A novel precursor towards buffer layer materials: the first solution based CVD of zinc oxysulfide

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Electronic Supplementary Information (ESI)

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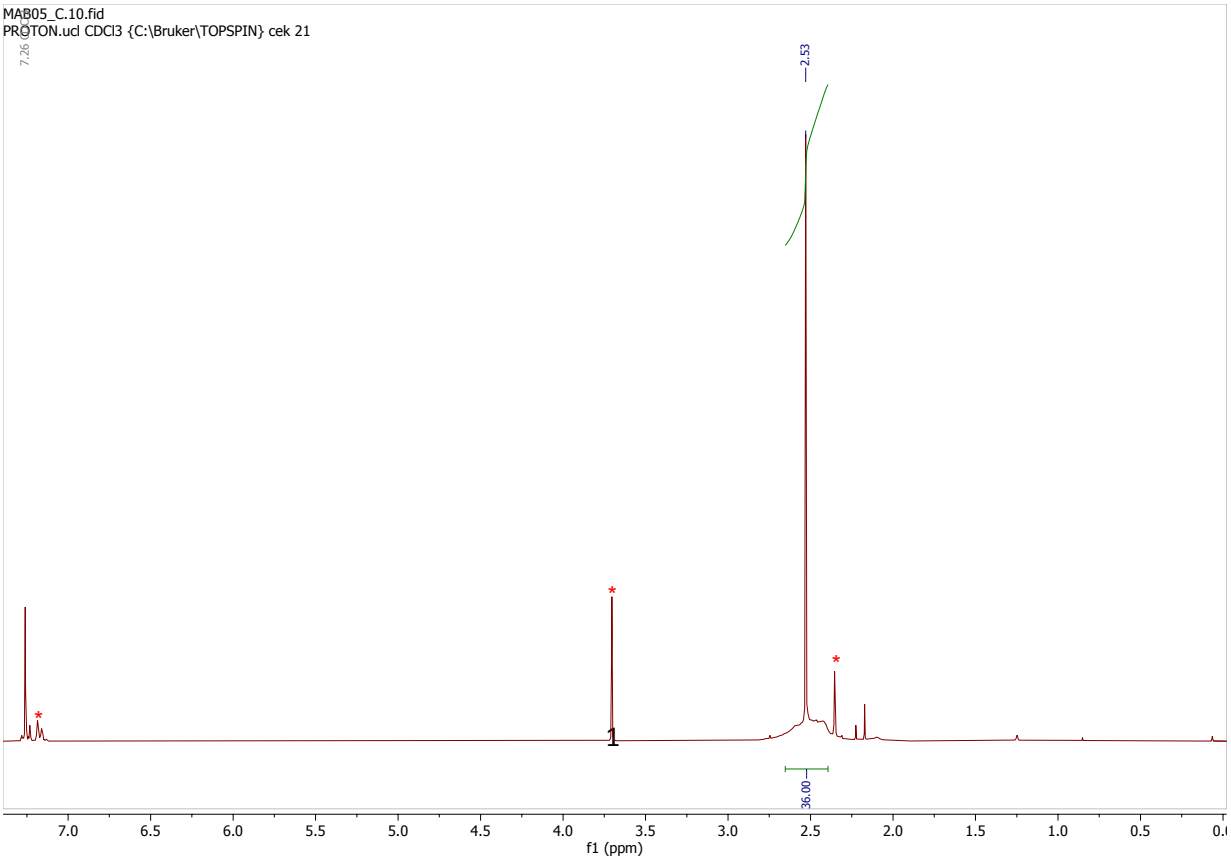
S1. ^{1}H NMR spectrum of **1**.

Red asterisks denote residual solvents.



S2. Crystallographic information for **1**

Table 1 Crystal data and structure refinement for **1**.

Identification code	xstr0983
Empirical formula	$C_{24}H_{36}O_{12}S_{14}Zn_8$
Formula weight	1488.33
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	22.8318(2)
b/Å	22.2511(2)
c/Å	12.24570(10)
α/°	90
β/°	102.3260(10)
γ/°	90
Volume/Å^3	6077.81(9)
Z	4
ρ_{calc}g/cm^3	1.627
μ/mm^{-1}	8.275
F(000)	2960.0
Crystal size/mm^3	0.12 × 0.1 × 0.04
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.928 to 152.744
Index ranges	-28 ≤ h ≤ 28, -27 ≤ k ≤ 27, -15 ≤ l ≤ 15
Reflections collected	62293
Independent reflections	6355 [R_{int} = 0.0478, R_{sigma} = 0.0188]
Data/restraints/parameters	6355/0/313
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0290, wR_2 = 0.0783
Final R indexes [all data]	R_1 = 0.0311, wR_2 = 0.0807
Largest diff. peak/hole / e Å^{-3}	0.82/-0.68

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for xstr0983. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Zn01	7124.7(2)	7789.0(2)	7144.6(2)	34.74(8)
Zn02	6535.4(2)	6656.9(2)	4604.7(2)	33.53(8)
Zn03	6776.0(2)	8488.7(2)	3585.1(2)	35.25(8)
Zn04	6931.2(2)	6287.8(2)	7258.4(2)	36.32(8)
S005	7275.3(2)	6953.6(2)	6109.2(4)	29.29(11)
S006	6739.0(3)	9331.8(3)	4661.9(5)	45.68(14)
S007	5587.6(2)	7018.6(3)	4581.6(6)	48.58(15)
S008	7120.8(3)	6970.8(3)	1339.3(5)	48.80(15)
S009	6745.6(4)	5317.9(3)	6622.7(6)	58.43(19)
S00A	8672.8(3)	6366.1(5)	8276.4(5)	63.1(2)
S00B	6141.5(15)	6597.1(13)	8098(2)	46.6(13)

O00C	6875.2(7)	6739.2(8)	3246.6(13)	38.6(3)
O00D	6827.8(7)	8422.7(7)	6001.7(14)	39.5(3)
O00E	6536.3(8)	5759.5(8)	4568.8(14)	47.2(4)
O00F	6266.7(7)	7793.7(8)	3915.2(14)	40.9(3)
O00G	6122(7)	7698(3)	7587(6)	23(3)
O00H	7596.1(8)	6138.3(10)	8610.9(16)	54.4(5)
C00I	6612.7(10)	5322.2(11)	5198(2)	41.2(5)
C00J	8134.5(11)	6177.6(10)	8984.1(19)	38.7(5)
C00K	6674.8(11)	6736.4(12)	2214(2)	42.6(5)
C00L	6844.5(11)	8976.7(11)	5932(2)	40.6(5)
C00M	5780.6(10)	7715.2(12)	4180(2)	44.0(5)
C00N	8350.3(14)	6048.7(14)	10213(2)	53.0(6)
C00O	6586.1(16)	4718.9(13)	4651(2)	57.1(7)
C00P	6099(5)	7377(4)	8178(9)	31(3)
C00Q	6959(2)	9359.9(15)	6956(3)	80.0(12)
C00R	6057.7(14)	6515(2)	1748(3)	77.3(11)
C00S	5359.8(15)	8231.1(18)	4196(5)	92.8(15)
C00T	5645.9(18)	7597.7(19)	8785(4)	58.8(13)
C1	5546(7)	6911(8)	8688(14)	80(6)
S2	6320(30)	6552(7)	8043(15)	99(6)
O3	6386(8)	7727.8(14)	7779(7)	53(2)
C4	6086(6)	7120(30)	8122(11)	107(14)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for xstr0983. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zn01	41.12(16)	36.23(16)	28.90(14)	-0.93(11)	12.02(11)	-2.10(11)
Zn02	27.73(14)	40.91(16)	31.51(15)	0.38(11)	5.35(11)	-3.54(10)
Zn03	30.51(15)	44.97(17)	31.43(15)	3.65(12)	9.22(11)	1.02(11)
Zn04	39.88(16)	37.80(16)	31.99(15)	1.43(11)	9.26(12)	-6.07(11)
S005	26.6(2)	35.0(2)	26.7(2)	-0.93(18)	6.70(17)	-2.96(17)
S006	59.3(3)	38.4(3)	42.1(3)	6.2(2)	16.9(3)	5.4(2)
S007	26.8(2)	58.0(4)	63.4(4)	9.9(3)	15.3(2)	-3.5(2)
S008	52.4(3)	68.4(4)	25.4(2)	-4.2(2)	7.8(2)	-0.8(3)
S009	100.6(6)	39.5(3)	41.4(3)	-3.2(2)	29.1(3)	-11.3(3)
S00A	34.0(3)	117.6(7)	36.1(3)	13.3(3)	4.0(2)	0.6(3)
S00B	50.1(17)	40.4(15)	58.7(12)	5.0(7)	32.7(6)	-0.3(8)
O00C	34.6(7)	49.9(9)	31.3(7)	-2.8(6)	7.4(6)	-3.8(6)
O00D	41.9(8)	38.2(8)	38.3(8)	3.9(6)	8.4(6)	-0.5(6)
O00E	51.3(10)	46.6(10)	39.4(9)	2.7(7)	0.1(7)	-3.5(7)
O00F	31.8(7)	48.3(9)	44.3(9)	0.9(7)	11.4(6)	-3.0(6)
O00G	12(5)	21(2)	39(3)	-4.4(17)	14(2)	-0.3(17)
O00H	42.2(9)	69.2(12)	50.4(10)	20.1(9)	6.8(8)	-9.3(8)
C00I	35.9(11)	41.4(12)	49.1(13)	-6.9(10)	15.6(9)	-4.5(9)
C00J	46.9(12)	36.5(11)	31.4(10)	-1.9(8)	5.2(9)	-0.5(9)

C00K	38.3(11)	54.0(14)	33.7(11)	-10.7(10)	3.7(9)	-1.3(10)
C00L	43.7(12)	42.7(12)	37.7(11)	0.4(9)	13.6(9)	1.9(9)
C00M	26.6(10)	57.6(14)	47.8(13)	8.5(11)	7.6(9)	2.3(9)
C00N	67.4(17)	58.0(16)	31.5(11)	-0.5(11)	5.7(11)	-3.5(13)
C00O	80(2)	44.2(14)	50.6(15)	-9.6(11)	20.9(14)	0.7(13)
C00P	37(3)	25(7)	32(3)	-4(2)	9(2)	-2(2)
C00Q	146(4)	48.5(17)	43.2(15)	-6.2(13)	15.9(19)	6.1(19)
C00R	42.6(15)	129(3)	55.3(18)	-19.9(19)	-1.2(13)	-14.8(18)
C00S	45.6(17)	74(2)	168(5)	38(3)	42(2)	20.0(16)
C00T	54(2)	62(2)	71(3)	-5.8(19)	38.0(19)	1.0(17)
C1	69(9)	95(11)	94(11)	31(9)	56(8)	21(8)
S2	130(18)	75(5)	97(6)	25(4)	36(7)	17(7)
O3	68(7)	38.9(14)	64(2)	-5.6(12)	39(3)	-5.2(17)
C4	39(4)	250(40)	39(4)	17(10)	18(3)	32(9)

Table 4 Bond Lengths for xstr0983.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Zn01	S005	2.3169(6)	S008	C00K	1.709(3)
Zn01	S008[1]	2.3096(7)	S009	C00I	1.706(3)
Zn01	O00D	2.0002(16)	S00A	Zn03[1]	2.3138(7)
Zn01	O00G	2.470(14)	S00A	C00J	1.701(3)
Zn01	O3	2.006(13)	S00B	C00P	1.742(8)
Zn02	S005	2.3141(5)	O00C	C00K	1.250(3)
Zn02	S007	2.3032(6)	O00D	C00L	1.237(3)
Zn02	O00C	1.9882(16)	O00E	C00I	1.230(3)
Zn02	O00E	1.9972(19)	O00F	C00M	1.233(3)
Zn03	S005[1]	2.3354(5)	O00G	C00P	1.026(13)
Zn03	S006	2.3049(7)	O00H	C00J	1.220(3)
Zn03	S00A[1]	2.3137(7)	C00I	C00O	1.495(3)
Zn03	O00F	2.0267(17)	C00J	C00N	1.508(3)
Zn04	S005	2.2944(5)	C00K	C00R	1.487(4)
Zn04	S009	2.3029(7)	C00L	C00Q	1.492(4)
Zn04	S00B	2.361(3)	C00M	C00S	1.500(4)
Zn04	O00H	2.0210(19)	C00P	C00T	1.480(11)
Zn04	S2	1.94(6)	C1	S2	2.24(7)
S005	Zn03[1]	2.3355(5)	C1	C4	1.61(3)
S006	C00L	1.716(2)	S2	C4	1.39(7)
S007	C00M	1.712(3)	O3	C4	1.60(6)
S008	Zn01[1]	2.3096(7)			

[1]3/2-X,3/2-Y,1-Z

Table 5 Bond Angles for xstr0983.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
S005	Zn01	O00G	107.88(18)	C00L	S006	Zn03	97.40(8)
S008[1]	Zn01	S005	116.95(2)	C00M	S007	Zn02	91.22(8)
S008[1]	Zn01	O00G	114.2(2)	C00K	S008	Zn01[1]	90.51(8)
O00D	Zn01	S005	104.50(5)	C00I	S009	Zn04	108.67(9)
O00D	Zn01	S008[1]	118.85(5)	C00J	S00A	Zn03[1]	108.68(8)
O00D	Zn01	O00G	91.14(15)	C00P	S00B	Zn04	111.8(4)
O00D	Zn01	O3	97.5(3)	C00K	O00C	Zn02	136.23(16)
O3	Zn01	S005	113.11(18)	C00L	O00D	Zn01	137.70(16)
O3	Zn01	S008[1]	104.4(4)	C00I	O00E	Zn02	141.06(17)
S007	Zn02	S005	115.75(3)	C00M	O00F	Zn03	138.35(18)
O00C	Zn02	S005	106.90(5)	C00P	O00G	Zn01	113.7(10)
O00C	Zn02	S007	119.40(5)	C00J	O00H	Zn04	144.68(17)
O00C	Zn02	O00E	94.08(7)	O00E	C00I	S009	127.97(19)
O00E	Zn02	S005	107.38(5)	O00E	C00I	C00O	116.3(2)
O00E	Zn02	S007	110.76(6)	C00O	C00I	S009	115.7(2)
S006	Zn03	S005[1]	113.40(2)	O00H	C00J	S00A	127.36(19)
S006	Zn03	S00A[1]	112.79(3)	O00H	C00J	C00N	116.7(2)
S00A[1]	Zn03	S005[1]	114.66(3)	C00N	C00J	S00A	115.96(19)
O00F	Zn03	S005[1]	101.45(5)	O00C	C00K	S008	119.61(18)
O00F	Zn03	S006	114.48(5)	O00C	C00K	C00R	120.1(3)
O00F	Zn03	S00A[1]	98.67(5)	C00R	C00K	S008	120.2(2)
S005	Zn04	S009	117.40(2)	O00D	C00L	S006	121.38(18)
S005	Zn04	S00B	118.19(7)	O00D	C00L	C00Q	121.0(2)
S009	Zn04	S00B	108.54(6)	C00Q	C00L	S006	117.7(2)
O00H	Zn04	S005	108.25(5)	O00F	C00M	S007	120.3(2)
O00H	Zn04	S009	100.05(7)	O00F	C00M	C00S	120.7(3)
O00H	Zn04	S00B	101.59(10)	C00S	C00M	S007	119.0(2)
S2	Zn04	S005	118.9(4)	O00G	C00P	S00B	129.9(9)
S2	Zn04	S009	110.6(7)	O00G	C00P	C00T	105.7(9)
S2	Zn04	O00H	97.8(7)	C00T	C00P	S00B	114.3(6)
Zn01	S005	Zn03[1]	119.43(2)	C4	C1	S2	38(2)
Zn02	S005	Zn01	119.74(2)	C4	S2	Zn04	130(3)
Zn02	S005	Zn03[1]	120.13(2)	C4	O3	Zn01	126.8(14)
Zn04	S005	Zn01	94.13(2)	S2	C4	C1	96(4)
Zn04	S005	Zn02	90.959(19)	S2	C4	O3	124(2)
Zn04	S005	Zn03[1]	93.27(2)	O3	C4	C1	140(4)

[1]3/2-X,3/2-Y,1-Z

Table 6 Torsion Angles for xstr0983.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
Zn01[1]	S008	C00K	O00C	-3.1(2)	Zn03	S006	C00L	C00Q	169.8(3)
Zn01[1]	S008	C00K	C00R	178.6(3)	Zn03[1]	S00A	C00J	O00H	-2.0(3)
Zn01	O00D	C00L	S006	158.64(14)	Zn03[1]	S00A	C00J	C00N	178.36(17)

Zn01	O00D	C00L	C00Q	-21.2(4)	Zn03	O00F	C00M	S007	-169.83(13)
Zn01	O00G	C00P	S00B	-68.8(15)	Zn03	O00F	C00M	C00S	7.9(5)
Zn01	O00G	C00P	C00T	148.7(5)	Zn04	S009	C00I	O00E	-10.0(3)
Zn01	O3	C4	C1	175.6(15)	Zn04	S009	C00I	C00O	170.05(18)
Zn01	O3	C4	S2	2(2)	Zn04	S00B	C00P	O00G	45.1(16)
Zn02	S007	C00M	O00F	8.4(2)	Zn04	S00B	C00P	C00T	-175.0(5)
Zn02	S007	C00M	C00S	-169.4(3)	Zn04	O00H	C00J	S00A	-7.9(5)
Zn02	O00C	C00K	S008	167.23(13)	Zn04	O00H	C00J	C00N	171.7(3)
Zn02	O00C	C00K	C00R	-14.5(4)	Zn04	S2	C4	C1	170(2)
Zn02	O00E	C00I	S009	3.4(4)	Zn04	S2	C4	O3	-14(3)
Zn02	O00E	C00I	C00O	-176.7(2)	S2	C1	C4	O3	-175(3)
Zn03	S006	C00L	O00D	-10.0(2)					

[1]3/2-X,3/2-Y,1-Z

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for xstr0983.

Atom	***x***	***y***	***z***	**U(eq)**
H00A	8780	6020	10386	80
H00B	8182	5676	10394	80
H00C	8227	6368	10641	80
H00D	6963	4635	4454	86
H00E	6273	4717	3989	86
H00F	6506	4417	5160	86
H00G	7360	9293	7372	120
H00H	6679	9258	7410	120
H00I	6911	9775	6743	120
H00J	5771	6794	1926	116
H00K	6004	6129	2066	116
H00L	5999	6478	951	116
H00M	4955	8101	3906	139
H00N	5458	8552	3742	139
H00O	5397	8370	4950	139
H00P	5326	7311	8713	88
H00Q	5489	7976	8474	88
H00R	5829	7650	9561	88
H1A	5204	6807	8114	121
H1B	5441	7232	9134	121
H1C	5670	6567	9152	121

Table 8 Atomic Occupancy for xstr0983.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
S00B	0.68(4)	O00G	0.40(4)	C00P	0.51(6)

C00T	0.764(10)	H00P	0.764(10)	H00Q	0.764(10)
H00R	0.764(10)	C1	0.251(11)	H1A	0.251(11)
H1B	0.251(11)	H1C	0.251(11)	S2	0.21(4)
O3	0.85(4)	C4	0.57(7)		

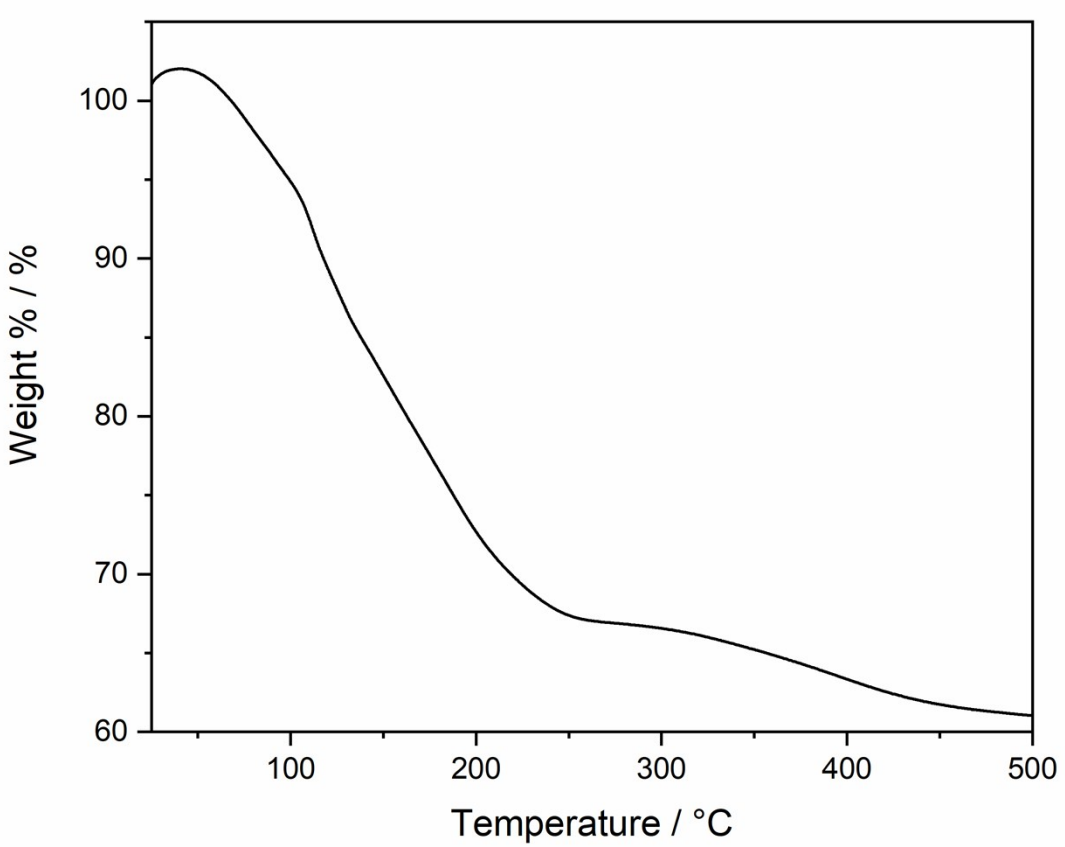
Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso
 At 1.5 times of:
  All C(H,H,H) groups
2. Others
 Sof(C00T)=Sof(H00P)=Sof(H00Q)=Sof(H00R)=FVAR(1)
 Sof(C1)=Sof(H1A)=Sof(H1B)=Sof(H1C)=FVAR(2)
3.a Idealised Me refined as rotating group:
 C00N(H00A,H00B,H00C), C00O(H00D,H00E,H00F), C00Q(H00G,H00H,H00I), C00R(H00J,
 H00K,H00L), C00S(H00M,H00N,H00O), C00T(H00P,H00Q,H00R), C1(H1A,H1B,H1C)

S3. TGA of **1**



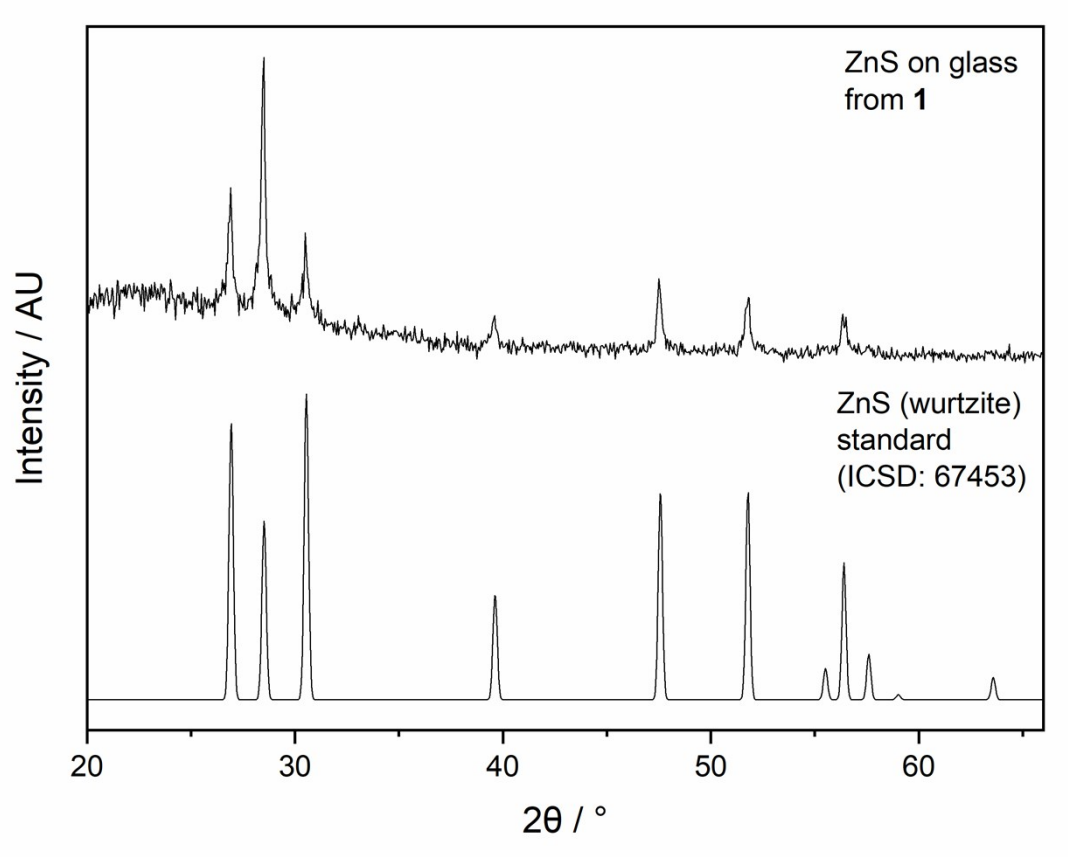
S4. AACVD of Zn(O,S) using alternative known precursors

Zinc acetate dihydrate and zinc diethyldithiocarbamate were added to an AACVD bubbler dissolved in methanol (20 cm^3) and THF (20 cm^3) respectively using the amounts listed in the table below. AACVD was carried out at 450 °C with a flow rate of 0.5 $Lmin^{-1}$.

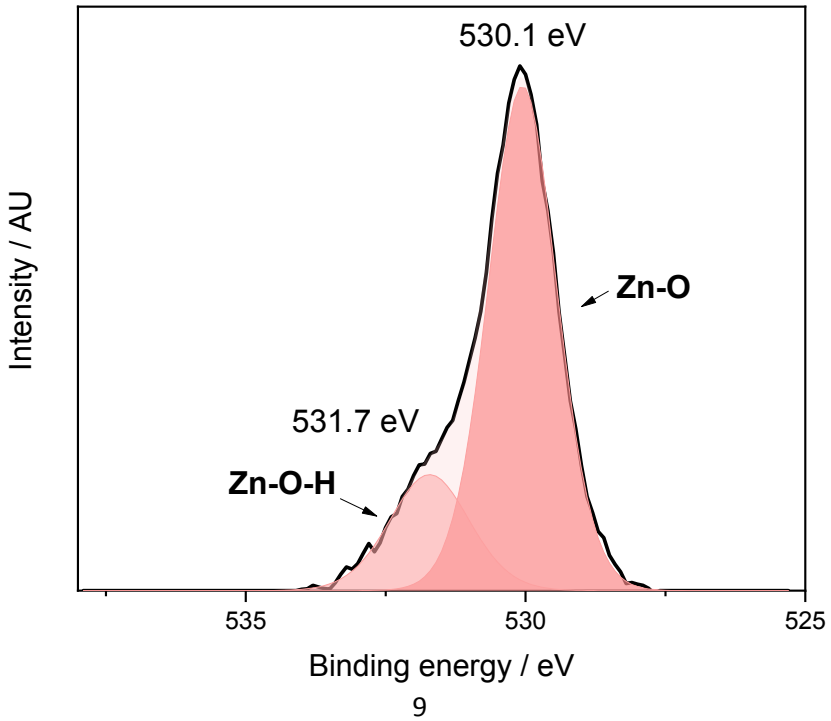
Amount of zinc acetate dihydrate / g	**Amount of zinc diethyldithiocarbamate / g**
0 (0 mmol)	0.7239 (2 mmol)
0.0439 (0.2 mmol)	0.6515 (1.8 mmol)
0.0878 (0.4 mmol)	0.5791 (1.6 mmol)
0.1317 (0.6 mmol)	0.5067 (1.4 mmol)
0.1756 (0.8 mmol)	0.4343 (1.2 mmol)
0.2195 (1.0 mmol)	0.3619 (1.0 mmol)
0.2634 (1.2 mmol)	0.2895 (0.8 mmol)
0.3073 (1.4 mmol)	0.2172 (0.6 mmol)
0.3512 (1.6 mmol)	0.1448 (0.4 mmol)
0.3951 (1.8 mmol)	0.0724 (0.2 mmol)
0.4390 (2.0 mmol)	0 (0 mmol)

S5. XRD pattern of ZnS deposited from **1**

AACVD of **1** carried out in toluene at 500 °C with a flow rate of 0.5 $Lmin^{-1}$.

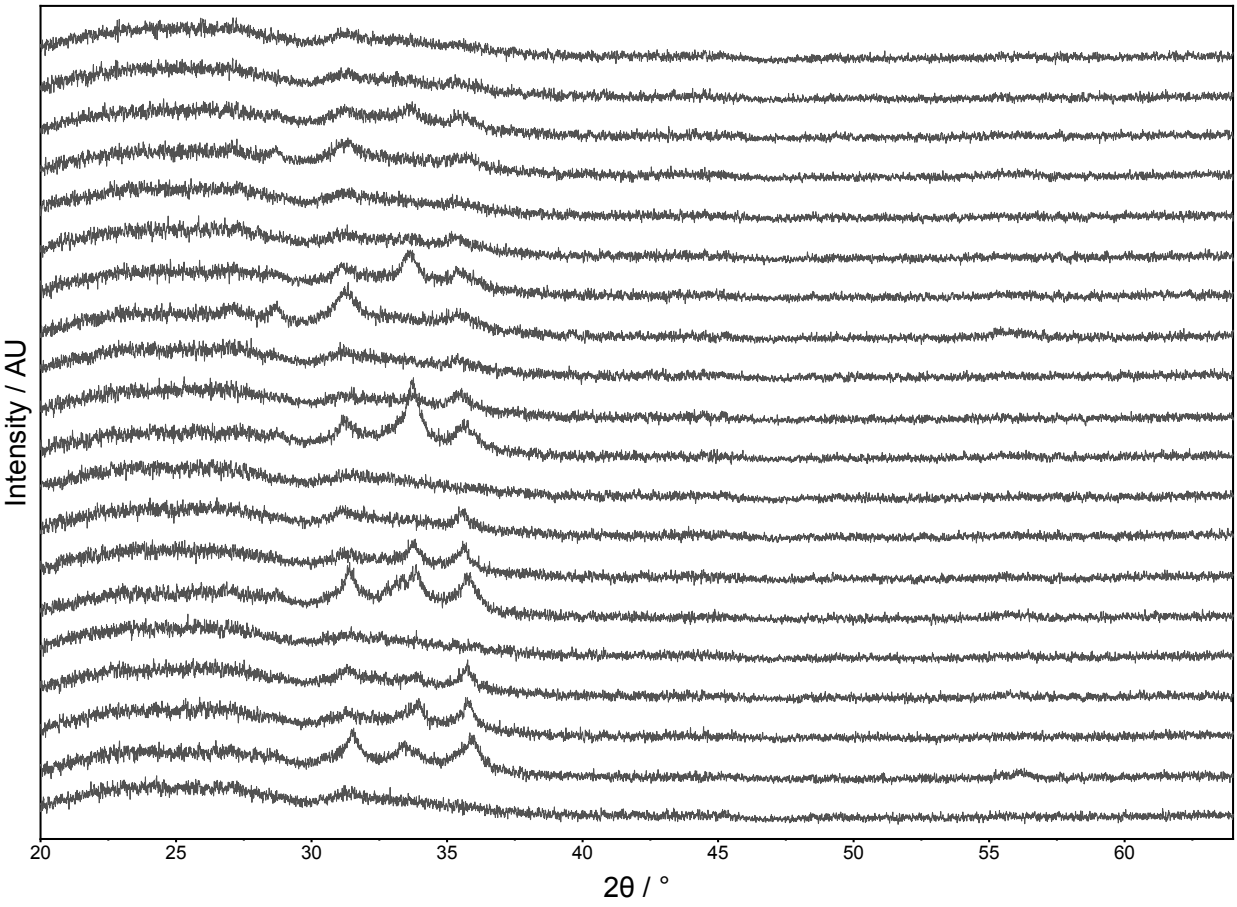


S6. XPS (300 s etch): O 1s spectrum of $ZnO_{0.884}S_{0.116}$



S7. XRD patterns of large area film

From bottom to top A1–A4, B1–B4, C1–C4, D1–D4, E1–E4.



S8. EDAX raw data of large area film

Position	O	S	Zn	Total	S/Zn
A4	66.73	2.66	30.61	100	0.086899706
A3	57.69	3.83	38.48	100	0.099532225
A2	48.53	4.79	46.68	100	0.102613539
A1	47.98	3.37	48.65	100	0.069270298
B1	27.14	7.09	65.77	100	0.107799909
B2	40.89	6.14	52.97	100	0.115914669
B3	62.24	4.36	33.4	100	0.130538922
B4	70.98	4.23	24.79	100	0.17063332
C1	25.21	8.36	66.42	100	0.125865703
C2	31.45	7.86	60.69	100	0.129510628
C3	68.75	4.79	26.46	100	0.181027967
C4	75.35	4.49	20.16	100	0.222718254
D1	28.06	9.09	62.84	100	0.144653087
D2	40.04	7.62	52.34	100	0.145586549
D3	73.06	4.75	22.2	100	0.213963964
D4	77.29	4.2	18.51	100	0.226904376
E1	39.87	7.74	52.38	100	0.147766323
E2	62.88	4.99	32.13	100	0.155306567
E3	77.02	3.82	19.17	100	0.199269692
E4	79.97	3.68	16.35	100	0.225076453

S9. UV/vis transmittance spectra of large area film