Electronic Supplementary Information

Synthesis and characterization of zinc di(*O*-2,2-dimethylpentan-3-yl dithiocarbonates) bearing pyridine or tetramethylethylenediamine coligands and investigation of their thermal conversion mechanisms towards nanocrystalline zinc sulfide

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^{13}C-NMR

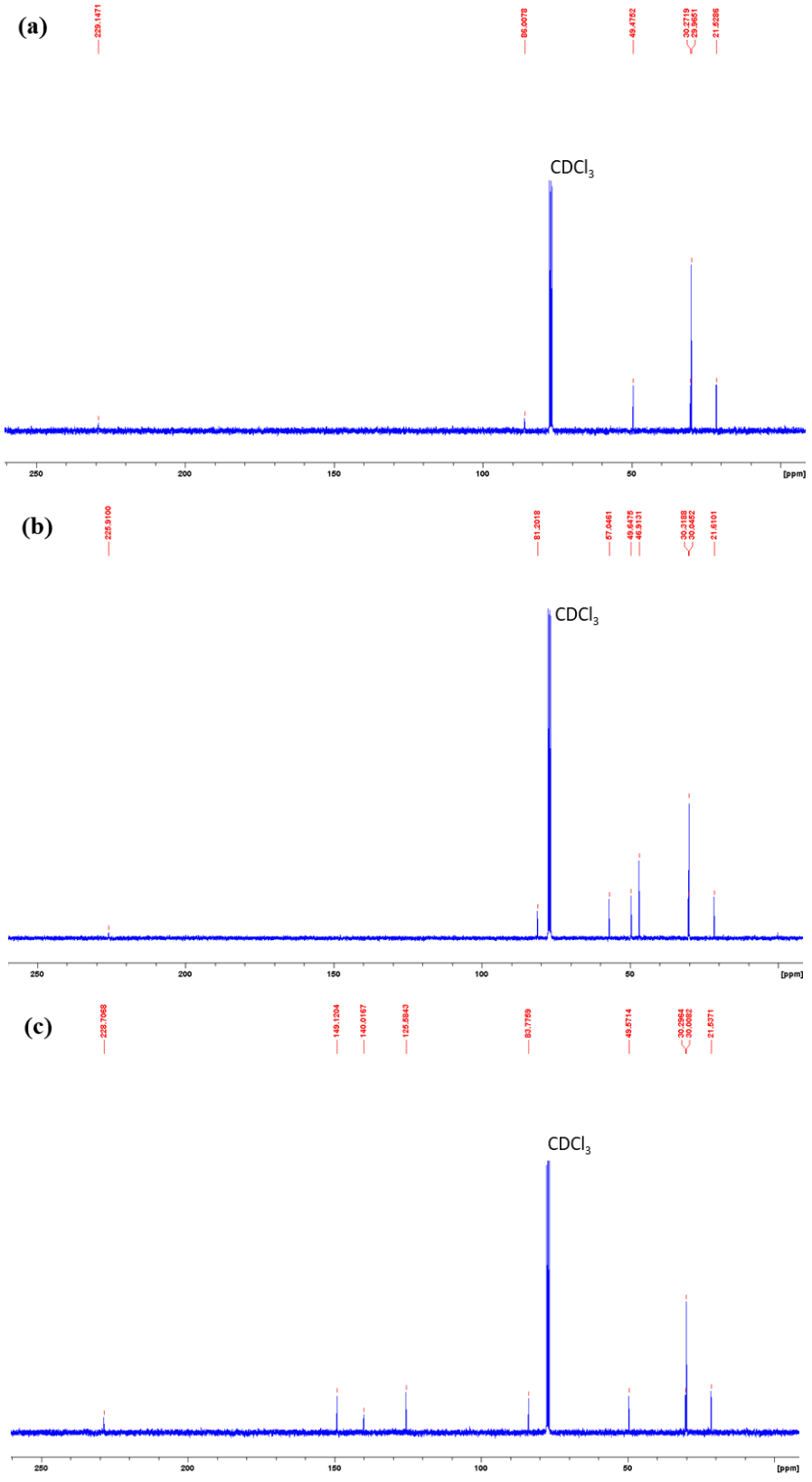

Fig. S1 ^{13}C- NMR spectra of **(a)** ZnHep, **(b)** ZnHepTMEDA and **(c)** ZnHepPyr.

^{1}H-NMR

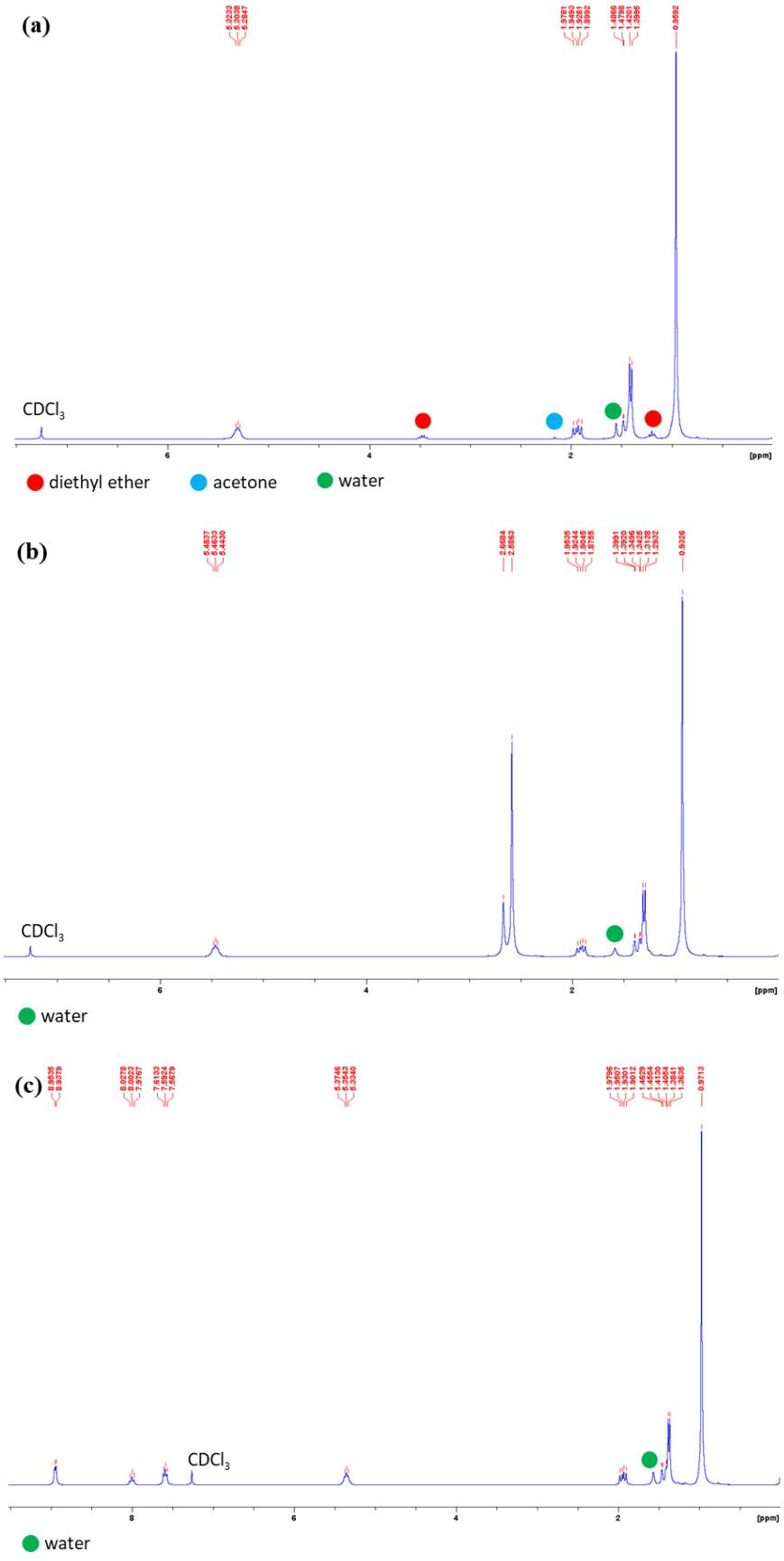

Fig. S2 ^{1}H- NMR spectra of (a) ZnHep, (b) ZnHepTMEDA and (c) ZnHepPyr.

Table S1 Assignment of the vibration bands of the zinc xanthate (ZnHep) and complexes (ZnHepTMEDA, ZnHepPyr)

Wavenumber (cm^{-1})			Assignment
ZnHep	**ZnHepTMEDA**	**ZnHepPyr**	
2966	2966	2964	ν_{as} CH (R-CH_3)
2875	2871	2873	ν_{s} CH (R-CH_3)
-	2801	-	ν_{s} CH, CH_3 (N-CH_3, N-CH_2)
-	-	1608	ν C=C
-	-	1483	ν C=N
1477	1477	1475	δ_{as} CH (R-CH_3),
1463	1461	1463	δ CH (-CH_2-) δ_{s} CH (N-CH_3, N-CH_2)
-	-	1444	ν C=N
1398	1393	1395	δ_{s} CH (R-CH_3)
1367	1365	1365	δ_{s} CH_3 (R(CH_3)$_3$)
1344	1330	1340	ω CH (-CH_2-)
-	1285	-	ν CN
1228	1224	1228	ν_{as} COC ($ROCS_2$)
1210	1171	1208	
1128	1122	1124	ρ CH_3, ν (S)CO, ν_{s} COC
1079	1081	1079	ν_{as} CCC
1057	1057	1059	ν_{as} SCS($ROCS_2$)
1034	1040	1038	ν C=S($ROCS_2$)

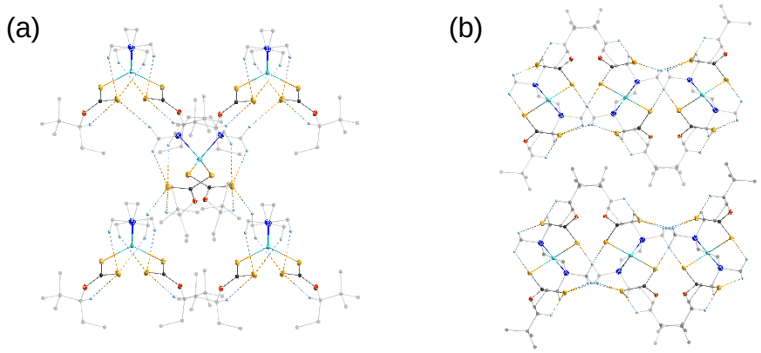

Fig. S3 (a) Offset view of the crystal packing diagram of ZnHepTMEDA along the a-axis. (b) View of the crystal packing diagram of ZnHepTMEDA forming the 2D sheets propagated by C–H···S hydrogen bonds. C–H···S hydrogen bonds highlighted by dashed bonds. All non-carbon atoms shown as 30% shaded ellipsoids. Hydrogen atoms not involved in interactions removed and carbon atoms grayed for clarity.

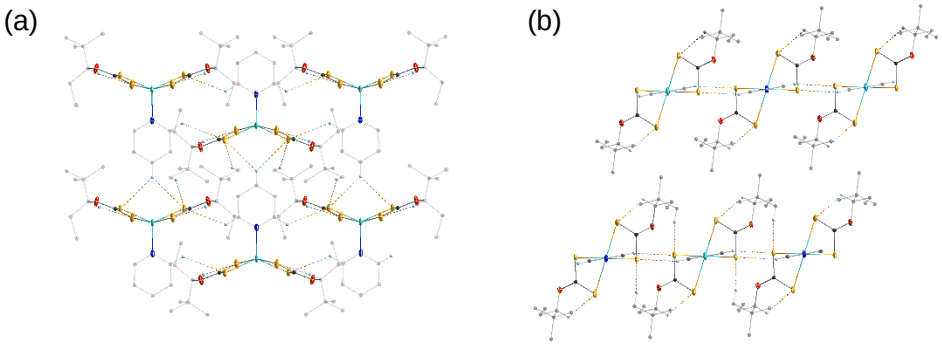

Fig. S4 (a) Offset view of the crystal packing diagram of ZnHepPyr along the a-axis. (b) View of the crystal packing diagram of ZnHepPyr forming the 2D sheets propagated by C–H···S hydrogen bonds. C–H···S hydrogen bonds highlighted by dashed bonds. All non-carbon atoms shown as 30% shaded ellipsoids. Hydrogen atoms not involved in interactions removed and carbon atoms grayed for clarity.

Table S2 List of bond lengths and angles for intra- and intermolecular secondary interactions in ZnHepTMEDA and ZnHepPyr

	Space Group	**Intramolecular Bonds (C—H···S) (Å)**	**Hydrogen (°)**	**Intermolecular Bonds (C—H···S) (Å)**	**Hydrogen (°)**
ZnHepTMEDA	*Pbcn*	2.52 (H2···S2) 2.84 (H9*B*···S2^{i}) 2.99 (H11*C*···S2^{i}) 3.02 (H11*A*···S1)	114 135 135 111	2.93 (H11*B*···S2^{ii})	151
ZnHepPyr	*C2/c*	2.54 (H2···S2)	115	2.96 (H5C···S1^{iii}) 2.96 (H11···S1) 3.02 (H9···S1^{iv})	150 134 127

Symmetry codes: (i) -*x*, *y*, -*z*+1/2; (ii) *x*+1/2, *y*-1/2, -*z*+1/2; (iii) -*x*, -*y*, -*z*; (iv) *x*, -*y*+1, *z*-1/2

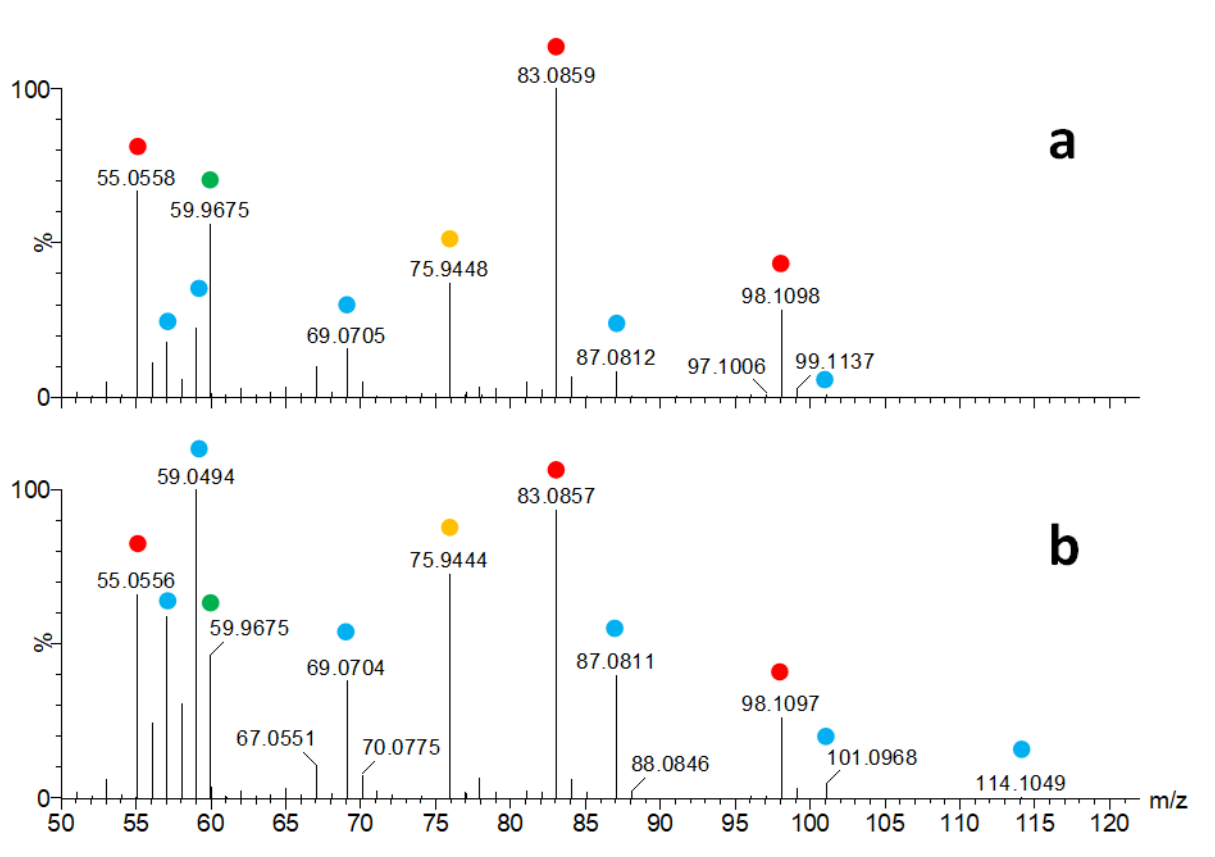

Fig. S5 DI/EI mass spectra showing volatile products formed during thermal decomposition of KHep (● 4,4-Dimethyl-2-pentene: M^+, C_7H_{14}, m/z_{calc}=98.1096Da; $[M\text{-}CH_3]^+$, C_6H_{11}, m/z_{calc}=83.0861Da; $C_4H_7^+$, m/z_{calc}=55.0548Da; relative intensities agree well to Wiley/NIST library spectra. ● COS: M^+, m/z_{calc}=59.9670Da. ● 2,2-Dimetyl-3-pentanol: M^+ not observed; $[M\text{-}2H]^+$, $C_7H_{14}O$, m/z_{calc}=114.1045Da; $[M\text{-}CH_3]^+$, $C_6H_{13}O$, m/z_{calc}=101.0966Da; $[M\text{-}C_2H_5]^+$, $C_5H_{11}O$, m/z_{calc}=87.0810Da; $C_5H_9^+$, m/z_{calc}=69.0704Da; $C_3H_7O^+$, m/z_{calc}=59.0497Da; $C_4H_9^+$, m/z_{calc}=57.0704Da; rel. intensities agree to Wiley/NIST spectra. ● CS_2: M^+, m/z_{calc}=75.9441Da). (**a**) Approx. 20% and (**b**) 80% thermal decomposition, respectively.

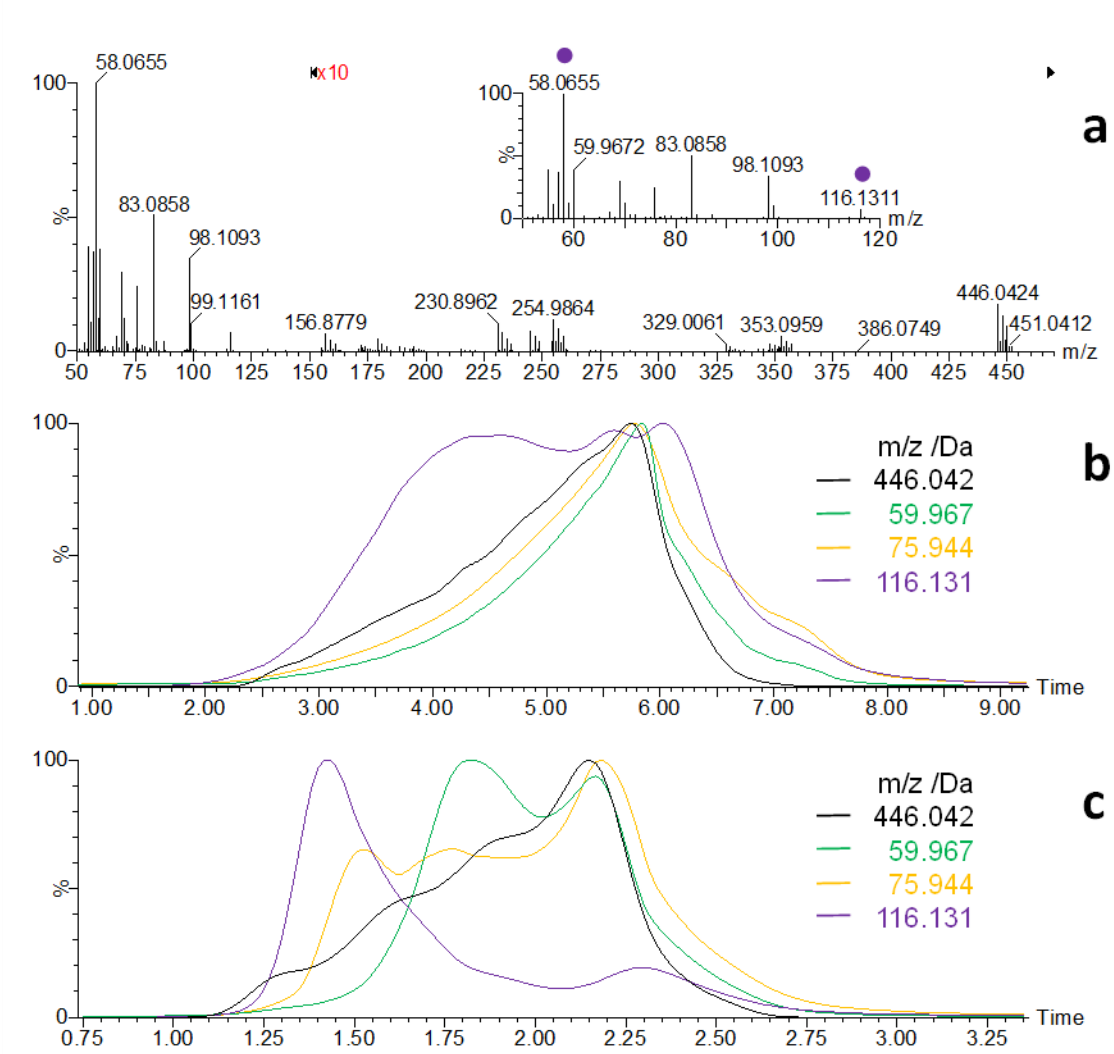

Fig. S6 DI/EI mass spectrometry of ZnHepTMEDA. (**a**) Mass spectrum after approx. 30% thermal decomposition / evaporation showing M^+ ion of ZnHep at m/z=446.0424Da (compare Fig. S4a) due to thermally triggered loss of TMEDA prior evaporation. Inset: expanded view of the low mass region showing xanthate decomposition products (compare Fig. S5) as well as TMEDA (● M^+, $C_6H_{16}N_2$, m/z_{calc}=116.1313Da; $[M\text{-}C_3H_8N]^+$, C_3H_8N, m/z_{calc}=58.0657Da). (**b**) Normalized extracted ion chromatograms at a heating rate of 20 and (**c**) 100 °C/min, respectively (M^+ of ZnHep, 446.042Da; M^+ of COS, 59.967Da; M^+ of CS_2, 75.994Da, M^+ of TMEDA, 116.131Da).

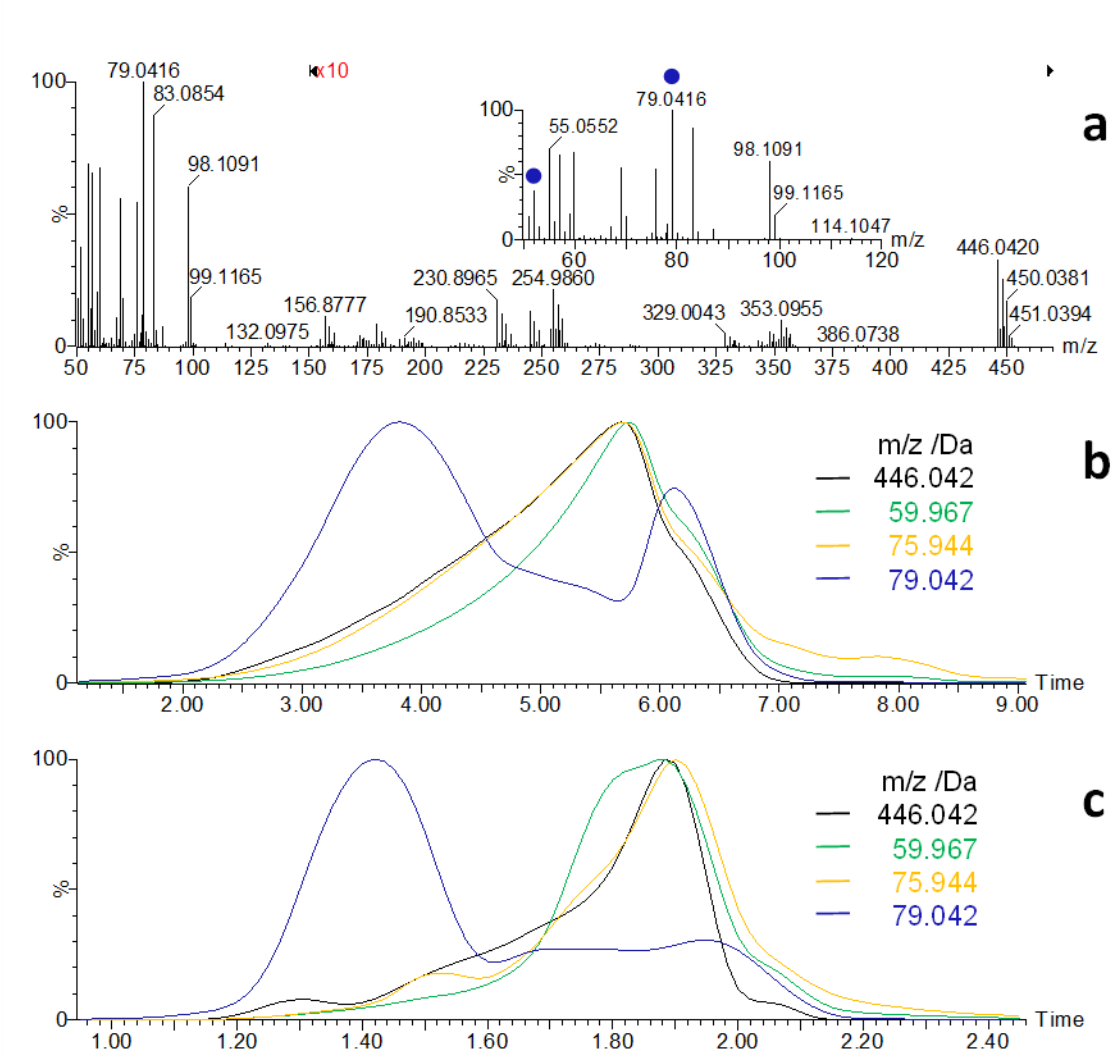

Fig. S7 DI/EI mass spectrometry of ZnHepPyr. (**a**) Mass spectrum after approx. 40 % thermal decomposition / evaporation showing M^+ of ZnHep at m/z=446.0420Da (compare Fig. S4a) due to thermally triggered loss of pyridine prior evaporation. Inset: expanded view of the low mass region showing xanthate decomposition products (compare Fig. S5) as well as pyridine (● M^+, C_5H_5N, m/z_{calc}=79.0422Da; $C_4H_4^+$, m/z_{calc}=52.0313Da). (**b**) Normalized extracted ion chromatograms at a heating rate of 20 and (**c**) 100 °C/min, respectively (M^+ of ZnHep, 446.042Da; M^+ of COS, 59.967Da; M^+ of CS_2, 75.994Da, M^+ of pyridine, 79.042Da).