Supporting Information

for

A single-source precursor route to anisotropic halogen-doped zinc oxide particles as a promising candidate for new transparent conducting oxide materials

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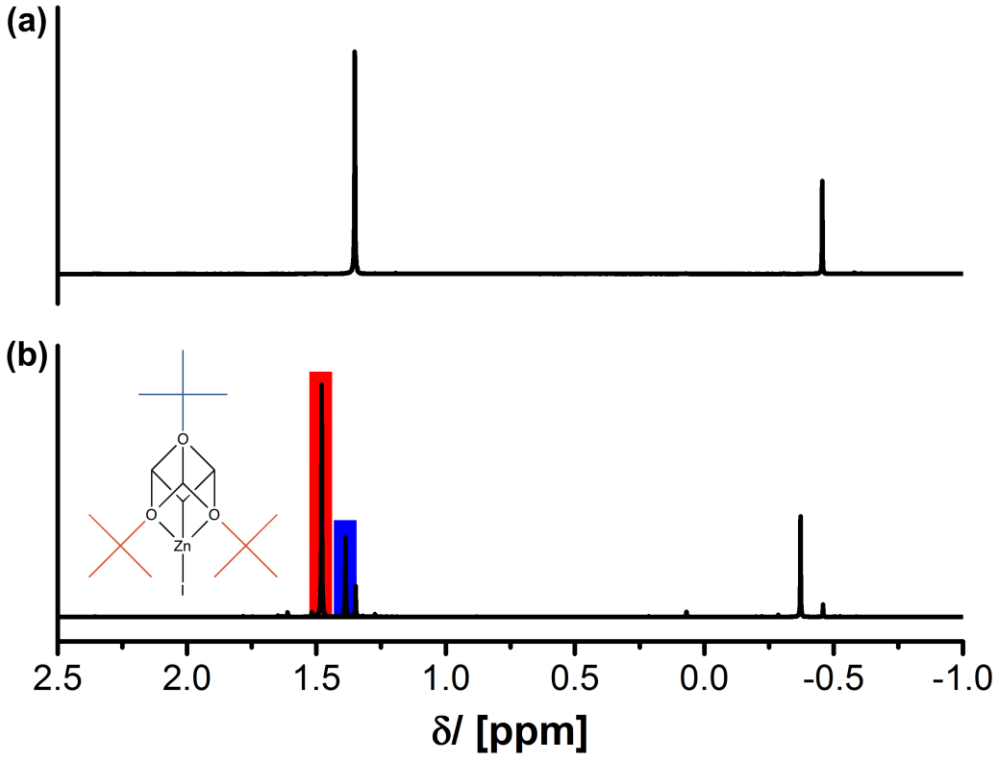
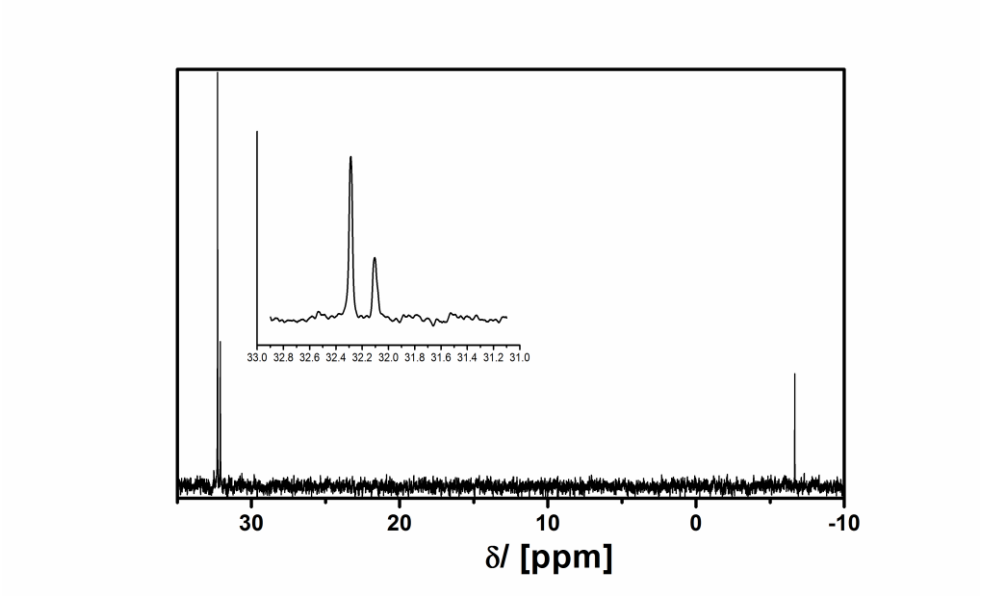

(a)
(b)
O
O
O
Y
Zn
I
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
δ/ [ppm]

(c)


33.0 32.8 32.6 32.4 32.2 32.0 31.8 31.6 31.4 31.2 31.0
30
20
10
0
-10
δ/ [ppm]

(d)

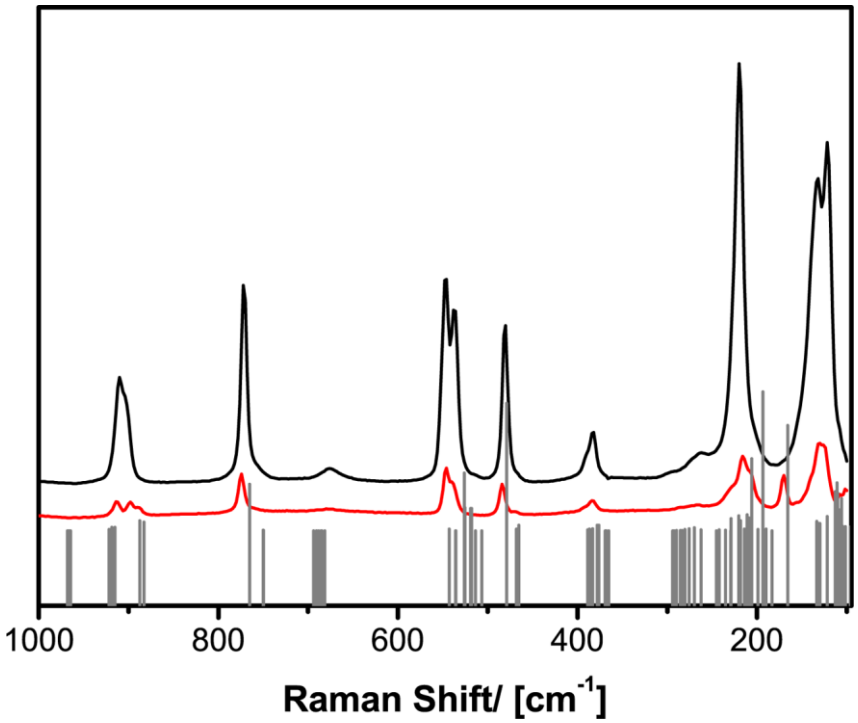
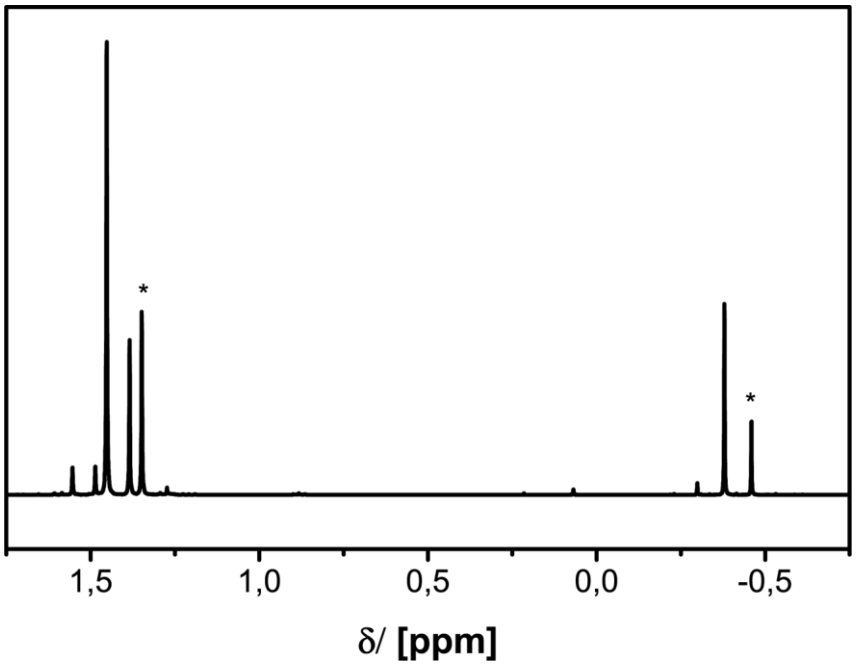


Figure S1: Additional analytical data for the molecular precursor compound **2a**. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the starting compound **1** [MeZnO*t*-Bu]$_4$ (a) and the monosubstituted iodo-compound **2a** [I(CH$_3$)$_3$Zn(O*t*-Bu)$_4$]. (c) ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of the monosubstituted iodo-compound **2a** [I(CH$_3$)$_3$Zn$_4$(O*t*-Bu)$_4$]. (d) FT-Raman spectra of [MeZnO*t*-Bu]$_4$ (black) and [I(CH$_3$)$_3$Zn$_4$(O*t*-Bu)$_4$] (**2a**) (red). Grey bars: DFT simulated vibration spectra of **2a**.

(a)



(b)

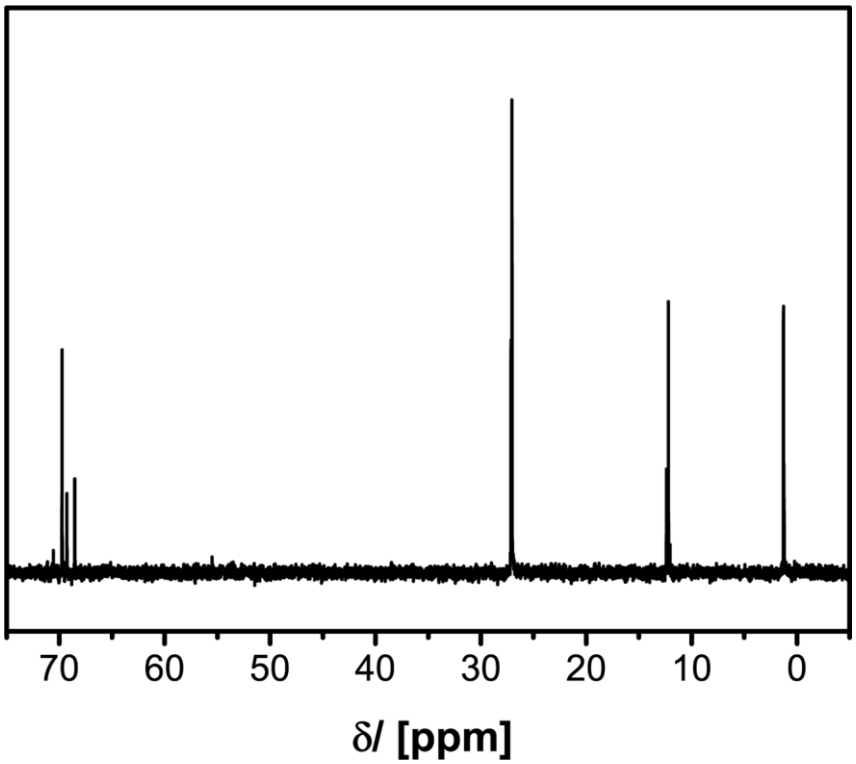
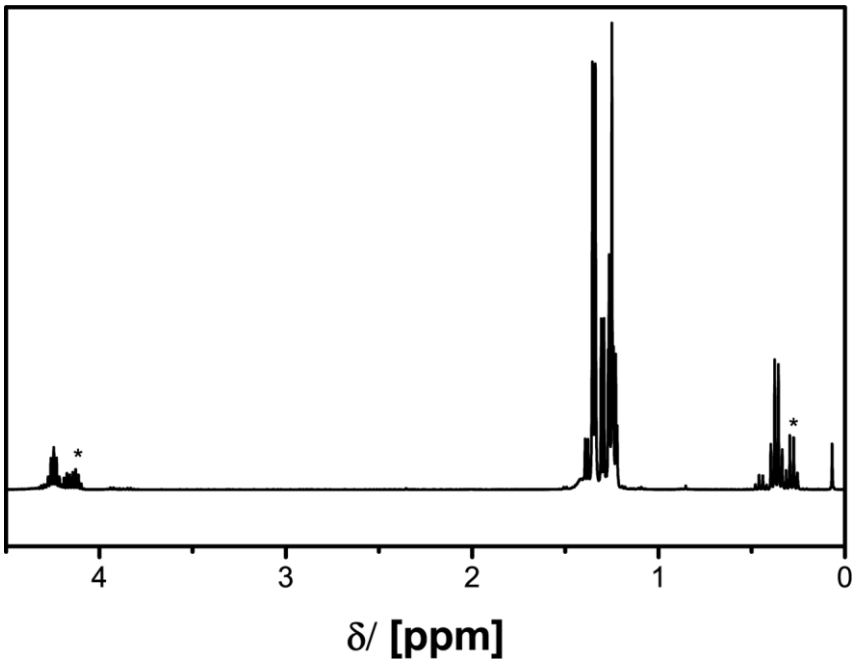
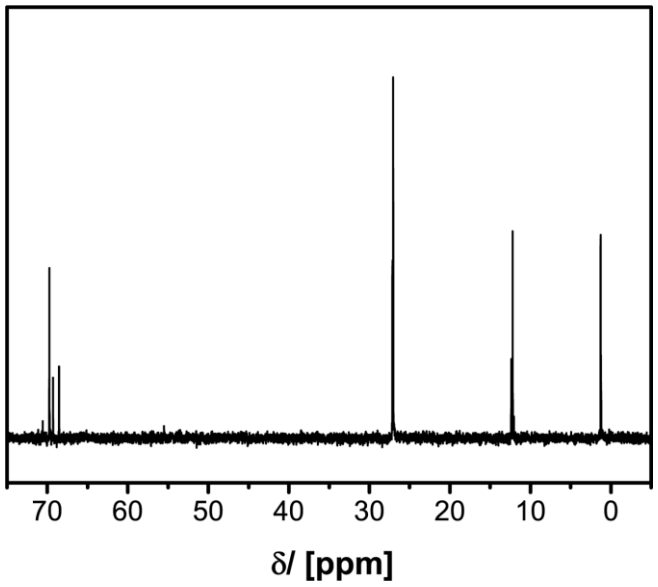


Figure S2: Additional analytical data for the molecular precursor compound **2b**. (a) ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the mono-substituted bromo-compound **2b** [$Br(CH_3)_3Zn_4(O$*t*-$Bu)_4$] (*residual starting compound [$MeZnO$*t*-$Bu]_4$). (b) ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of the mono-substituted bromo-compound **2b** [$Br(CH_3)_3Zn_4(O$*t*-$Bu)_4$].

(a)



(b)



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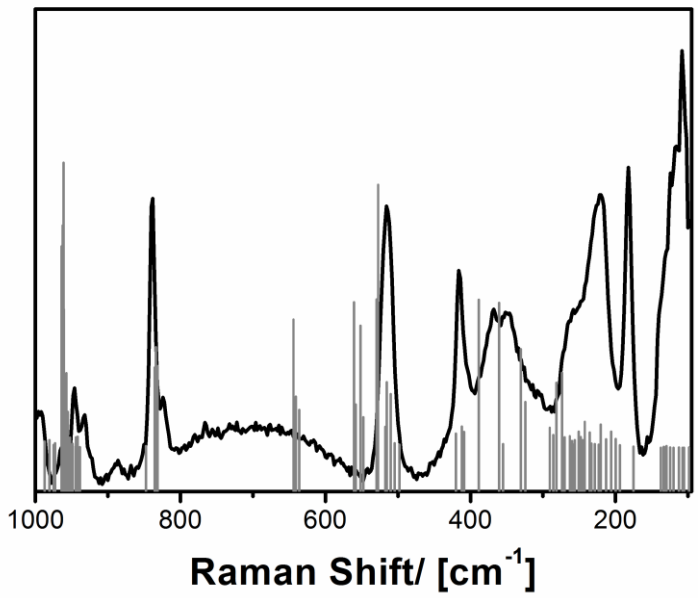


(d)

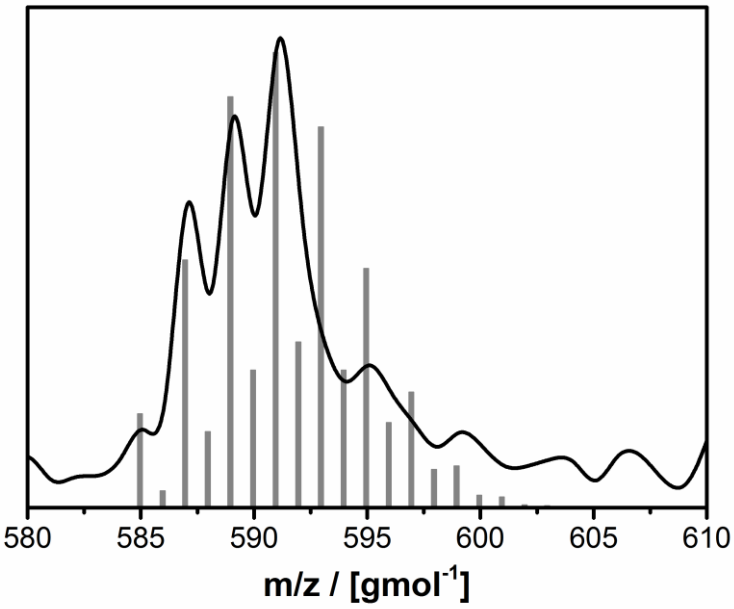
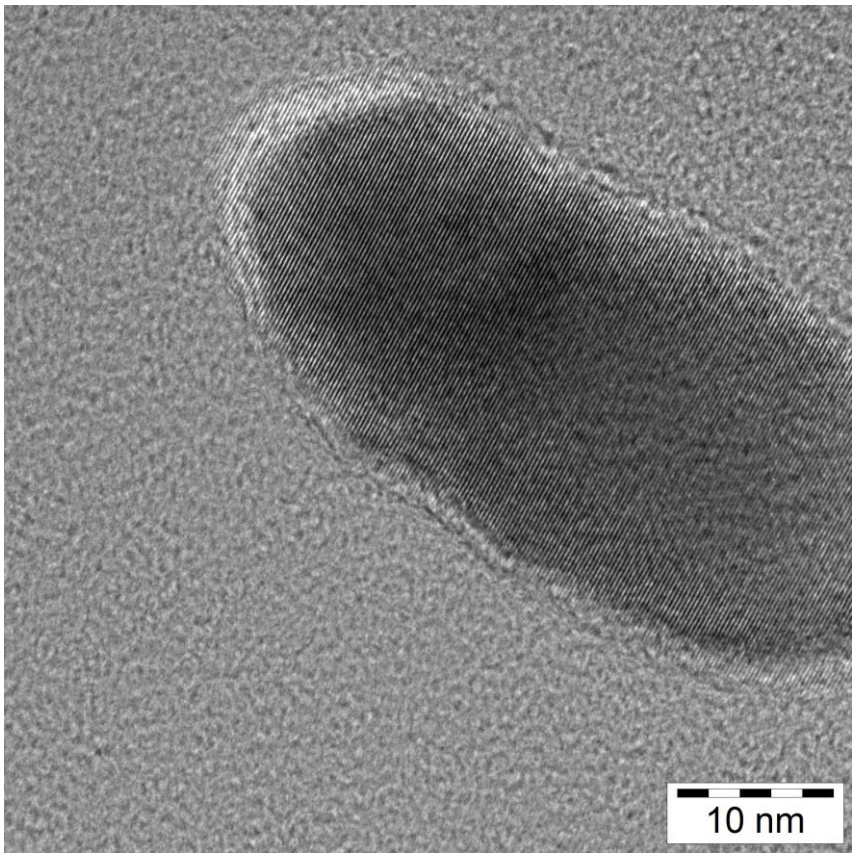


Figure S3: Additional analytical data for the molecular precursor compound **2c**. (a) ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the monosubstituted chloro-compound $[Cl(Et)_3Zn_4(OiPr)_4]$ (**2c**) (*residual starting compound $[EtZnOiPr]_4$). (b) ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of the monosubstituted chloro-compound $[Cl(Et)_3Zn_4(OiPr)_4]$ (**2c**). (c) FT-Raman of $[Cl(Et)_3Zn_4(OiPr)_4]$; experimental spectrum: black graph; spectrum simulated using DFT calculations: grey bars. EI-MS data (black graph: experimental signal) and calculated signal (grey bars) for the fragment $[Cl(Et)_2Zn(OiPr)_4]^+$ (m/z = 591.5).

(a)



(b)

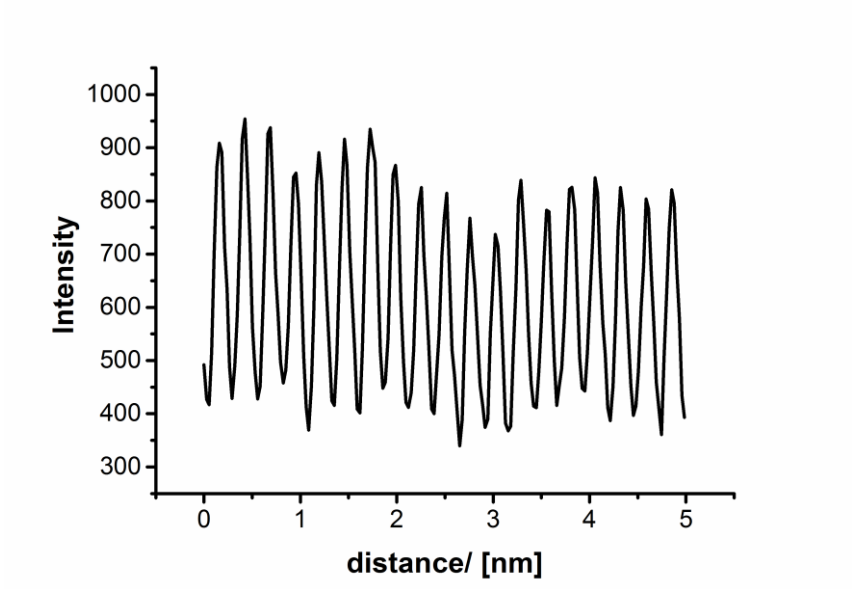


Figure S4: (a) HRTEM evaluation of $ZnO_{1-x}Cl_x$. (b) Evaluation of the lattice plane distances along *c*-direction from HR-TEM micrograph.

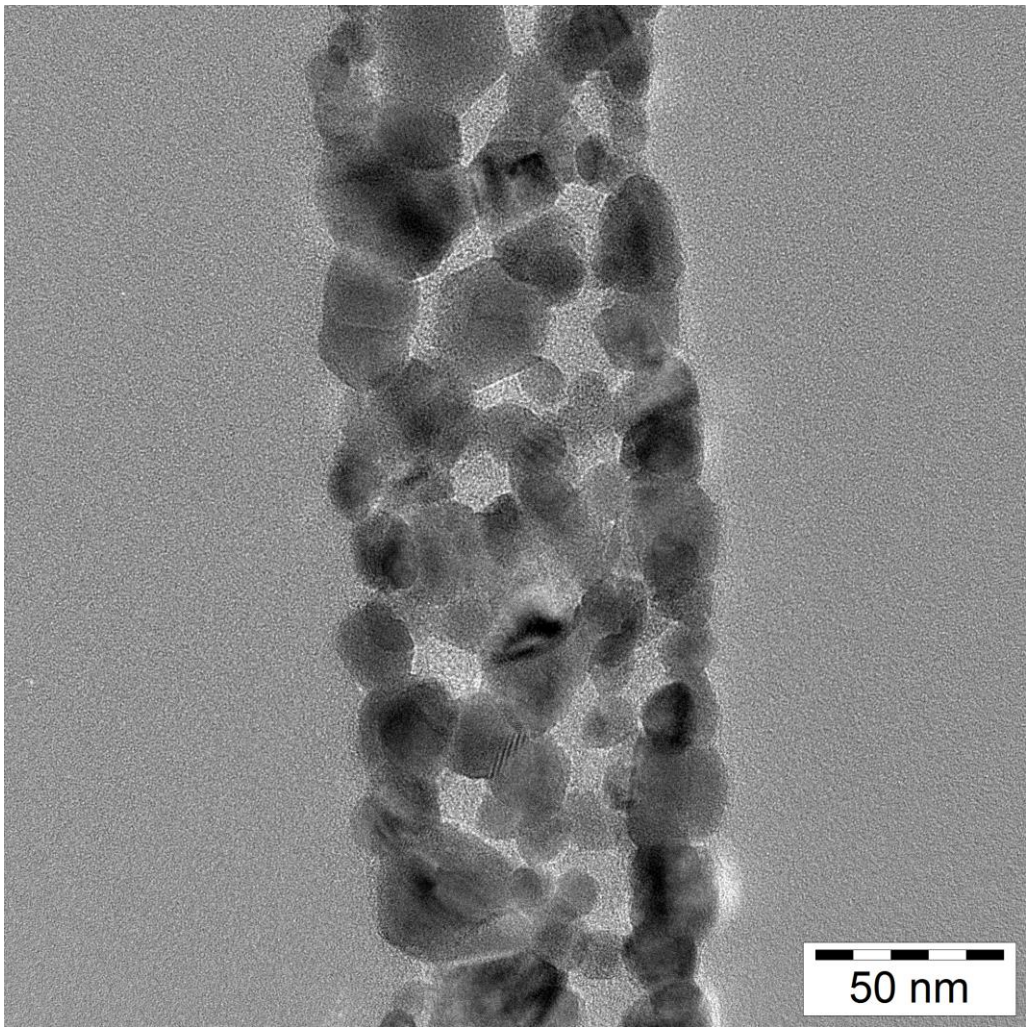
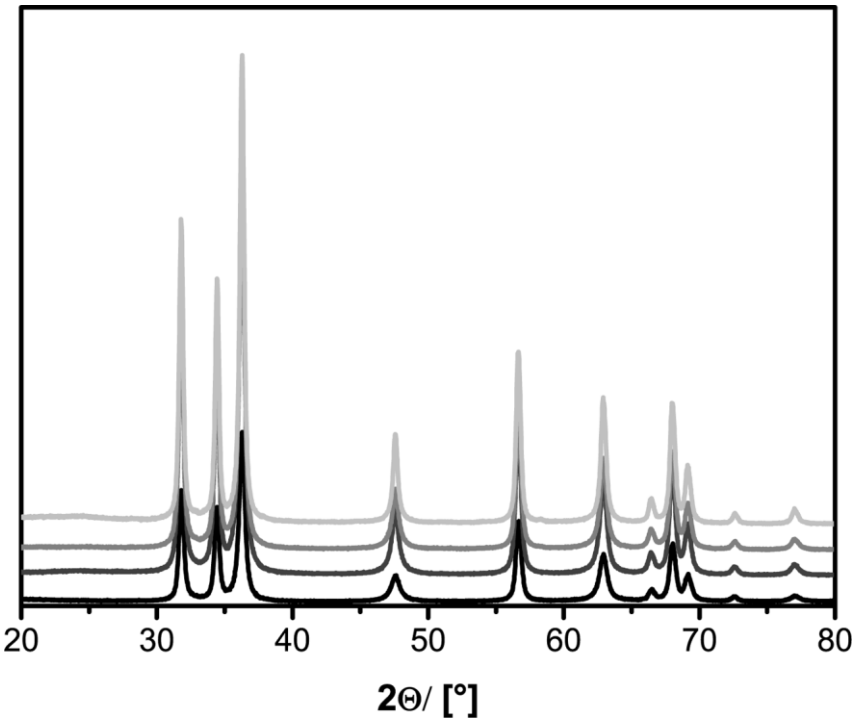


Figure S5: TEM micrograph of ZnO particles prepared from $[EtZnOiPr]_4$ as a precursor.

(a)

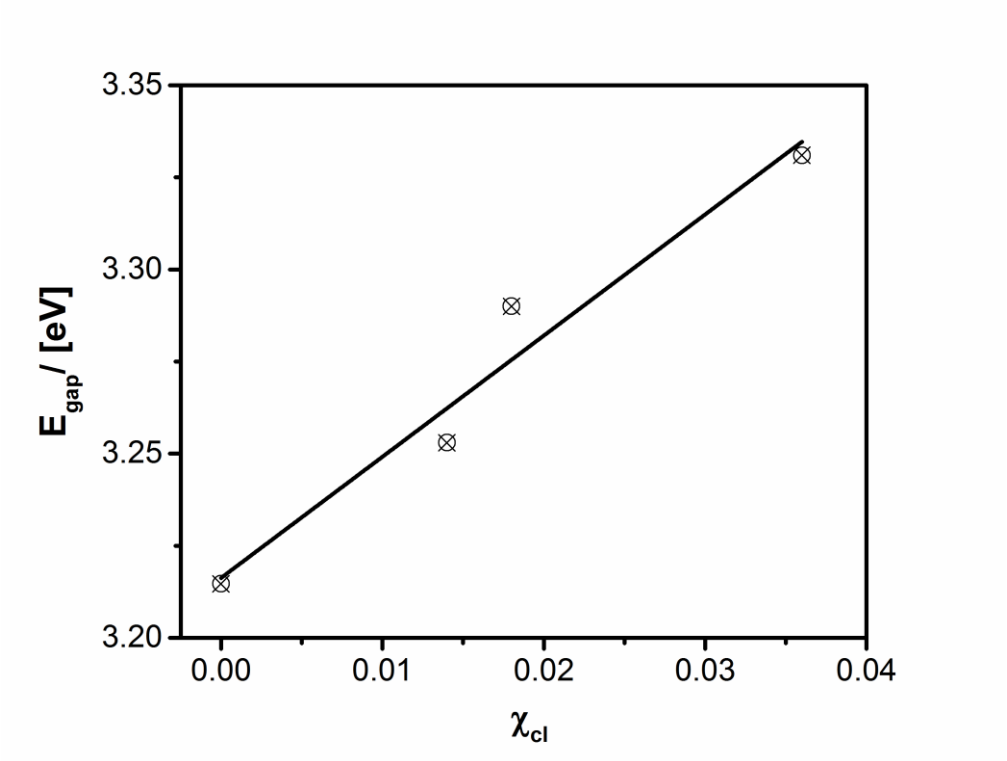


Composition and crystallite size of $ZnO_{1-x}Cl_x$

x in $ZnO_{1-x}Cl_x$	$D_{cryst[110]}$ [nm]
0.0	21.6
1.4	25.1
1.8	27.2
2.5	37.1

The crystallite size was calculated from the (110) diffraction signal using Scherrer equation.

(b)



(c)

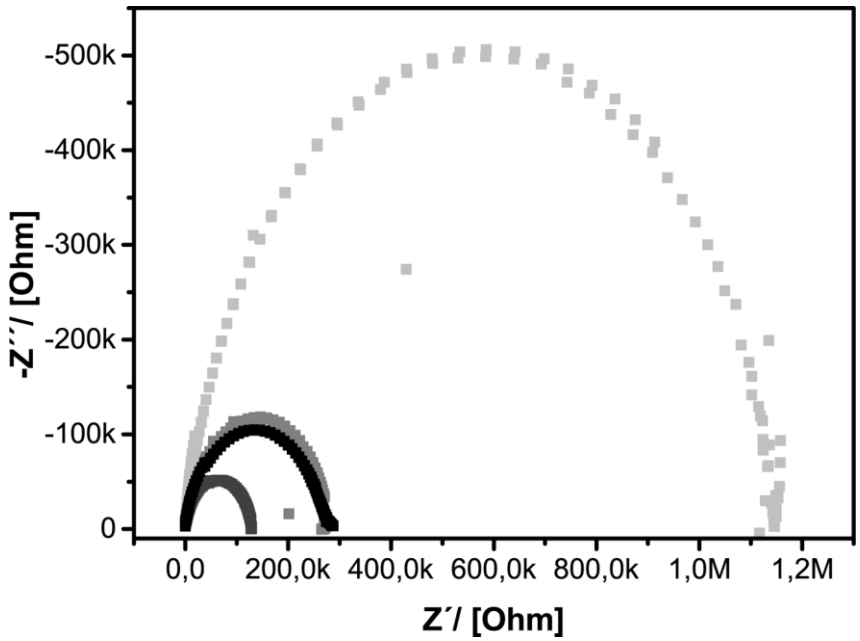
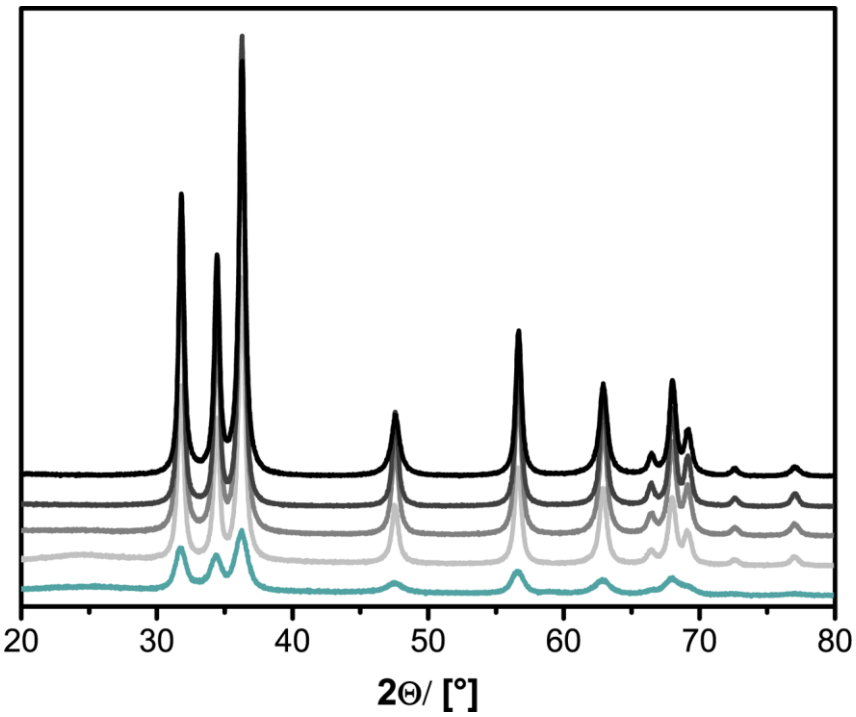


Figure S6: $ZnO_{1-x}Cl_x$ materials with different doping concentrations. (a) PXRD of $ZnO_{1-x}Cl_x$ materials synthesized from precursor mixtures of $[Et_3Cl_1Zn_4(OiPr)_4]$ (**2c**) and $[EtZnOiPr]_4$: $x = 0.0\%$ (black), 1.4% (dark grey), 1.8% (grey) and 2.5% (light grey). (b) Correlation of E_{gap} determined from optical diffuse reflectance spectra and the mole fraction of chlorine. (c) Impedance spectra of $ZnO_{1-x}Cl_x$ (Nyquist Plot): $x = 0.0\%$ (black), 1.4% (dark grey), 1.8% (grey) and 2.5% (light grey).

(a)

T [°C]	x in $ZnO_{1-x}I_x$	$D_{cryst\ [110]}$ [nm]
200	0.088	7.7
250	0.024	15.1
300	0.007	15.7
350	0.005	19.9
350 (ZnO reference)	0.000	18.4

(b)



(c)

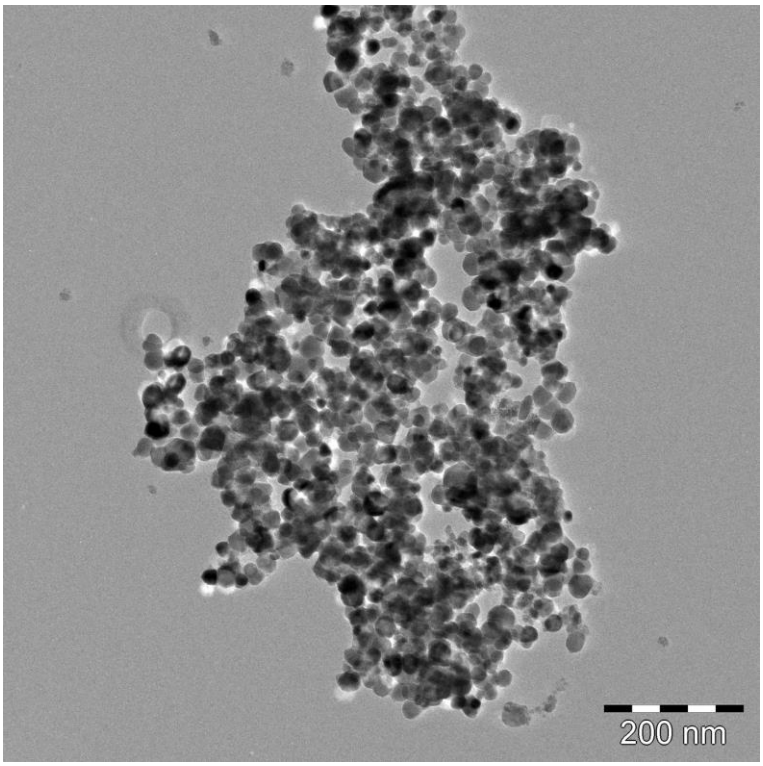
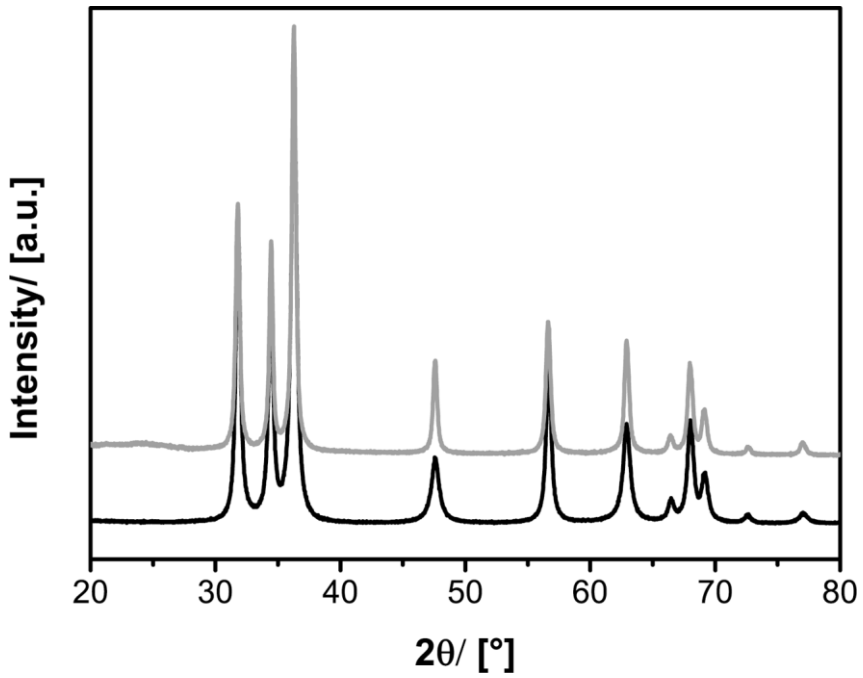


Figure S7: $ZnO_{1-x}I_x$ materials prepared from precursor **2a**. (a) $ZnO_{1-x}I_x$ synthesized from **2a** at different decomposition temperatures. (b) PXRD of $ZnO_{1-x}I_x$ materials synthesized at different temperatures from [$IMe_3Zn(O$*t*-$Bu)_4$]: 200 °C (blue), 250 °C (light grey), 300 °C (grey) and 350 °C (darkgrey). Black: ZnO reference (prepared from [$MeZnO$*t*-$Bu]_4$ at 350 °C). (c) TEM micrograph of $ZnO_{1-x}I_x$ particles (x = 0.005).

(a)



(b)

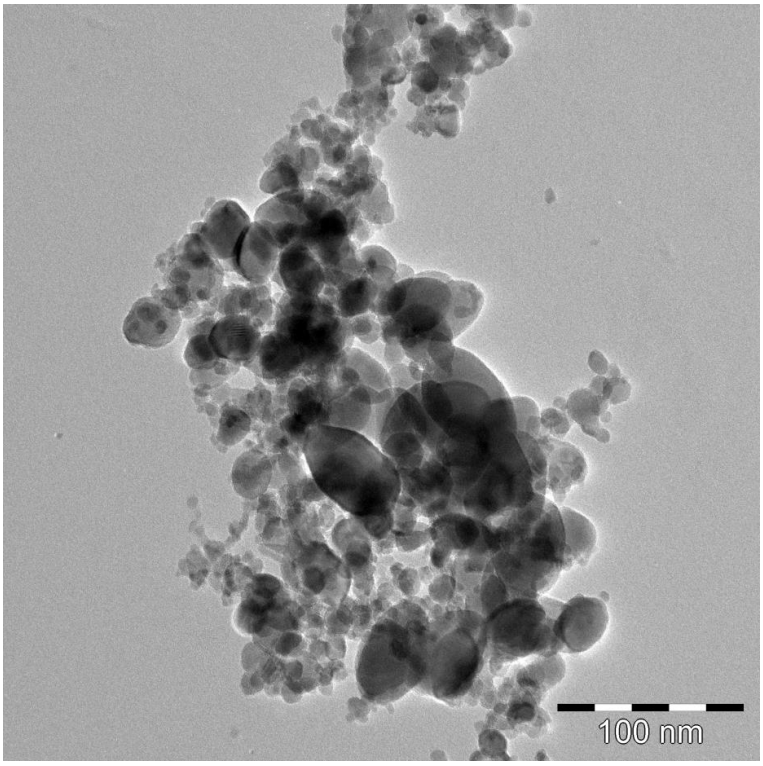


Figure S8: $ZnO_{1-x}Br_x$ material prepared from precursor **2b**. (a) PXRD of $ZnO_{1-x}Br_x$ (x = 0.022) and ZnO reference (black) prepared at 350 °C. (b) TEM micrograph of $ZnO_{1-x}Br_x$ particles.