

## Supplementary Information for

### Indium tris-guanidinate: A promising class of precursors for water assisted atomic layer deposition of $\text{In}_2\text{O}_3$ thin films

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#### Experimental Details

All the compounds were synthesized using standard Schlenk techniques due their sensitivity towards oxygen and moisture.  $\text{InCl}_3$  (Alfa Aesar, 99.999% metals basis) and  $\text{LiN}(\text{CH}_3)_2$  (Sigma-Aldrich, 99.99%) were used without further purification. Handling of all the compounds was carried out under inert gas atmosphere (Argon) in a glove box (MBraun, Labmaster 100). The solvents ( $\text{Et}_2\text{O}$ , *n*-hexane) were purified by a solvent purification system (MBraun SPS). Deuterated solvents ( $d_6$ -benzene,  $d_8$ -toluene) for NMR-measurements were degassed by repeated freezing in liquid nitrogen and subsequent evaporation of the overlaying gas phase. All the solvents were stored over activated molecular sieves (4 Å). The NMR-spectra were recorded on a Bruker Advance 250 instrument and referenced to internal solvent proton signals. The spectra were corrected to the TMS (tetramethylsilane) standard value. For both compounds, temperature dependent NMR-experiments were carried out at -30, 30, 100, 120 and 140 °C in heavy walled NMR tubes (Norrell, Pyrex glas; wall thickness: 1.4 mm; inner diameter: 2.20 mm). Cooling and heating of each sample was performed in one session. NMR decomposition studies were carried out for both the compounds where highly concentrated solutions of each compound in  $d_8$ -toluene, sealed in heavy walled NMR tubes were heated in an oven at two different temperatures (125 and 160 °C). Prior, to this a reference spectrum at room temperature was recorded for each tube. In between the heat treatments, the tubes were cooled to room temperature and  $^1\text{H}$ -NMR spectra were measured. As reference the integral of the deuterated solvent multiplet was taken. Thermogravimetric (TG) and isothermal TG studies were carried out on a Seiko 6 TG/DTA 3200 under ambient pressure ( $\text{N}_2$  flow rate: 300 ml  $\text{min}^{-1}$ ). In the case of TG studies a heating rate of 5 K  $\text{min}^{-1}$  was applied and 10 mg of the compound was used. Single crystal X-ray analysis was carried out on an Oxford Excalibur diffractometer. The structures were solved by direct methods using SHELXS-97 and refined against  $F^2$  on all data by full-matrix least-squares with SHELXL-97.<sup>1</sup> The crystallographic data and structure refinement parents are listed in Tables 1 and 2 (ESI) for compounds **1** and **2** respectively.

#### Synthesis of compound 1, $[\text{In}\{(\text{PrN})_2\text{CN}(\text{CH}_2\text{CH}_3)_2\}_3]$

25 ml (1.6 M, 0.04 mol) of *n*-Butyllithium was added drop wise to a solution of 4.15 ml  $\text{HN}(\text{CH}_2\text{CH}_3)_2$  in 50 ml  $\text{Et}_2\text{O}$  at -78 °C. After two hours of stirring, 6.2 ml (0.04 mol) *N,N'*-Diisopropylcarbodiimide was added under stirring at -78 °C. The mixture became clear after one minute of stirring leading to the formation of lithium guanidinate. After 12 hours stirring, a solution of 2.94 g (0.013 mol)  $\text{InCl}_3$  in 50 ml  $\text{Et}_2\text{O}$  and 5 ml THF was added and the mixture was stirred additionally for two more days. The resulting  $\text{LiCl}$  was allowed to settle down and the liquid phase was filtered and subsequently concentrated to a volume of about 100 ml. The solvent was completely evaporated before 200 ml *n*-hexane was added. After storing three days in the freezer (-30°C), a colourless precipitate was formed, which was dried under reduced pressure at 60 °C. Recrystallization of the product by dissolving in *n*-hexane and very slow cooling resulted in the formation of single crystals. Yield: 7.14 g (75 %)

$^1\text{H}$ -NMR (250 MHz,  $\text{C}_6\text{D}_6$ ),  $\delta$  = 3.80 (sept, 6H), 3.14 (m, 12H), 1.46 (dd, 36H), 1.07 (t, 18H).

$^{13}\text{C}$ -NMR (200 MHz,  $\text{C}_6\text{D}_6$ ),  $\delta$  = 47.73, 26.69, 25.45, 11.74.

Elemental analysis (theoretical values in brackets): C 57.1 % (55.8 %), H 10.3 % (10.2 %) and N 15.4 % (17.8 %).

MS/ESI:  $m/z$  (%) = 709 (n. d.) [ $\text{M}^+$ ], 511 (100) [ $\text{M}^+ - \text{L}$ ], 314 (46) [ $\text{M}^+ - 2\text{L}$ ], 114 (38) [ $\text{In}^+$ ], 385 (4) [ $\text{M}^+ - \text{L} - \text{L}^2$ ], 314 (35) [ $\text{M}^+ - \text{L} - \text{L}^2 - \text{NET}_2$ ], 198 (82) [ $\text{L}^+$ ], 126 (12) [ $\text{L}^{2+}$ ].

( $\text{L} = [(\text{PrN})_2\text{CN}(\text{CH}_2\text{CH}_3)_2]$ ,  $\text{L}^2 = \text{CDI}$ )

<sup>1</sup> G. M. Sheldrick, SHELXS-97, Program for solution of crystal structures, University of Gottingen, Germany, 1997; G. M. Sheldrick, SHELXL-97, Program for refinement of crystal structures, University of Gottingen, Germany, 1997.

### Synthesis of compound 2, [In[(<sup>t</sup>PrN)<sub>2</sub>CN(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>]

To a slurry of 5.51 g (0.1 mol) LiN(CH<sub>3</sub>)<sub>2</sub> in 200 ml Et<sub>2</sub>O, 15.5 ml (0.1 mol) N,N'-Diisopropylcarbodiimide was added. The mixture became clear after one minute of stirring, leading to the formation of the lithiated guanidinate. The solution was stirred further for 4 hours at room temperature. Then a solution of 7.37 g (0.033 mol) InCl<sub>3</sub> in 100 ml Et<sub>2</sub>O and 20 ml THF was added. After stirring for 24 hours over night the solvent was completely evaporated under reduced pressure. About 200 ml *n*-hexane was added and the solution was stirred again for 24 hours. The resulting LiCl was allowed to settle down and the liquid phase was filtered and subsequently concentrated to a volume of about 150 ml. After two hours in the freezer (-30 °C) a white precipitate in the form of needles was formed. After 48 hours of storage in the freezer, the remaining solvent was evaporated under reduced pressure. The colorless, solid product was dried under reduced pressure at 60 °C. Recrystallization of the crude product by dissolving in *n*-hexane and very slow cooling yielded single crystals.

Yield: 12.1 g (65 %)

<sup>1</sup>H-NMR (250 MHz, C<sub>6</sub>D<sub>6</sub>), δ = 3.82 (sept, 6H), 2.76 (s, 18H), 1.45 (dd, 36H).

<sup>13</sup>C-NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>), δ = 47.73, 26.69, 25.45, 11.74.

Elemental analysis (theoretical values in brackets): C 51.9 % (51.8 %), H 9.5 % (9.7 %) and N 19.7 % (20.2 %).

MS/ESI: *m/z* (%) = 625 (n. d.) [M<sup>+</sup>], 455 (3) [M<sup>+</sup> - L], 411 (3) [M<sup>+</sup> - L - NMe<sub>2</sub>], 241 (9) [M<sup>+</sup> - L - NMe<sub>2</sub> - L], 284 (2) [M<sup>+</sup> - L - NMe<sub>2</sub> - L<sup>2</sup>], 114 (5) [In<sup>+</sup>], 170 (3) [L<sup>+</sup>], 126 (9) [L<sup>2+</sup>], 43 (55) [NMe<sub>2</sub><sup>+</sup>].

(L = [(<sup>t</sup>PrN)<sub>2</sub>CN(CH<sub>3</sub>)<sub>2</sub>], L<sup>2</sup> = CDI)

### Atomic layer deposition (ALD) of In<sub>2</sub>O<sub>3</sub>

Both the In compounds were used for the growth of In<sub>2</sub>O<sub>3</sub> thin films on 2 inch p-type Si (100) substrates in a commercial flow-type hot-wall ALD reactor (F-120, ASM Microchemistry Ltd., Finland), using N<sub>2</sub> as carrier and purging gas (99.999%) and H<sub>2</sub>O (HPLC quality, Baker analysed) as co-reactant. In addition, 2 inch borosilicate glass and sapphire (Al<sub>2</sub>O<sub>3</sub> (0001)) substrates were also used for the ALD of In<sub>2</sub>O<sub>3</sub>. The substrates were cleaned by standard procedure (isopropanol and acetone), followed by ultrasonic water bath for 10 minutes and dried under argon stream. The solvents used for cleaning were of HPLC quality (Baker analyzed). In-tris guanidinate precursor was filled (inside the MBraun glove box) in open boat type of crucible and transferred to the ALD reactor. About 150 mg of the precursor was used for each deposition and evaporated at 130°C. ALD experiments were carried out in the pressure range of 1 – 5 mbar. ALD-deposited films were stored in a dessicator, and the film analysis was carried out under ambient conditions.

### In<sub>2</sub>O<sub>3</sub> thin film characterization

The crystallinity of the ALD films was investigated by grazing-incidence X-ray diffraction (GI-XRD) on a Bruker D8 Discover diffractometer (Cu K $\alpha$  radiation (1.5418 Å)). For each measurement the step interval was set to 0.01° in the range from 20 to 60 ° with a incident angle of 1°. Determination of thin film thickness and refractive index was carried out on a J. A. Woollam M-88 Ellipsometer in the range 300 – 800 nm using an incident angle of 75 °. The surface morphology was investigated by atomic force microscopy (AFM) in the tapping mode on a Nanoscope Multimode III AFM (Digital Instruments) unit. UV/Vis spectra were measured on a CARY 5000 device (Varian Australia Pty., Ltd.). Rutherford-back scattering (RBS) and nuclear reaction analysis (NRA) were performed at RUBION, the central service unit for ion beams and radio nucleotides at Ruhr-University Bochum. For RBS, 2 MeV He<sup>2+</sup> ions were used. A beam intensity of about 50 nA with a tilt of 7 ° to the sample was applied, while the backscattered particles were detected at an angle of 160 °. Film stoichiometry was estimated using the software RBX.<sup>2</sup> X-ray photoelectron spectroscopy (XPS) was performed in a Versaprobe spectrometer from Physical Electronics (PHI 5000 VersaProbe), using monochromated Al K $\alpha$  excitation source (1486.6 eV). The spectrometer was calibrated by assigning to the Au 4f<sub>7/2</sub> line the binding energy (BE) of 84.0 eV with respect to the Fermi level. For sputtering, Ar<sup>+</sup> (1 kV, 2 minutes) was employed.

<sup>2</sup> Kótai, E. Nucl. Instrum. Methods 1994, B85, 588.

Table 1 Selected crystal data and structure refinement parameters for compound 1

CCDC	819611
Formula	C <sub>33</sub> H <sub>72</sub> InN <sub>9</sub>
FW/g mol <sup>-1</sup>	709.82
T/K	111
Crystal system	Monoclinic
Space group	C 1 2/c
a/Å	16.4523(3)
b/Å	12.8122(1)
c/Å	19.7849(2)
$\alpha$ /°	90.0
$\beta$ /°	98.503(6)
$\gamma$ /°	90.0
V/Å <sup>3</sup>	4124.62(374)
Z	4
$\rho$ /g cm <sup>-3</sup> (calc)	1.143
$\mu$ /mm <sup>-1</sup>	0.604
R indices [I > 2 $\sigma$ ]	$R_1 = 0.0299$ $wR_2 = 0.0670$
Rint	0.0959
Reflections collected; unique	32012; 3638

Table 2 Selected crystal data and structure refinement parameters for compound 2

CCDC	831071
Formula	C <sub>27</sub> H <sub>60</sub> InN <sub>9</sub>
FW/g mol <sup>-1</sup>	625.66
T/K	113
Crystal system	Monoclinic
Space group	P2(1)/n
a/Å	16.2217(6)
b/Å	11.1470(3)
c/Å	23.0289(9)
$\alpha$ /°	90.0
$\beta$ /°	109.239(3)
$\gamma$ /°	90.0
V/Å <sup>3</sup>	3931.6(2)
Z	4
$\rho$ /g cm <sup>-3</sup> (calc)	1.057
$\mu$ /mm <sup>-1</sup>	0.626
R indices [I > 2 $\sigma$ ]	$R_1 = 0.0399$ $wR_2 = 0.1020$
Rint	0.0381
Reflections collected; unique	29196; 6896

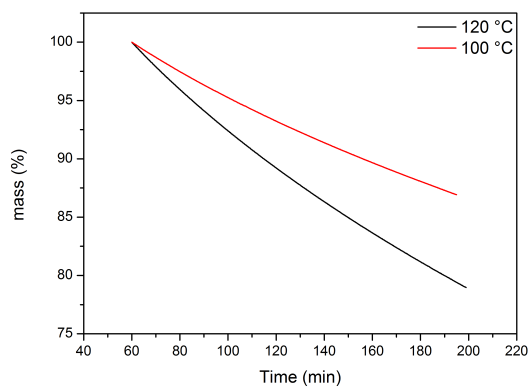


Fig. S 1 Isothermal TG analysis of compound 1,  $[\text{In}[(i\text{Pr})_2\text{CN}(\text{CH}_2\text{CH}_3)_2]_3]$ .

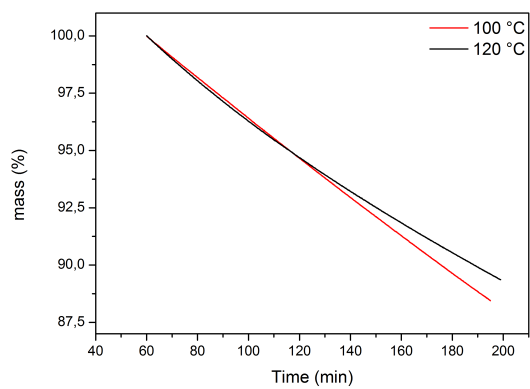


Fig. S 2 Isothermal TG analysis of compound 2,  $[\text{In}[(i\text{Pr})_2\text{CN}(\text{CH}_3)_2]_3]$

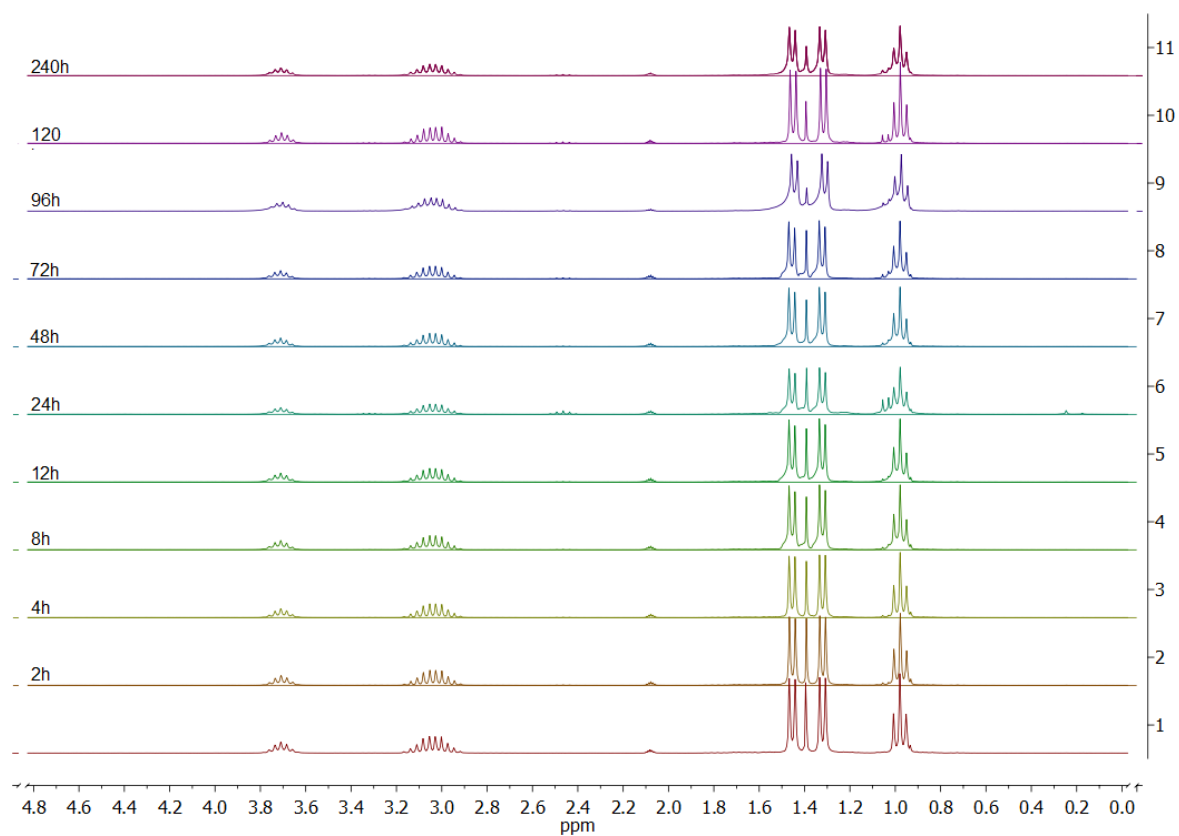


Fig. S 3 <sup>1</sup>H-NMR spectra of compound **1**, recorded in the course of the decomposition study performed at 125 °C and for different periods of heat treatment.

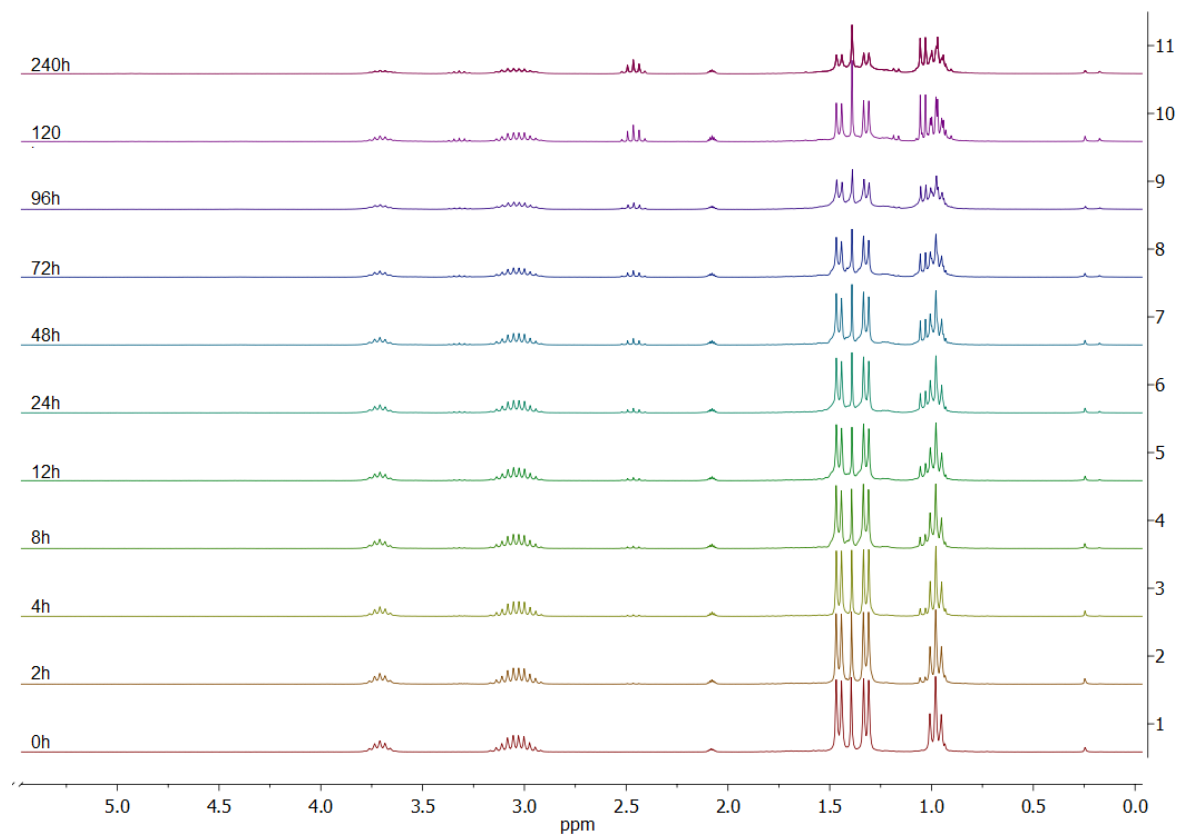


Fig. S 4 <sup>1</sup>H-NMR spectra of compound **1**, recorded in the course of the decomposition study performed at 160 °C and for different periods of heat treatment.

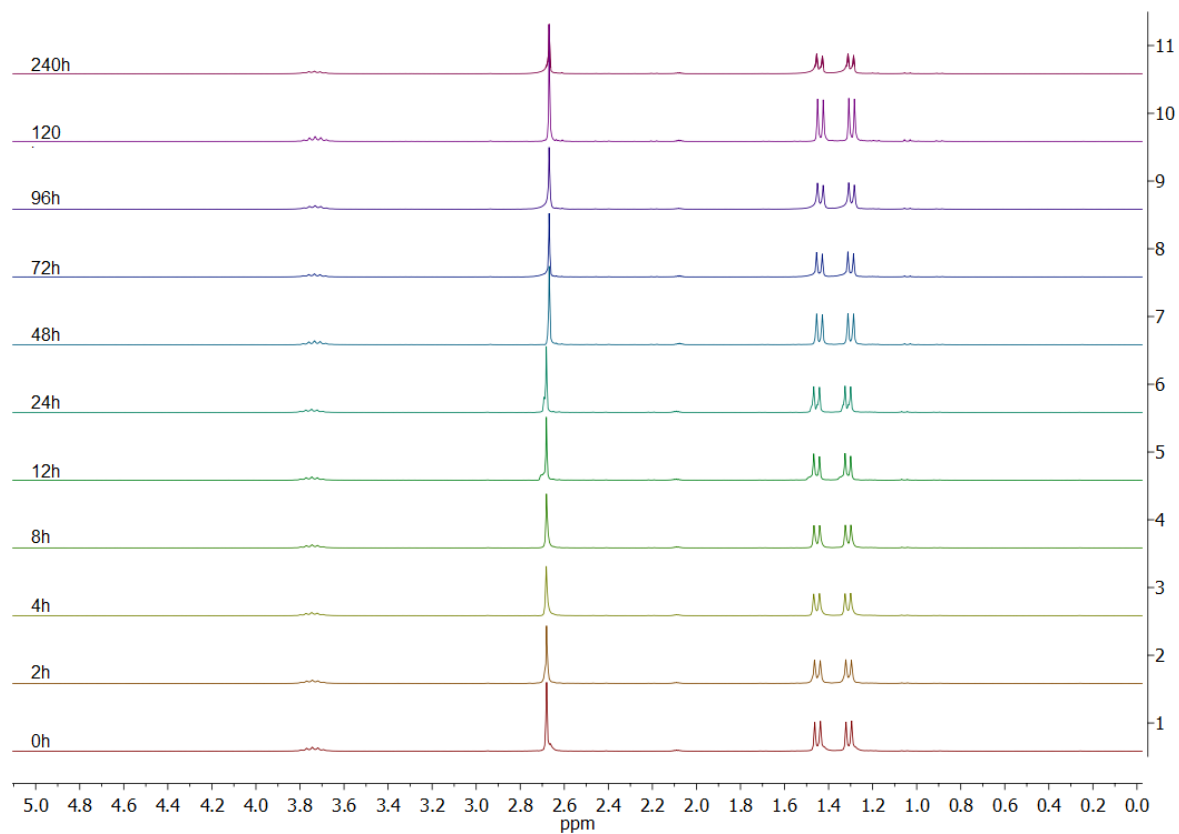


Fig. S 5 <sup>1</sup>H-NMR spectra of compound 2, recorded in the course of the decomposition study performed at 125 °C and for different periods of heat treatment.

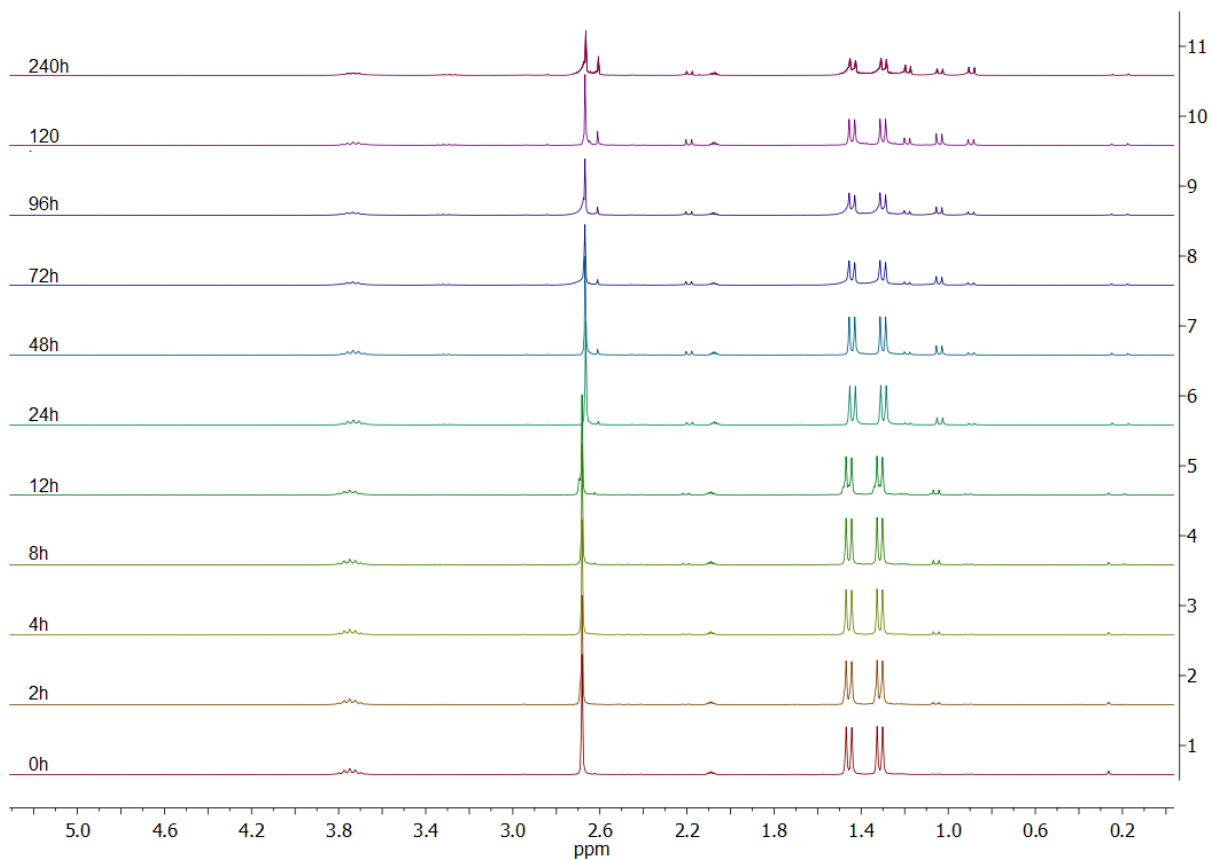


Fig. S 6 <sup>1</sup>H-NMR spectra of compound 2, recorded in the course of the decomposition study performed at 160 °C and for different periods of heat treatment.

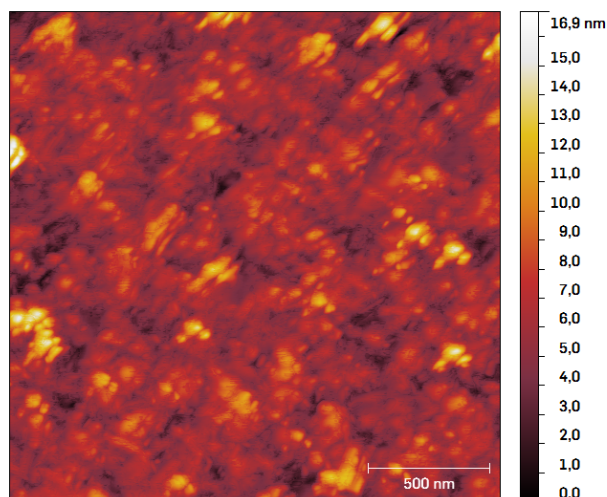


Fig. S 7 AFM micrograph of a 30 nm  $\text{In}_2\text{O}_3$  film grown at 230 °C on Si (100), using compound 2.

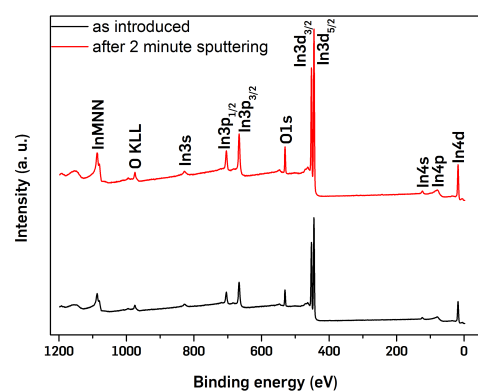


Fig. S 8 XPS survey spectra of an  $\text{In}_2\text{O}_3$  film grown at 230 °C on Si (100), deposited using compound 2.

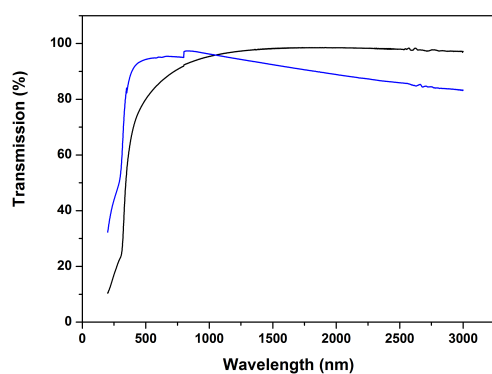


Fig. S 9 Black line: Transmission spectra of a 30 nm  $\text{In}_2\text{O}_3$  film on glass at 230 °C, deposited using compound 2. Blue line: Bare glass substrate