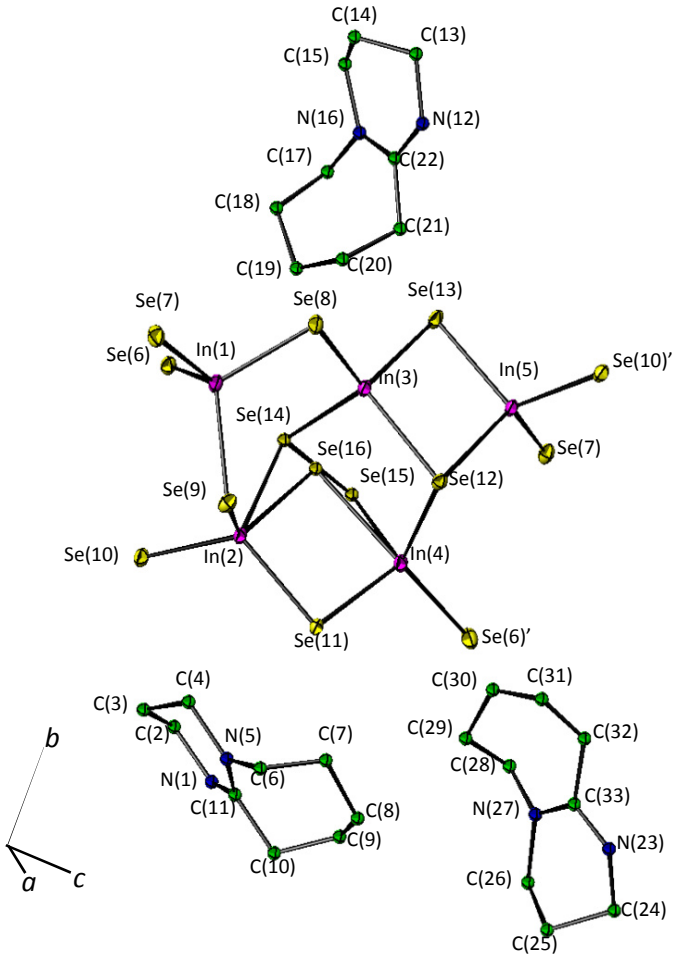

Figure S3. Local coordination diagram of non-hydrogen atoms for $[C_9H_{17}N_2]_3[In_5Se_{8.07}(Se_2)_{0.93}]$ (**1**) showing the atom labelling scheme and ellipsoids at 50% probability.

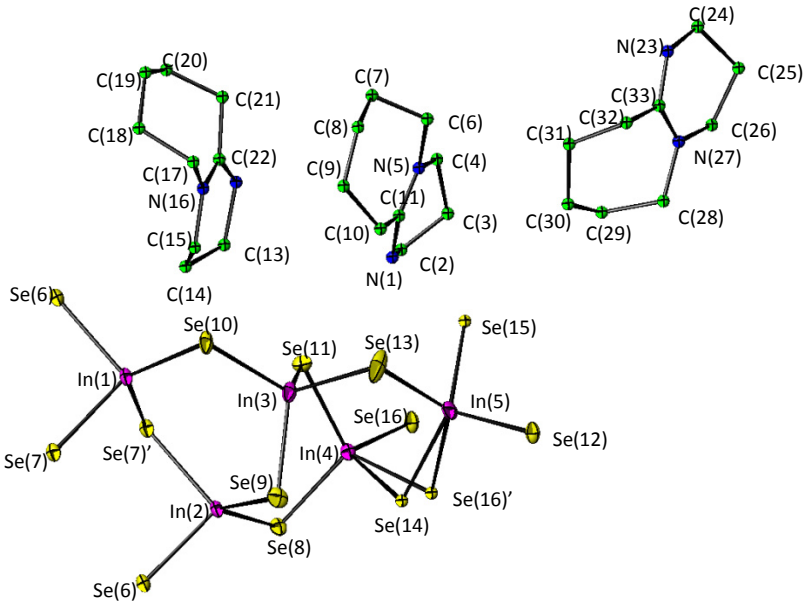

Figure S4. Local coordination diagram of non-hydrogen atoms for $[C_9H_{17}N_2]_3[In_5Se_{8.74}(Se_2)_{0.26}]$ (**2**) showing the atom labelling scheme and ellipsoids at 50% probability.

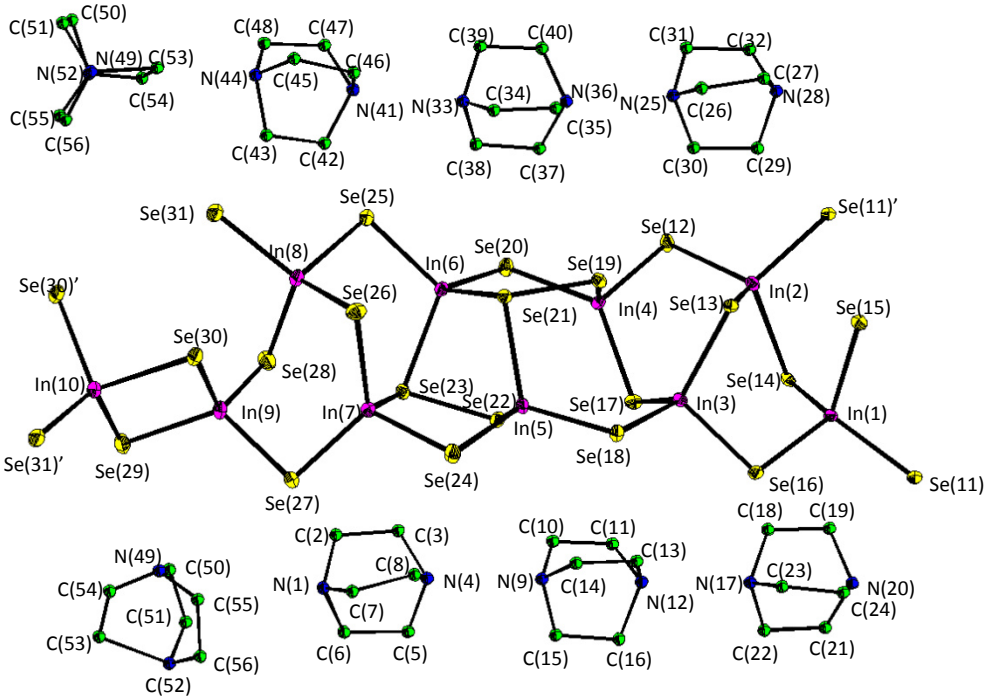

Figure S5. Local coordination diagram of non-hydrogen atoms for $[C_6H_{12}N_2]_4[C_6H_{14}N_2]_3[In_{10}Se_{15}(Se_2)_3]$ (**3**) showing the atom labelling scheme and ellipsoids at 50% probability.

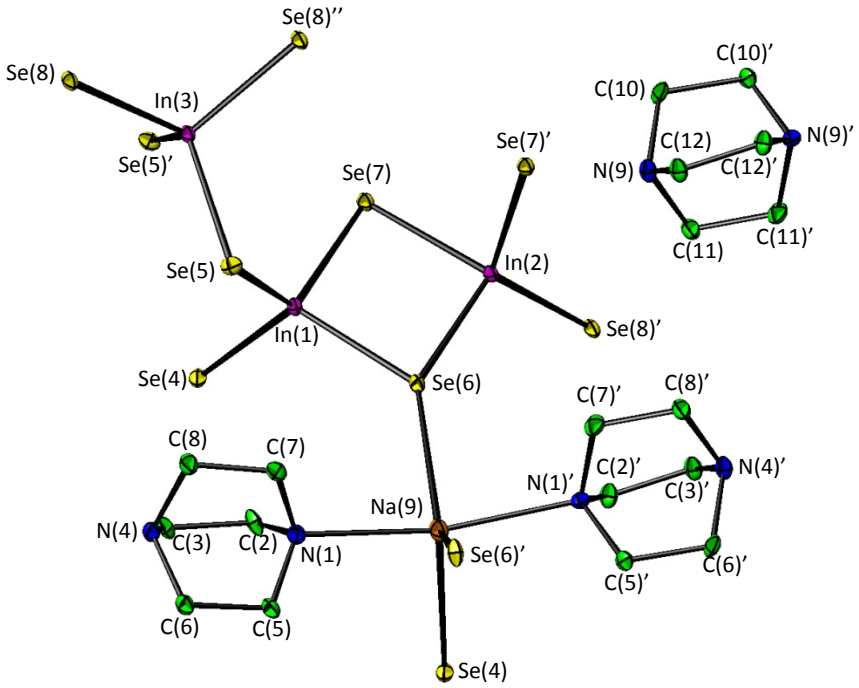

Figure S6. Local coordination diagram of non-hydrogen atoms for $[C_6H_{14}N_2][(C_6H_{12}N_2)_2NaIn_5Se_9]$ (**4**) showing the atom labelling scheme and ellipsoids at 50% probability

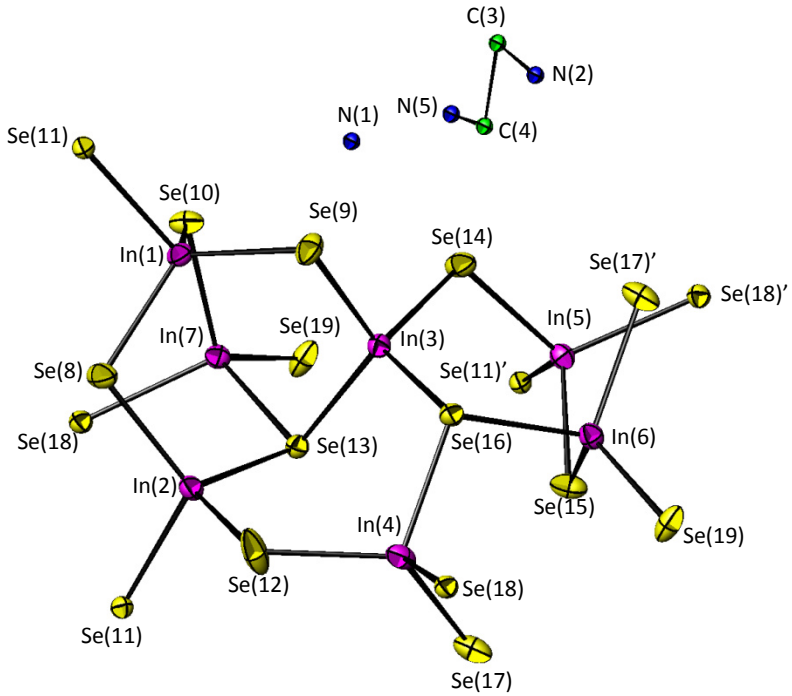

Figure S7. Local coordination diagram of non-hydrogen atoms for $[enH_2][NH_4][In_7Se_{12}]$ (**5**) showing the atom labelling scheme and ellipsoids at 50% probability

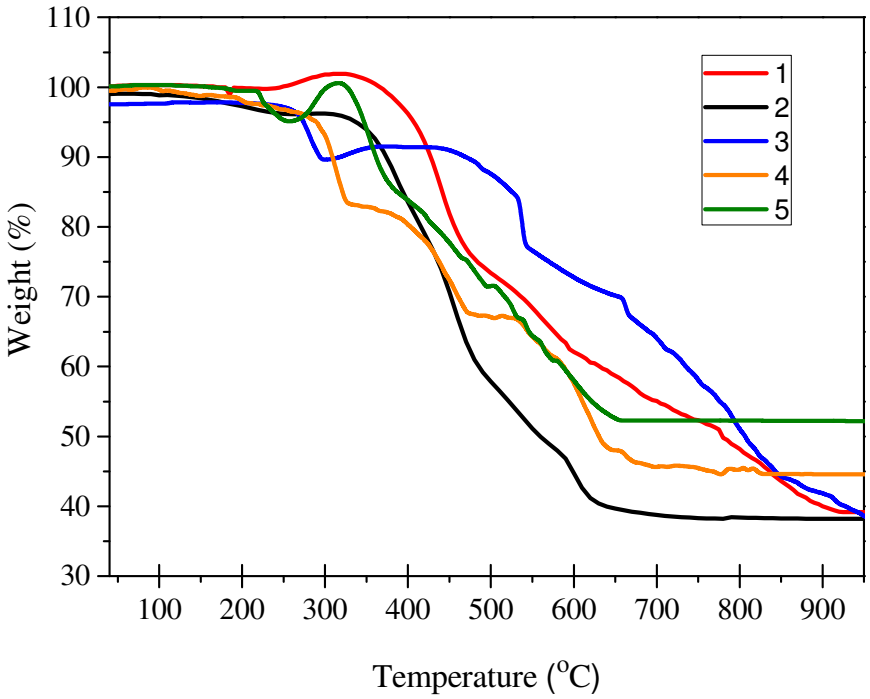

Figure S8. Thermogravimetric data, collected under a flowing O_2 atmosphere, for compounds **1-5.**

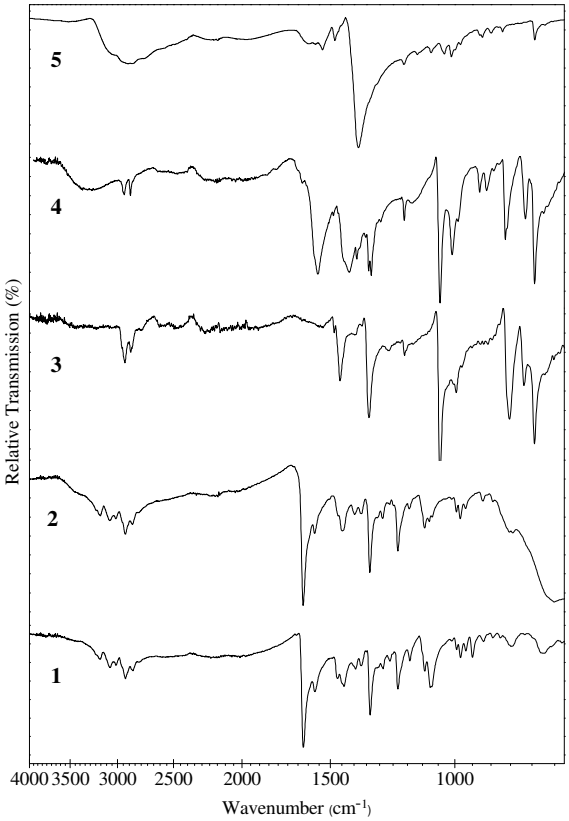

Figure S9. FT-IR data for compounds **1-5.**

Synthesis of previously reported $[In_{10}Se_{18}]^{6-}$ and $[In_{33}Se_{56}]^{13-}$: Crystals of $[In_{10}Se_{18}]^{6-}$ were obtained from a mixture of In:Se:DABCO on a 1.46:3:6 molar ratio, using 3 mL of deionised water as solvent. The reaction mixture was heated at 185°C for 10 days in a 23 mL autoclave. $[In_{33}Se_{56}]^{13-}$ was obtained from a mixture of In:Se:DABCO with a molar ratio of 0.365:0.75:2, using 1mL of deionised water as solvent. This mixture was heated at 170°C for 10 days in a 23 mL autoclave. Lattice parameters determined by single-crystal X-ray diffraction, which are given in Table S2, are in good agreement with the previously reported values.[1]

Table S2: Lattice parameters determined for the $[In_{10}Se_{18}]^{6-}$ and $[In_{33}Se_{56}]^{13-}$ frameworks.

Compound	$[In_{10}Se_{18}]^{6-}$	$[In_{33}Se_{56}]^{13-}$
Space group	$I\,4_1/acd$	$R32$
Crystal system	Tetragonal	Trigonal
a (Å)	20.8153(16)	22.3302(13)
c (Å)	33.130(3)	34.6223(19)

[1] (a) Wang, C.; Bu, X.; Zheng, N.; Feng, P. *Chem. Commun.*, **2002**, 1344-1345; (b) Wang, C.; Bu, X.; Zheng, N.; Feng, P.; *Angew. Chem. Int. Ed*, **2002**, 41, 1959-1961.