Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

One-pot synthesis of ultrastable pentanuclear alkylzinc complexes

Hana Bunzen,* Maciej Grzywa, Andreas Kalytta-Mewes, Dirk Volkmer

Chair of Solid State and Materials Chemistry, Institute of Physics, University of Augsburg, Universitätsstraße 1, D-86159 Augsburg, Germany

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Characterization of complexes 1 and 2

A) NMR

Compound **1**:
^{1}H NMR (400 MHz, $CDCl_3$, 20˚C): δ = 7.78 (s, 12H, $H_{arom.}$), 7.37 (s, 6H, $H_{benzene}$), 2.35 (s, 36H, H_{Me}), 1.86 (t, 12H, J=8.1 Hz, $H_{Zn\text{-}Et}$), 1.19 (q, 8H, J=8.1 Hz, $H_{Zn\text{-}Et}$).
^{13}C NMR (100 MHz, $CDCl_3$, 20˚C): δ = 141.76 ($C_{arom.}$), 136.07 ($C_{arom.}$), 128.32 ($C_{benzene}$), 115.04 + 114.94 ($C_{arom.}$), 20.84 + 20.77 (C_{Me}), 13.29 ($C_{Zn\text{-}Et}$), -1.95 ($C_{Zn\text{-}Et}$).

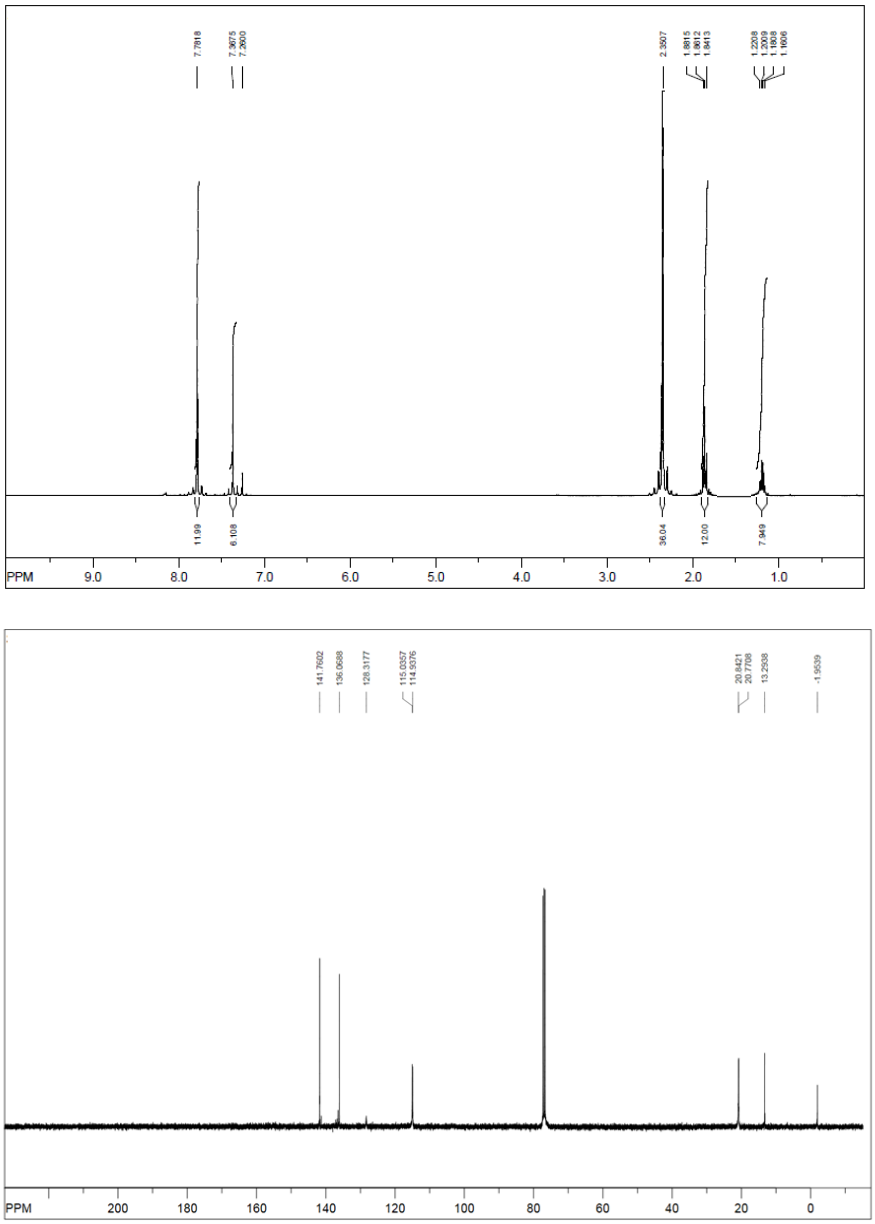

Figure S1. ^{1}H and ^{13}C NMR spectra of $[Zn_5Et_4(Me_2bta)_6]$ (**1**) in $CDCl_3$.

Compound **2**:
^{1}H NMR (400 MHz, $CDCl_3$, 20˚C): δ = 7.76 (s, 12H, $H_{arom.}$), 2.32 (s, 36H, H_{Me}), 0.26 (s, 12H, $H_{Zn\text{-}Me}$).
^{13}C NMR (100 MHz, $CDCl_3$, 20˚C): δ = 141.82 ($C_{arom.}$), 136.00 ($C_{arom.}$), 115.01 + 114.91 ($C_{arom.}$), 20.76 + 20.69 (C_{Me}), -14.70 + (-14.74) ($C_{Zn\text{-}Me}$).

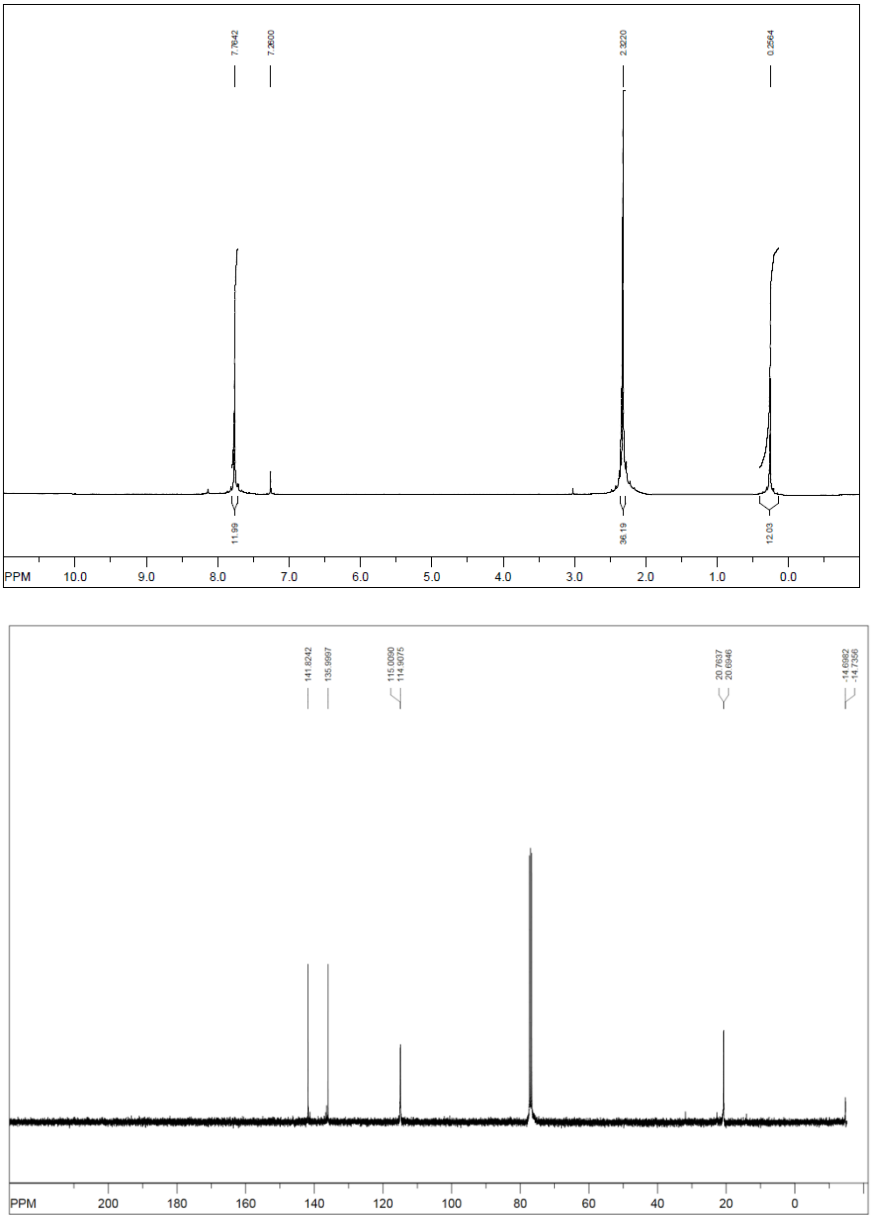

Figure S2. ^{1}H and ^{13}C NMR spectra of $[Zn_5Me_4(Me_2bta)_6]$ (**2**) in $CDCl_3$.

B) IR

Compound **1**:
2973 (CH_3, m), 2929 (CH_3, m), 2852 (CH_2, m), 1575 (w), 1465 (m), 1450 (m), 1375 (w), 1294 (w), 1197 (s), 1170 (s), 1025 (w), 1001 (s), 850 (s), 826 (m), 688 (m), 674 (s), 598 (s), 495 (s), 465 (m), 436 (m) cm^{-1}.

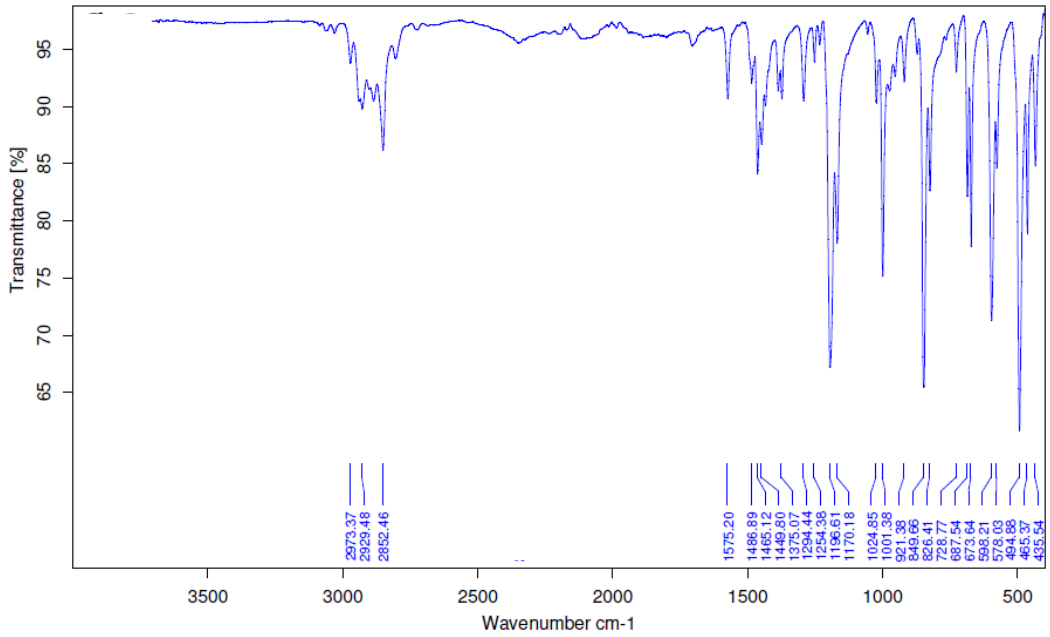

Figure S3. IR spectrum of $[Zn_5Et_4(Me_2bta)_6]$ (**1**).

Compound **2**:
2931 (CH_3, m), 2906 (CH_3, m), 1574 (w), 1464 (m), 1452 (m), 1376 (w), 1294 (w), 1198 (s), 1165 (s), 1025 (w), 1001 (s), 852 (s), 827 (m), 658 (s), 531 (m), 497 (s), 466 (m), 437 (m) cm^{-1}.

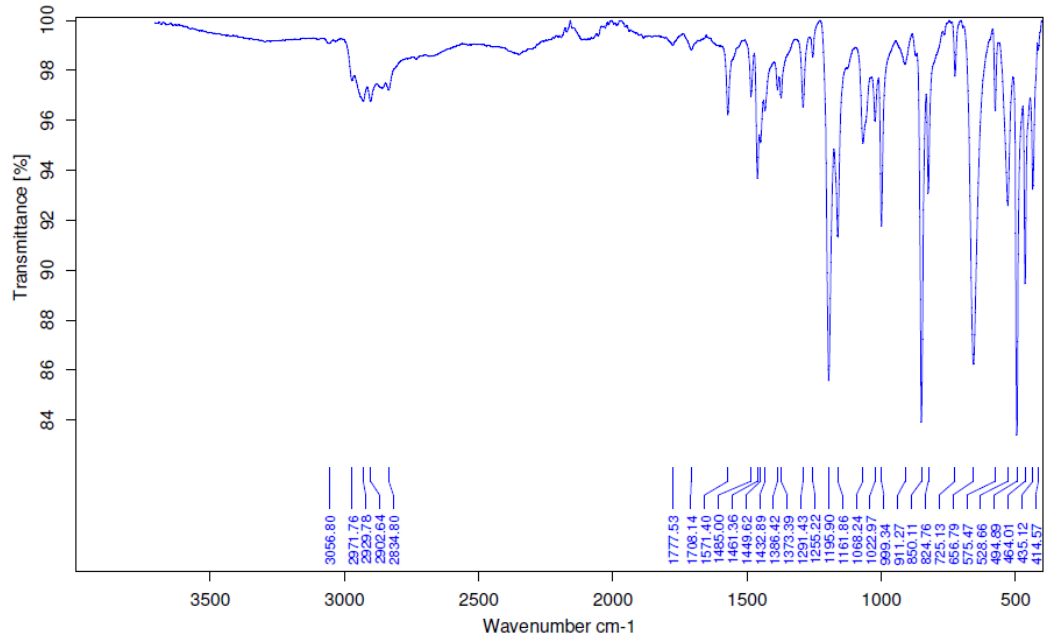

Figure S4. IR spectrum of $[Zn_5Me_4(Me_2bta)_6]$ (**2**).

C) MS

Measurement details: The samples were injected into the ESI source with a flow rate of 8 µL/min and measured in an ESI positive mode. The ion-source voltage was 3.20-3.80 kV for capillary and 60-100 V for cone voltage. The collision energy was set to 16-20.0 eV. The spectra are an average of spectra collected within 2 min. The mass spectra were externally calibrated using phosphoric acid. The composition of the ions was verified by a comparison between experimental and theoretical mass values and isotopic distributions.

Compound **1**:
ESI-MS (m/z): 1343.22 $[M+Na]^+$

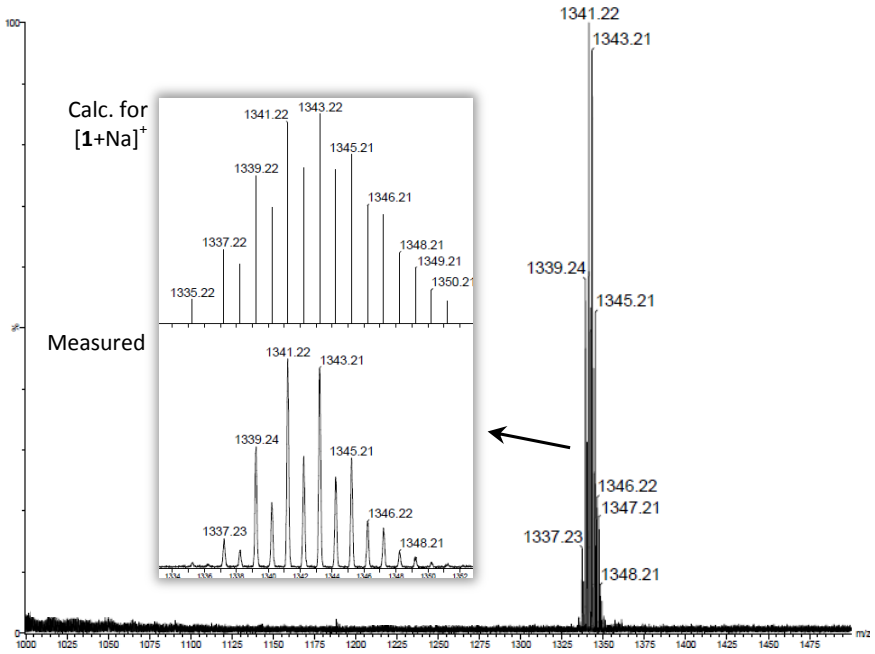

Figure S5. MS spectrum of $[Zn_5Et_4(Me_2bta)_6]$ (**1**).

Compound **2**:
ESI-MS (m/z): 1287.16 $[M+Na]^+$

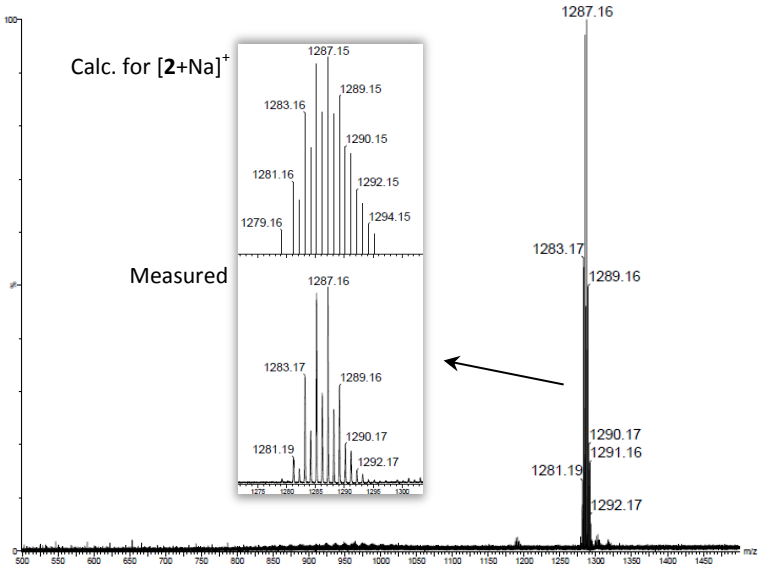

Figure S6. MS spectrum of $[Zn_5Me_4(Me_2bta)_6]$ (**2**).

D) XRPD

Compound **1**:

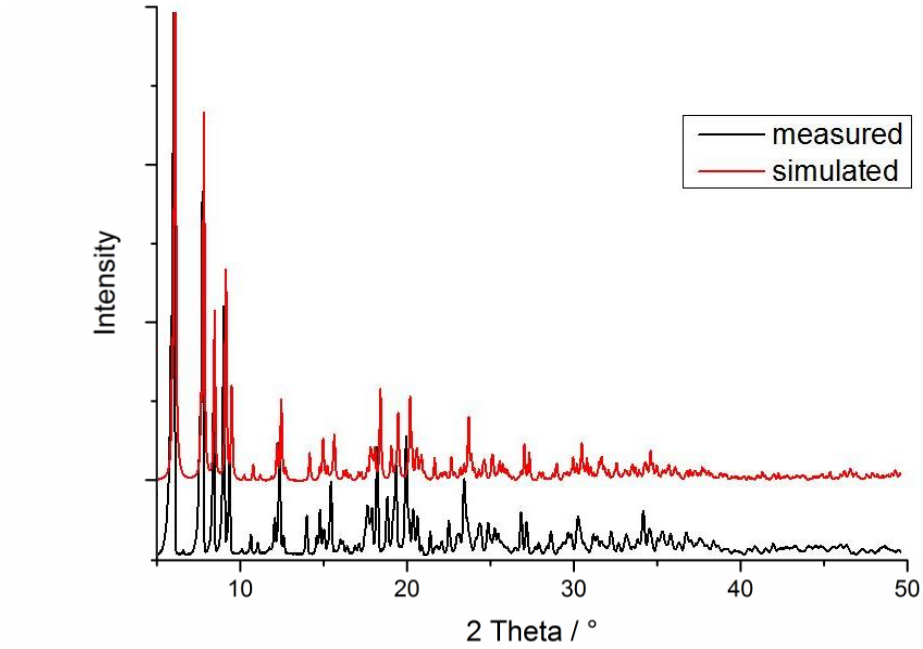

Figure S7. XRPD pattern of $[Zn_5Et_4(Me_2bta)_6]$ (**1**). The simulated powder pattern was created on the basis of the single-crystal X-ray diffraction data of **1** using program Mercury.[1]

Compound **2**:

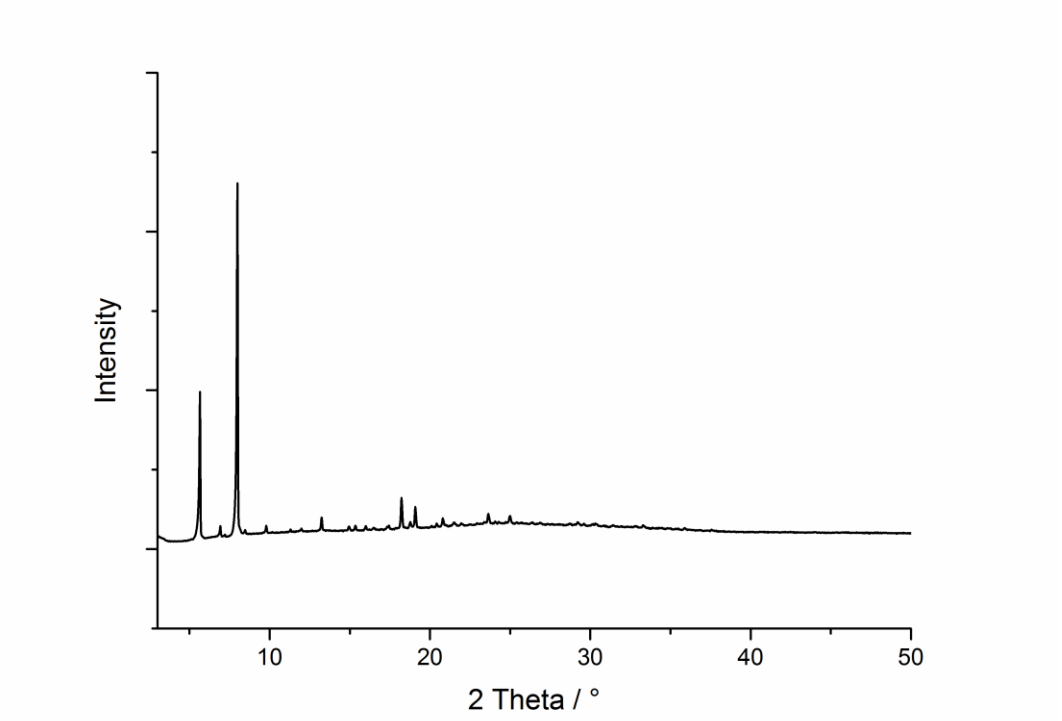

Figure S8. XRPD pattern of $[Zn_5Et_4(Me_2bta)_6]$ (**2**).

Thermal stability

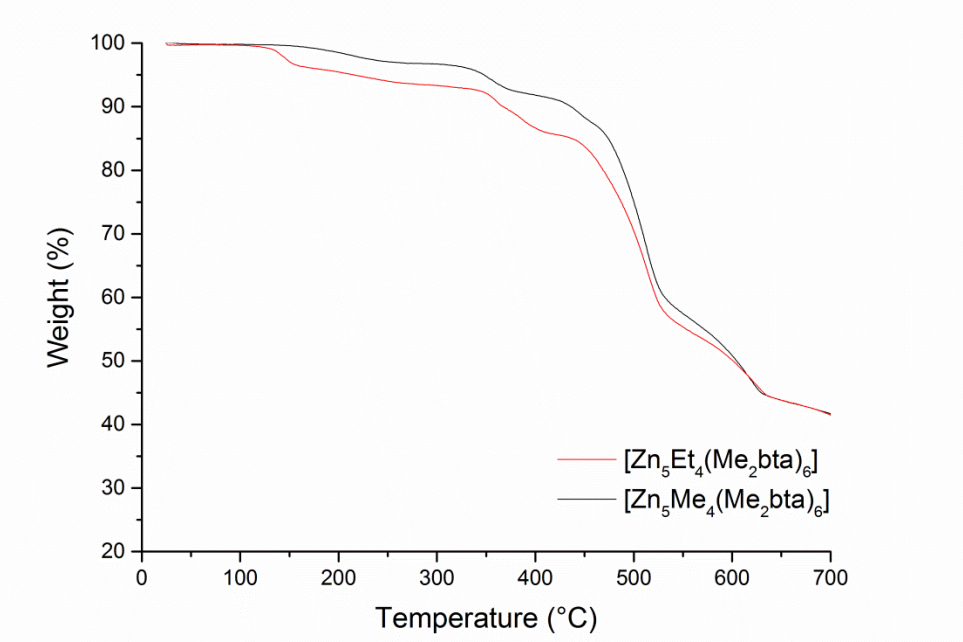

Figure S9. Comparison of thermal stability of complex **1** (red) and **2** (black) by TG analysis under N_2 flow.

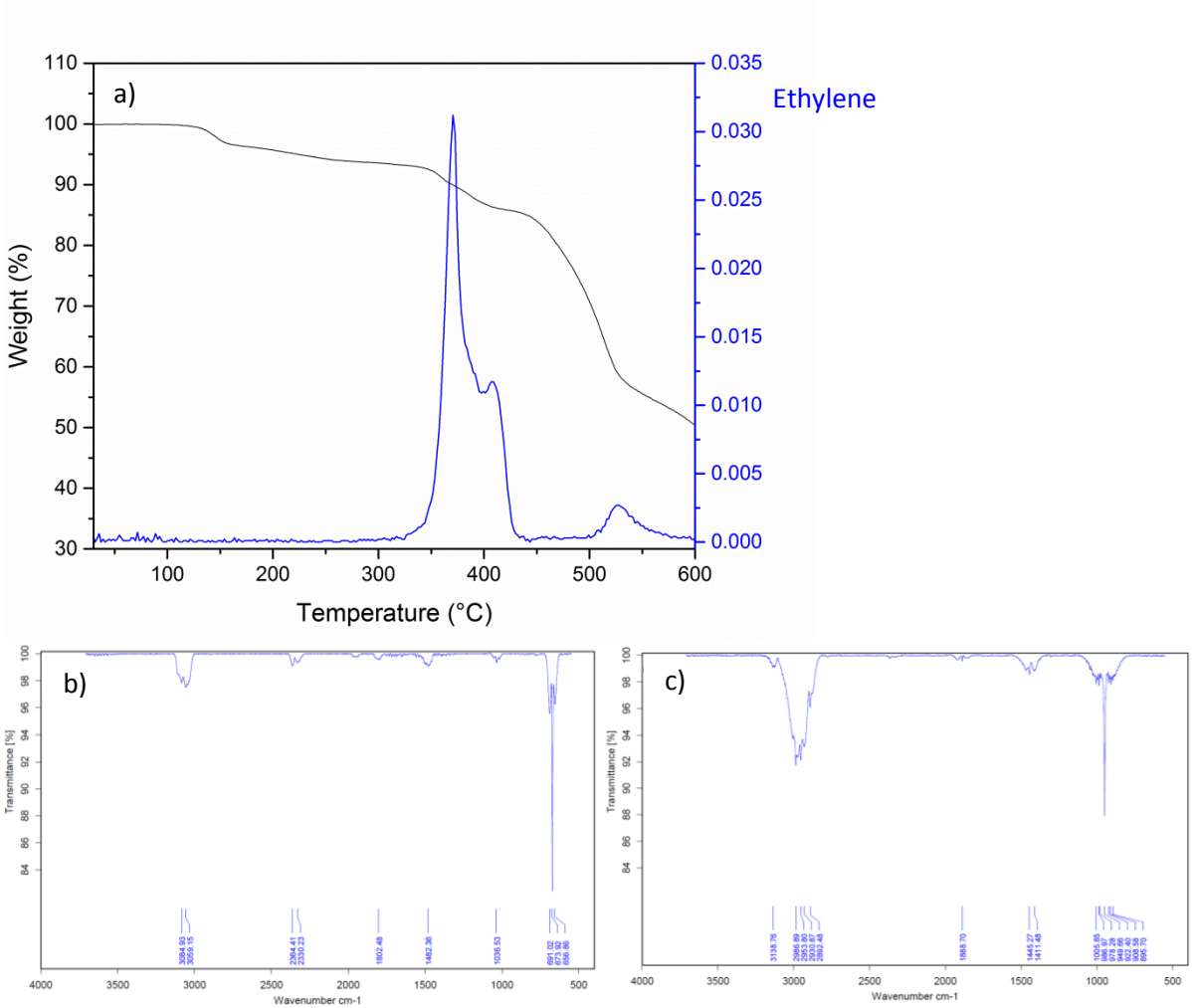

Figure S10. IR-TG analysis of $[Zn_5Et_4(Me_2bta)_6]$ (**1**, a), and IR spectra of (b) benzene detected by the IR-TG analysis in a gas phase at 138 °C and (c) ethylene detected in a gas phase at 355 °C.

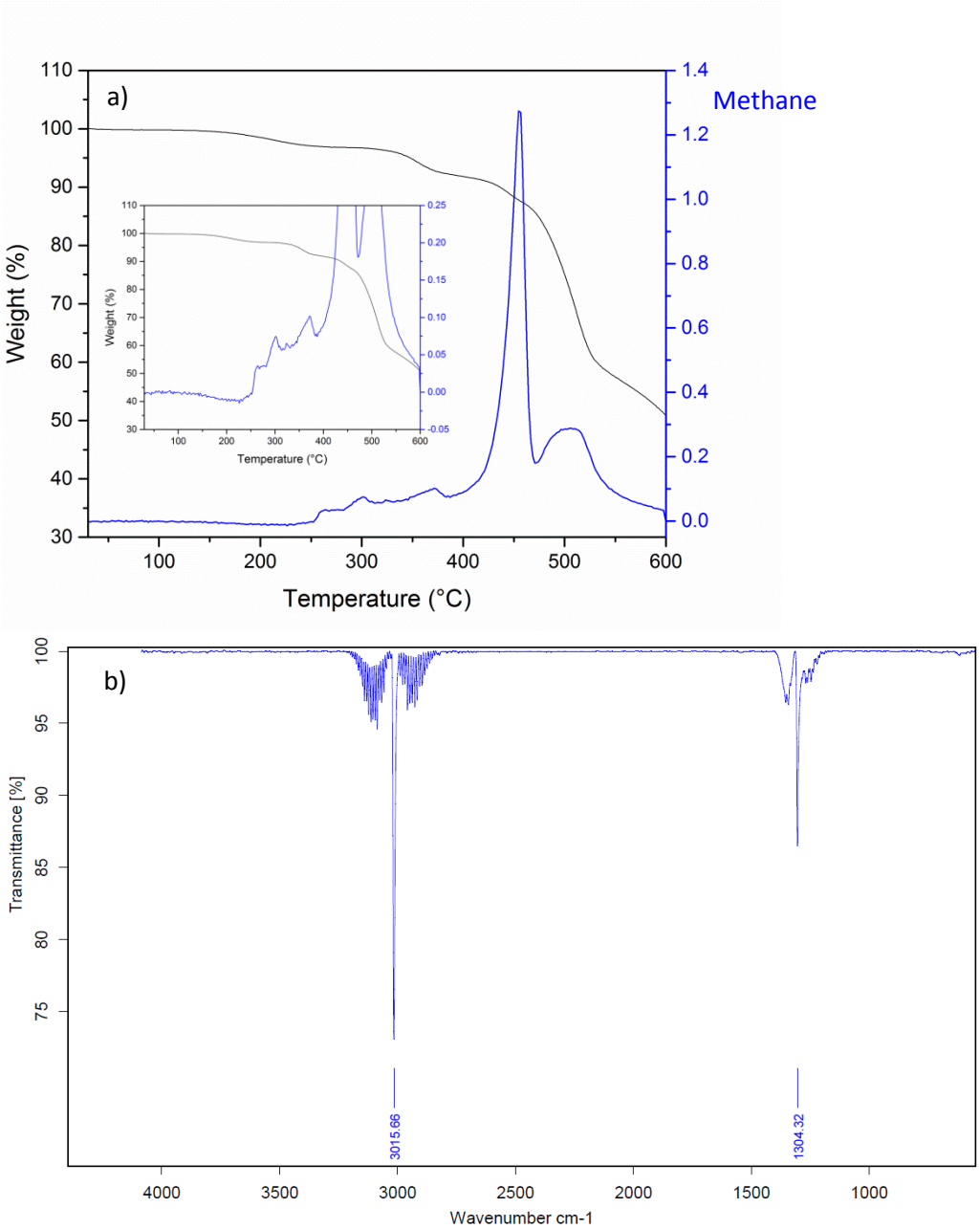

Figure S11. IR-TG analysis of $[Zn_5Me_4(Me_2bta)_6]$ (**2**, a), and IR spectra of (b) methane detected by the IR-TG analysis in a gas phase at 302 °C.

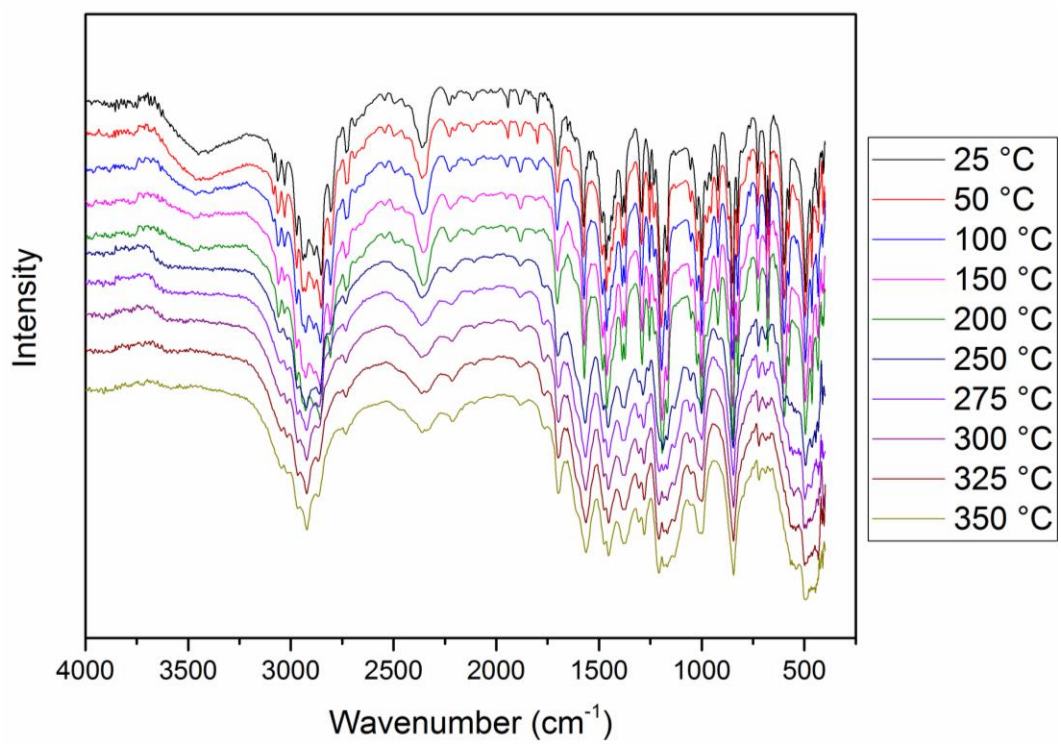

Figure S12. VT-DRIFT spectra of $[Zn_5Et_4(Me_2bta)_6]$ (**1**).

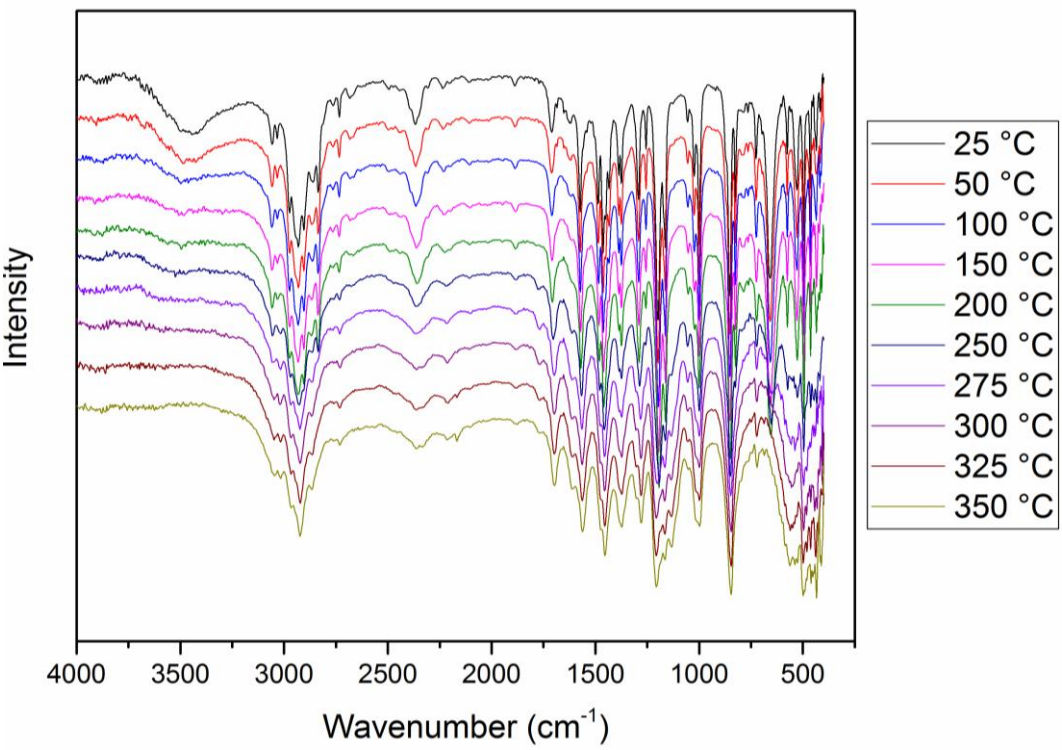

Figure S13. VT-DRIFT spectra of $[Zn_5Me_4(Me_2bta)_6]$ (**2**).

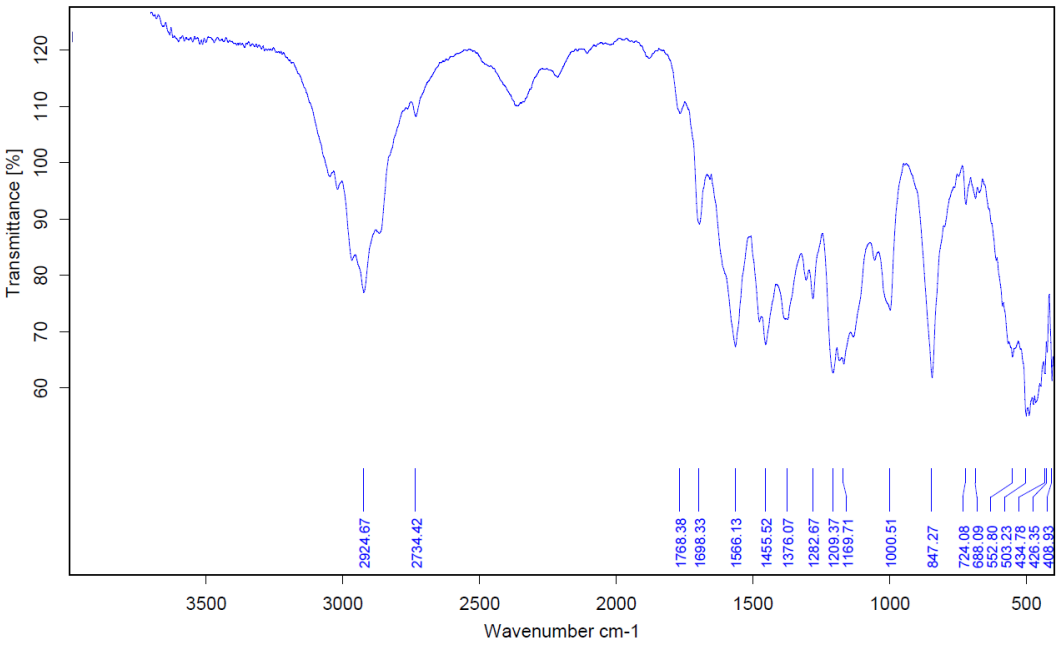

Figure S14. DRIFT spectrum of compound **1** at 300 °C.

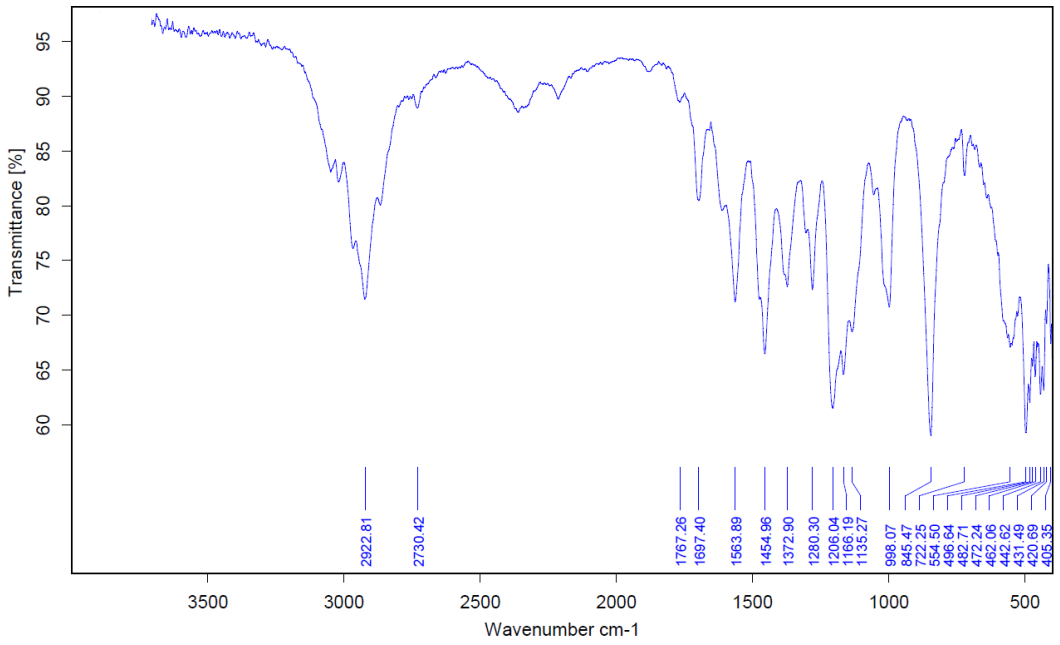

Figure S15. DRIFT spectrum of compound **2** at 300 °C.

Chemical stability

A) Stability in water:

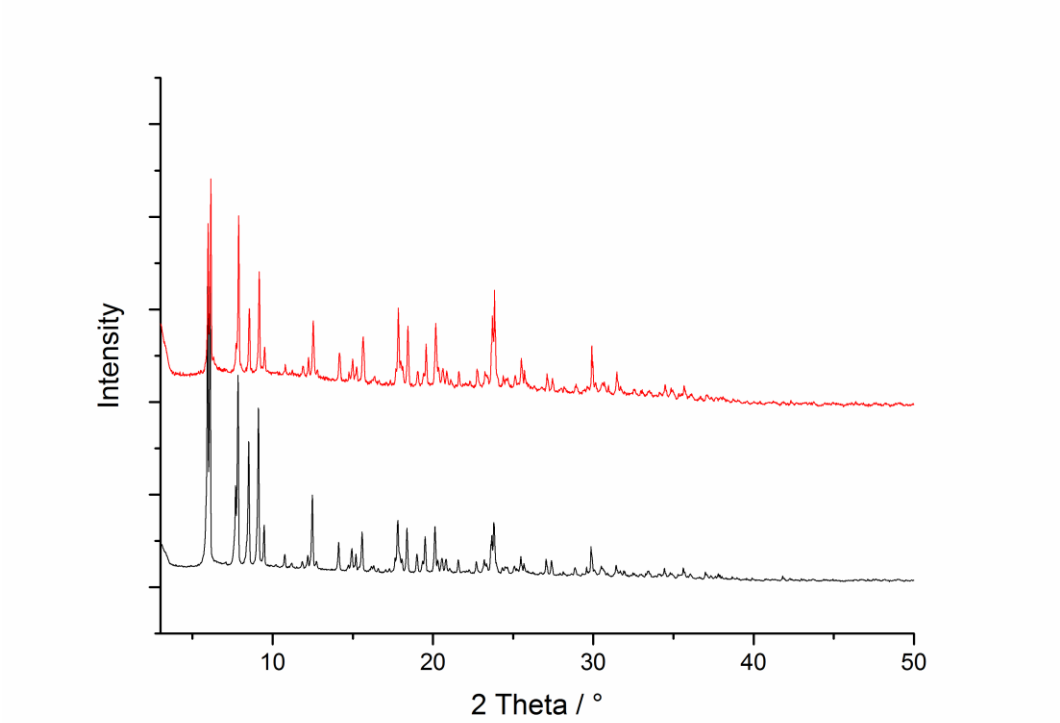

Figure S16. XRPD patterns of $[Zn_5Et_4(Me_2bta)_6]$ (**1**) before (black) and after (red) being dispersed in water for one week.

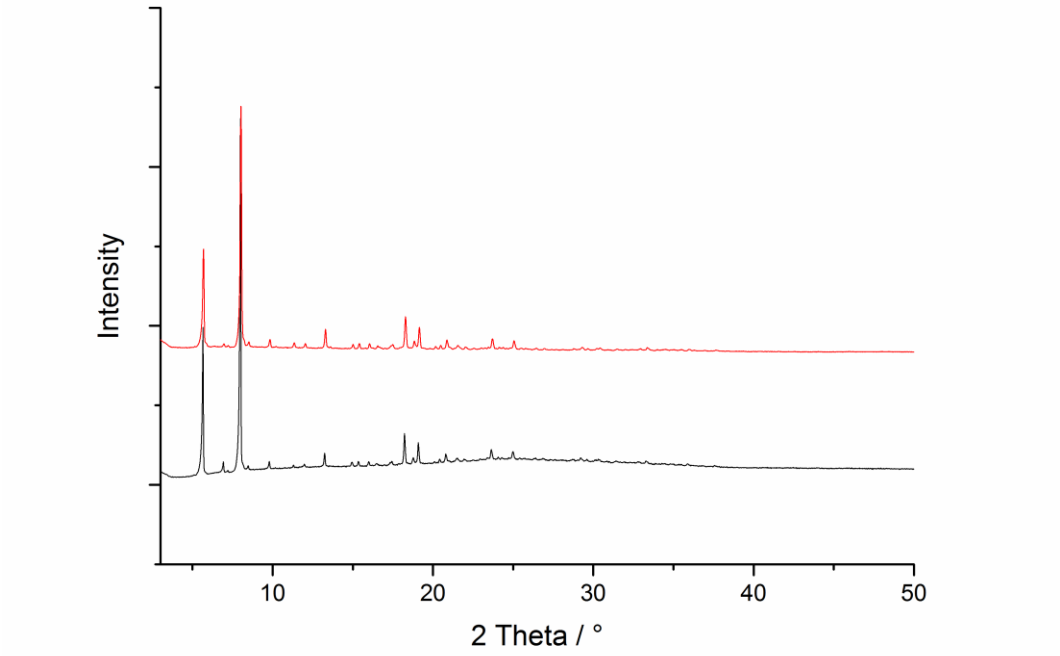

Figure S17. XRPD patterns of $[Zn_5Me_4(Me_2bta)_6]$ (**2**) before (black) and after (red) being dispersed in water for one week.

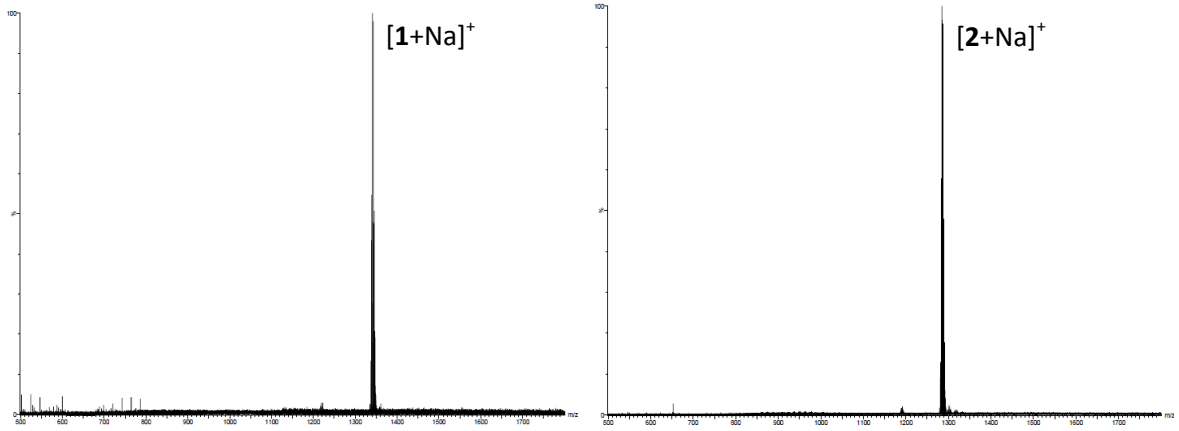

Figure S18. MS spectra of **1** (left) and **2** (right) after being dispersed in water for one week.

B) Reaction with benzaldehyde in $CDCl_3$:

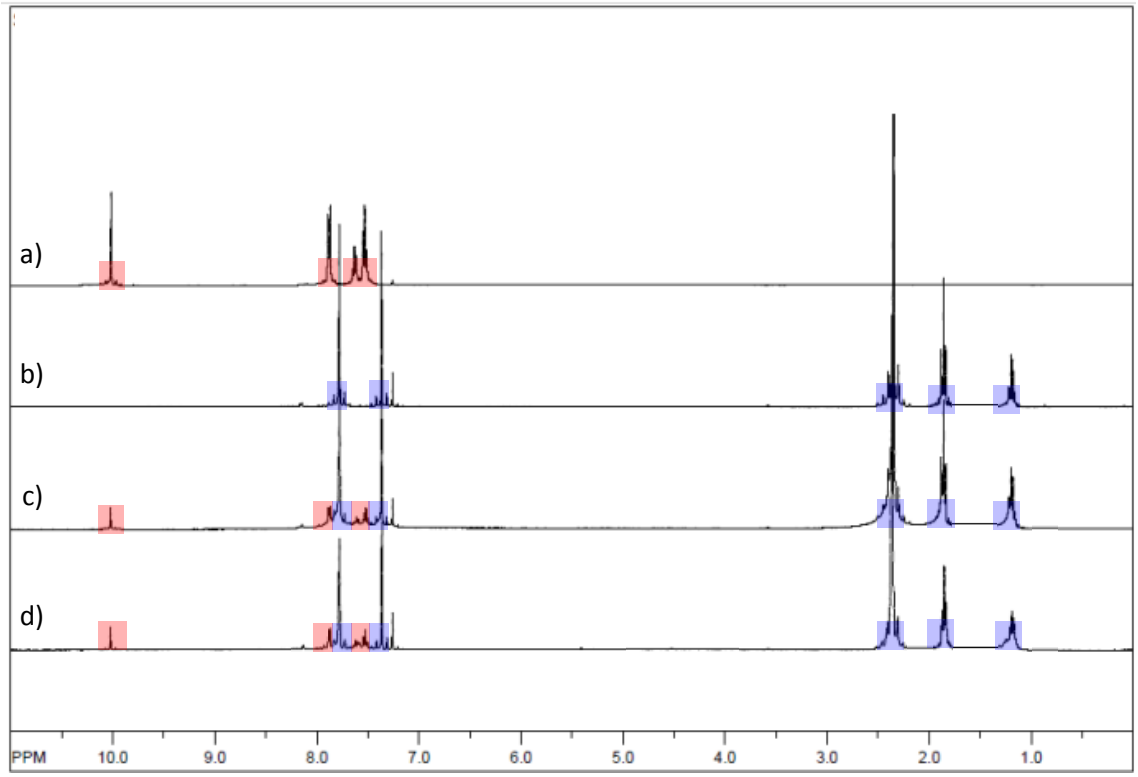

Figure S19. NMR spectra of benzaldehyde (a), complex **1** (b), and their mixture (1:1 molar ratio) in deuterated chloroform after 1 h (c) and 3 days (d) after mixing the components. Signals corresponding to benzaldehyde are marked in red color, signals corresponding to complex **1** are marked in blue.

C) Reaction with trifluoroacetic acid-d_1 in $CDCl_3$:

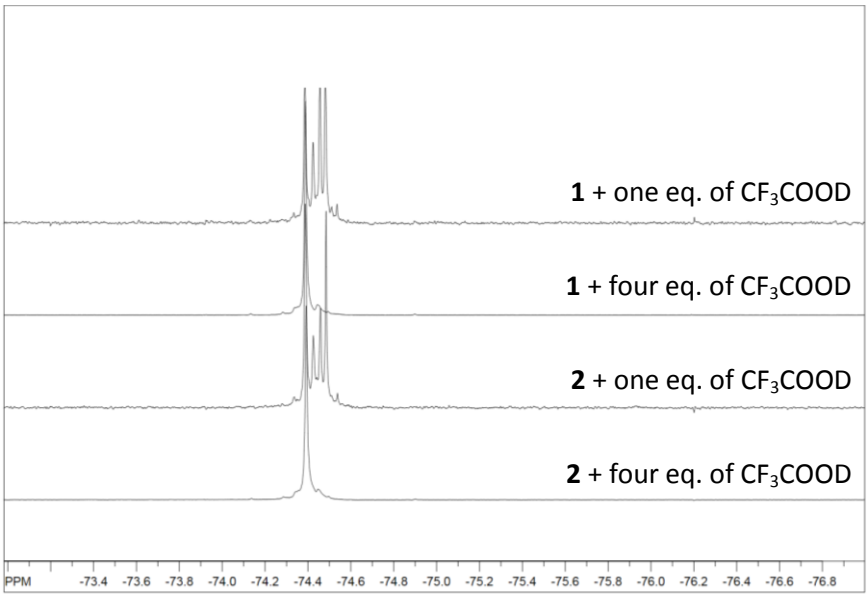

Figure S20. ^{19}F NMR spectra of complexes **1** and **2** upon mixing with one and four molar equivalents of trifluoroacetic acid in $CDCl_3$.

Compound **4**:
^{1}H NMR (400 MHz, $CDCl_3$, 20˚C): δ = 7.87 (s, 12H, $H_{arom.}$), 7.36 (s, 6H, $H_{benzene}$), 2.40 (s, 36H, H_{Me}), 0.86 (s, H_{ethane}); ^{13}C NMR (100 MHz, $CDCl_3$, 20˚C): δ = 164.00 + 163.62 (C_{COO}), 141.04 ($C_{arom.}$), 139.22 ($C_{arom.}$), 128.32 ($C_{benzene}$), 118.07 (C_{CF3}), 114.84 + 114.75 ($C_{arom.}$), 21.00 + 20.92 (C_{Me}); ^{19}F NMR (376 MHz, $CDCl_3$, 20˚C): δ = -74.40.
IR: 2928 (CH_3, w), 1688 (COO asym. stretch, bs), 1573 (w), 1490 (w), 1462 (m), 1431 (COO sym. stretch), 1376 (w), 1296 (w), 1195 (s), 1170 (s), 1145 (CF asym. stretch, s), 1025 (w), 1002 (m), 851 (s), 832 (m), 795 (m), 728 (m), 498 (s), 469 (m), 435 (m) cm^{-1}.
ESI-MS (m/z): 1612.00 $[M\text{-}CO_2]^+$, 1688.00 $[M+MeOH+D]^+$.

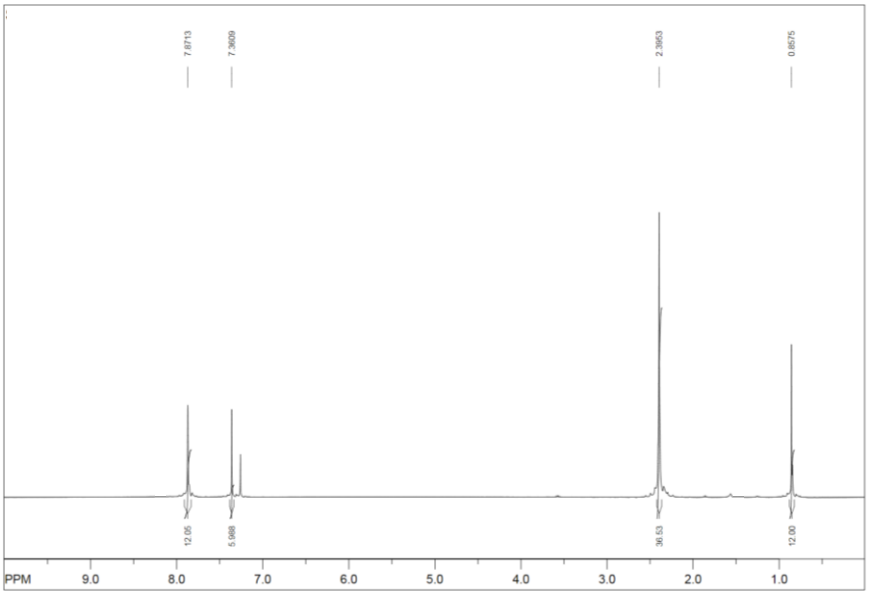

Figure S21. ^{1}H NMR spectrum of compound **4** which was prepared by a reaction of compound **1** with four molar equivalents of trifluoroacetic acid-d_1 in $CDCl_3$.

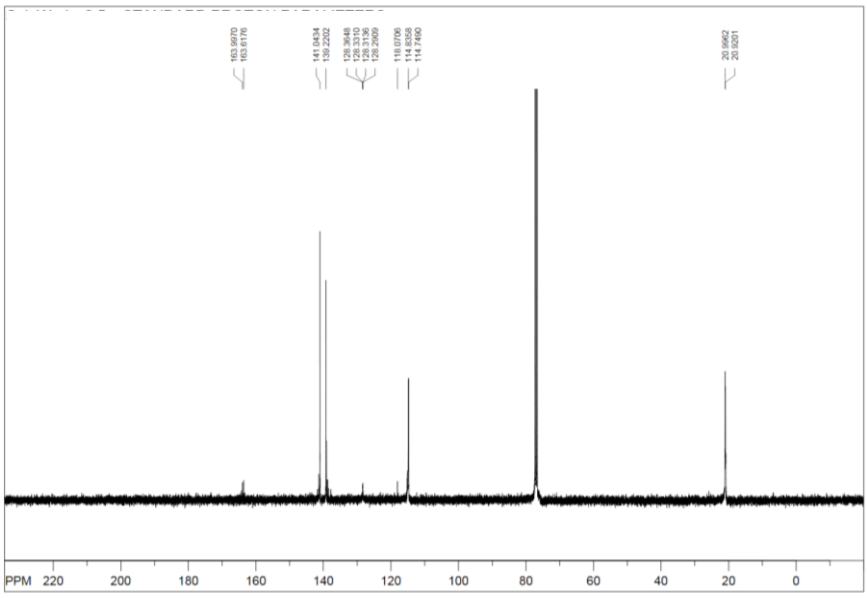

Figure S22. ^{13}C NMR spectrum of compound **4** which was prepared by a reaction of compound **1** with four molar equivalents of trifluoroacetic acid-d_1 in $CDCl_3$.

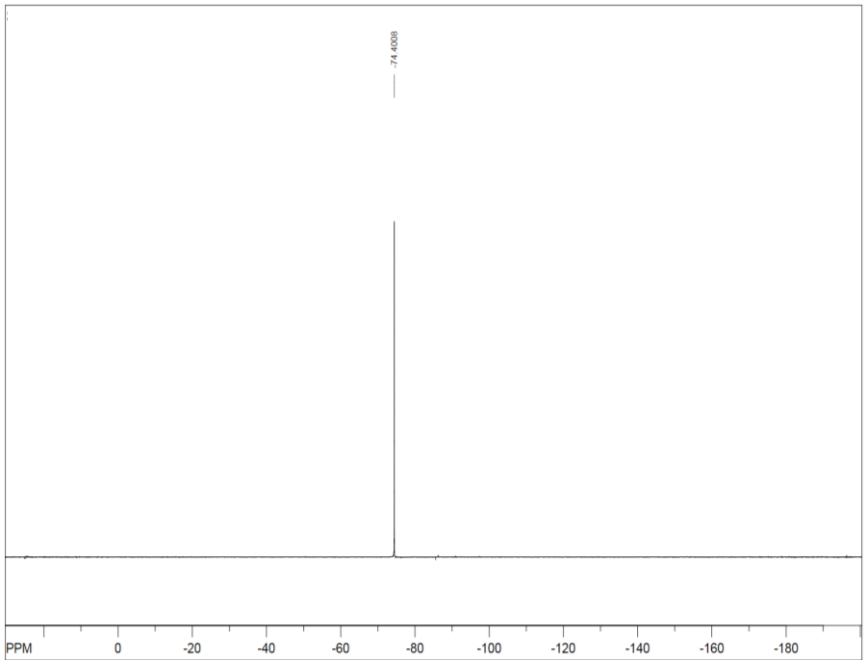

Figure S23. ^{19}F NMR spectrum of compound **4** which was prepared by a reaction of compound **1** with four molar equivalents of trifluoroacetic acid-d_1 in $CDCl_3$.

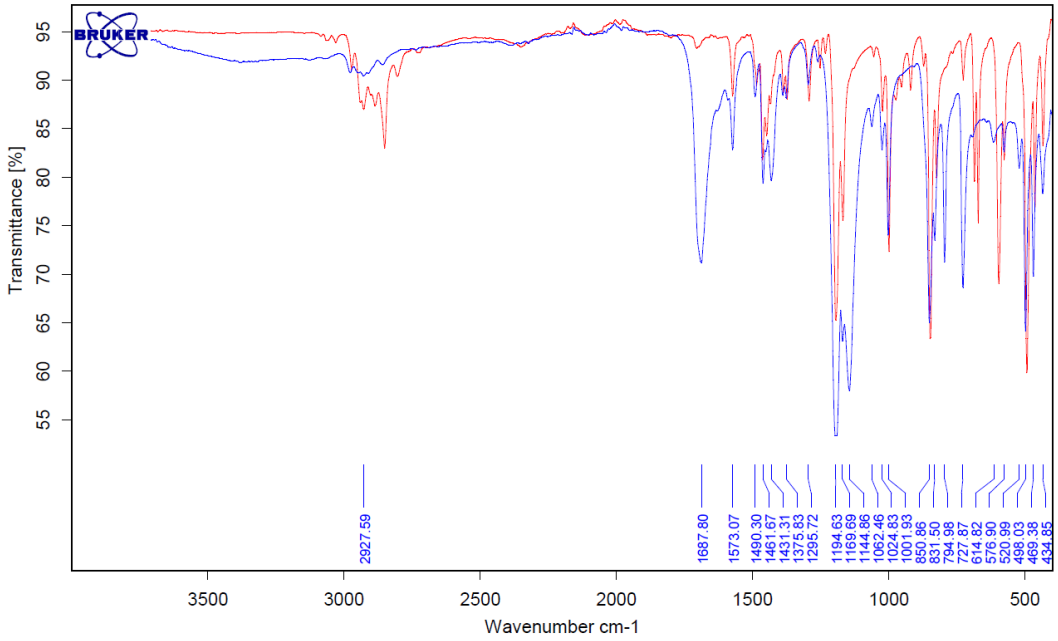

Figure S24. IR spectra of compound **1** (red) and compound **4** (blue).

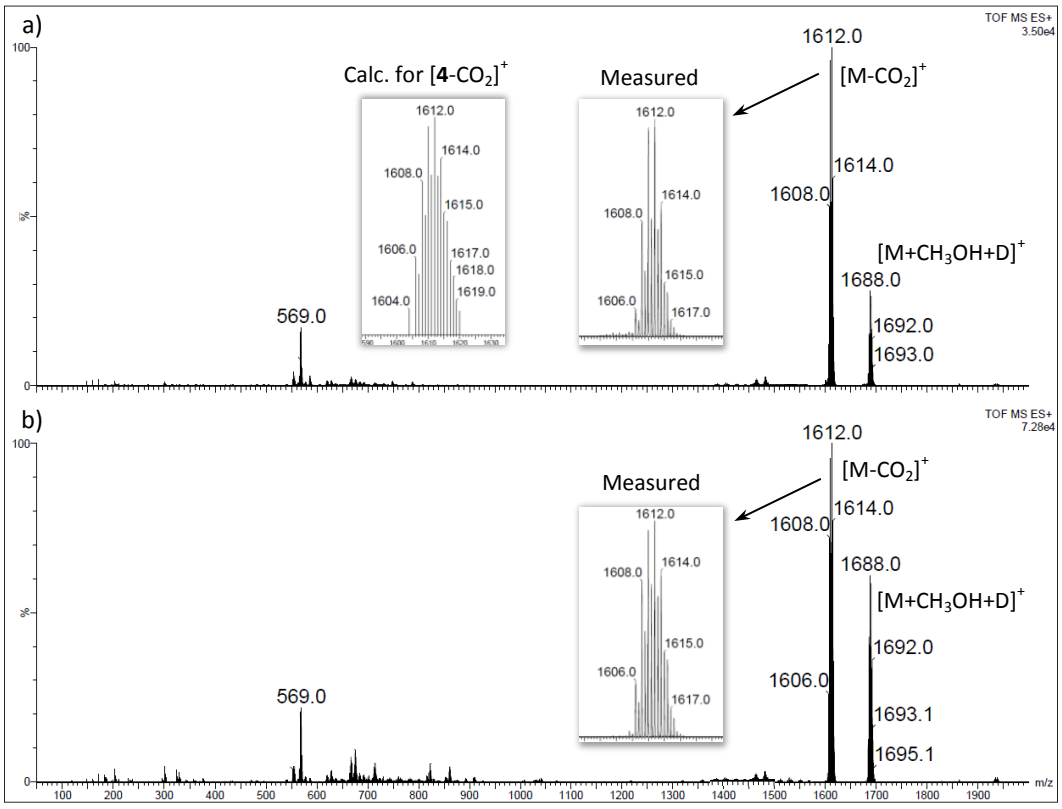

Figure S25. MS spectra of the product of the reaction of a) compound **1** with four molar equivalents of trifluoroacetic acid-d_1 and b) compound **2** with four molar equivalents of trifluoroacetic acid-d_1 measured in an ESI positive mode in a CH_3OH-$CDCl_3$ mixture (100:1).

Crystallographic analysis of complex 1

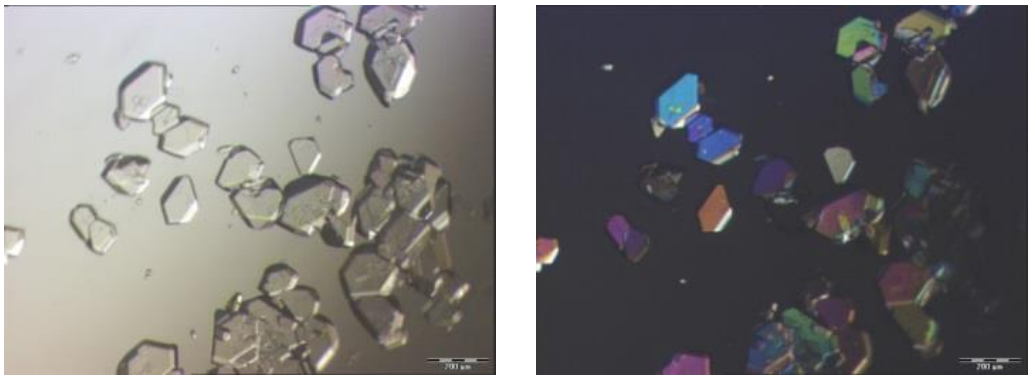

Figure S26. Optical microscope images of single crystals of **1** in non-polarized (left) and polarized light (right) (scale bar: 200 µm).

Table S1. Crystal data and structure refinement for compound **1** ($C_{56}H_{68}N_{18}Zn_5.C_6H_6$).

Empirical formula	C62 H74 N18 Zn5	
Formula weight	1398.24	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$ (no. 14)	
Unit cell dimensions	a = 15.2540(4) Å	α= 90°.
	b = 18.4800(5) Å	β= 104.1820(10)°.
	c = 23.6173(6) Å	γ = 90°.
Volume	6454.7(3) $Å^3$	
Z	4	
Density (calculated)	1.439 Mg/m^3	
Absorption coefficient	1.885 mm^{-1}	
F(000)	2888	
Crystal size	0.10 x 0.09 x 0.02 mm^3	
Theta range for data collection	2.25 to 27.94°.	
Index ranges	-20<=h<=20, -24<=k<=24, -30<=l<=31	
Reflections collected	180327	
Independent reflections	15462 [R(int) = 0.0689]	
Completeness to theta = 27.94°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15462 / 6 / 803	
Goodness-of-fit on F^2	0.937	
Final R indices [I>2sigma(I)]	R1 = 0.0285, wR2 = 0.0594	
R indices (all data)	R1 = 0.0464, wR2 = 0.0663	
Largest diff. peak and hole	0.471 and -0.308 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for compound **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zn(1)	7180(1)	5138(1)	8448(1)	11(1)
Zn(2)	5172(1)	5450(1)	7223(1)	14(1)
Zn(3)	6889(1)	3447(1)	9184(1)	14(1)
Zn(4)	9174(1)	5045(1)	7843(1)	15(1)
Zn(5)	7406(1)	6627(1)	9488(1)	13(1)
N(1)	5884(1)	3826(1)	8487(1)	14(1)
N(2)	6007(1)	4429(1)	8205(1)	13(1)
N(3)	5338(1)	4521(1)	7725(1)	14(1)
N(4)	7147(1)	4401(1)	9631(1)	14(1)
N(5)	7218(1)	5027(1)	9364(1)	13(1)
N(6)	7352(1)	5576(1)	9743(1)	14(1)
N(7)	7935(1)	3599(1)	8764(1)	14(1)
N(8)	8064(1)	4217(1)	8509(1)	13(1)
N(9)	8785(1)	4183(1)	8283(1)	15(1)
N(10)	5533(1)	6150(1)	7915(1)	14(1)
N(11)	6251(1)	6046(1)	8364(1)	13(1)
N(12)	6298(1)	6556(1)	8771(1)	13(1)
N(13)	8341(1)	6453(1)	8994(1)	14(1)
N(14)	8304(1)	5882(1)	8644(1)	14(1)
N(15)	8994(1)	5883(1)	8388(1)	14(1)
N(16)	7910(1)	5170(1)	7287(1)	14(1)
N(17)	7176(1)	5234(1)	7495(1)	14(1)
N(18)	6436(1)	5344(1)	7067(1)	14(1)
C(1)	5097(1)	3519(1)	8178(1)	14(1)
C(2)	4617(1)	2899(1)	8284(1)	18(1)
C(3)	3819(1)	2741(1)	7884(1)	20(1)
C(4)	3502(1)	3170(1)	7368(1)	20(1)
C(5)	3968(1)	3771(1)	7269(1)	18(1)
C(6)	4760(1)	3954(1)	7692(1)	14(1)
C(7)	3266(2)	2106(1)	7995(1)	30(1)
C(8)	2630(2)	2965(1)	6936(1)	29(1)
C(9)	8597(1)	3134(1)	8699(1)	16(1)
C(10)	9135(1)	3506(1)	8394(1)	17(1)

C(11)	9885(2)	3170(1)	8259(1)	24(1)
C(12)	10068(2)	2463(1)	8429(1)	28(1)
C(13)	9513(2)	2081(1)	8742(1)	26(1)
C(14)	8785(2)	2413(1)	8879(1)	21(1)
C(15)	9735(2)	1306(1)	8925(1)	39(1)
C(16)	10864(2)	2080(2)	8282(1)	41(1)
C(17)	7235(1)	4552(1)	10206(1)	15(1)
C(18)	7368(1)	5295(1)	10276(1)	14(1)
C(19)	7455(1)	5625(1)	10823(1)	18(1)
C(20)	7379(1)	5196(1)	11282(1)	19(1)
C(21)	7257(1)	4430(1)	11215(1)	19(1)
C(22)	7195(1)	4104(1)	10682(1)	18(1)
C(23)	7157(2)	3979(1)	11727(1)	30(1)
C(24)	7360(2)	5546(1)	11858(1)	27(1)
C(25)	5101(1)	6751(1)	8037(1)	13(1)
C(26)	5577(1)	7007(1)	8580(1)	13(1)
C(27)	5290(1)	7625(1)	8831(1)	16(1)
C(28)	4522(1)	7969(1)	8523(1)	16(1)
C(29)	4032(1)	7710(1)	7960(1)	15(1)
C(30)	4321(1)	7109(1)	7716(1)	15(1)
C(31)	3196(1)	8106(1)	7635(1)	21(1)
C(32)	4198(2)	8644(1)	8765(1)	25(1)
C(33)	9497(1)	6485(1)	8578(1)	16(1)
C(34)	9085(1)	6842(1)	8963(1)	15(1)
C(35)	9450(1)	7486(1)	9246(1)	18(1)
C(36)	10225(1)	7756(1)	9128(1)	20(1)
C(37)	10646(2)	7393(1)	8724(1)	23(1)
C(38)	10291(1)	6759(1)	8454(1)	21(1)
C(39)	11486(2)	7712(1)	8596(1)	35(1)
C(40)	10643(2)	8441(1)	9424(1)	27(1)
C(41)	7631(1)	5237(1)	6694(1)	14(1)
C(42)	6702(1)	5348(1)	6555(1)	14(1)
C(43)	6206(1)	5436(1)	5975(1)	18(1)
C(44)	6668(2)	5395(1)	5542(1)	20(1)
C(45)	7626(2)	5276(1)	5683(1)	20(1)
C(46)	8112(1)	5201(1)	6255(1)	17(1)
C(47)	6162(2)	5479(1)	4914(1)	31(1)
C(48)	8112(2)	5232(1)	5196(1)	28(1)

C(49)	6810(2)	2484(1)	9539(1)	26(1)
C(50)	6058(2)	2337(2)	9850(1)	38(1)
C(51)	10301(1)	5032(1)	7565(1)	26(1)
C(52)	10413(2)	4477(1)	7107(1)	29(1)
C(53)	7560(2)	7483(1)	10014(1)	23(1)
C(54)	6888(2)	7601(1)	10394(1)	31(1)
C(55)	4120(2)	5587(1)	6548(1)	25(1)
C(56)	3161(1)	5628(1)	6638(1)	32(1)
C(57)	4995(1)	5089(1)	9417(1)	43(1)
C(58)	5131(1)	5585(1)	10368(1)	44(1)
C(59)	5112(1)	5683(1)	9793(1)	44(1)
C(60A)	9548(5)	4981(13)	10437(3)	42(3)
C(61A)	9622(8)	4361(7)	10137(7)	41(3)
C(62A)	10087(10)	4380(7)	9702(5)	51(4)
C(60B)	9526(12)	4660(20)	10297(13)	14(5)
C(61B)	9841(19)	4271(14)	9900(20)	40(10)
C(62B)	10340(20)	4610(20)	9569(18)	40(9)

Table S3. Bond lengths [Å] and angles [°] for compound **1**.

Zn(1)-N(8)	2.1539(16)
Zn(1)-N(14)	2.1575(16)
Zn(1)-N(5)	2.1589(15)
Zn(1)-N(11)	2.1739(16)
Zn(1)-N(2)	2.1791(16)
Zn(1)-N(17)	2.2568(16)
Zn(2)-C(55)	1.982(2)
Zn(2)-N(10)	2.0513(16)
Zn(2)-N(18)	2.0587(16)
Zn(2)-N(3)	2.0663(16)
Zn(3)-C(49)	1.984(2)
Zn(3)-N(4)	2.0443(16)
Zn(3)-N(1)	2.0773(16)
Zn(3)-N(7)	2.0932(16)
Zn(4)-C(51)	1.984(2)
Zn(4)-N(16)	2.0631(16)
Zn(4)-N(9)	2.0672(17)
Zn(4)-N(15)	2.0738(16)
Zn(5)-C(53)	1.990(2)
Zn(5)-N(6)	2.0400(17)
Zn(5)-N(13)	2.0779(16)
Zn(5)-N(12)	2.0834(16)
N(1)-N(2)	1.334(2)
N(1)-C(1)	1.366(3)
N(2)-N(3)	1.337(2)
N(3)-C(6)	1.360(2)
N(4)-N(5)	1.334(2)
N(4)-C(17)	1.361(2)
N(5)-N(6)	1.335(2)
N(6)-C(18)	1.358(2)
N(7)-N(8)	1.329(2)
N(7)-C(9)	1.362(2)
N(8)-N(9)	1.335(2)
N(9)-C(10)	1.361(3)
N(10)-N(11)	1.338(2)
N(10)-C(25)	1.359(2)

N(11)-N(12)	1.336(2)
N(12)-C(26)	1.366(2)
N(13)-N(14)	1.332(2)
N(13)-C(34)	1.361(3)
N(14)-N(15)	1.337(2)
N(15)-C(33)	1.365(3)
N(16)-N(17)	1.334(2)
N(16)-C(41)	1.366(2)
N(17)-N(18)	1.333(2)
N(18)-C(42)	1.366(2)
C(1)-C(6)	1.393(3)
C(1)-C(2)	1.414(3)
C(2)-C(3)	1.377(3)
C(3)-C(4)	1.433(3)
C(3)-C(7)	1.506(3)
C(4)-C(5)	1.370(3)
C(4)-C(8)	1.513(3)
C(5)-C(6)	1.407(3)
C(9)-C(10)	1.397(3)
C(9)-C(14)	1.406(3)
C(10)-C(11)	1.406(3)
C(11)-C(12)	1.375(3)
C(12)-C(13)	1.437(3)
C(12)-C(16)	1.518(3)
C(13)-C(14)	1.374(3)
C(13)-C(15)	1.512(3)
C(17)-C(18)	1.391(3)
C(17)-C(22)	1.410(3)
C(18)-C(19)	1.405(3)
C(19)-C(20)	1.372(3)
C(20)-C(21)	1.431(3)
C(20)-C(24)	1.511(3)
C(21)-C(22)	1.376(3)
C(21)-C(23)	1.508(3)
C(25)-C(26)	1.392(3)
C(25)-C(30)	1.409(3)
C(26)-C(27)	1.404(3)
C(27)-C(28)	1.374(3)

C(28)-C(29)	1.439(3)
C(28)-C(32)	1.505(3)
C(29)-C(30)	1.372(3)
C(29)-C(31)	1.508(3)
C(33)-C(34)	1.393(3)
C(33)-C(38)	1.407(3)
C(34)-C(35)	1.409(3)
C(35)-C(36)	1.373(3)
C(36)-C(37)	1.439(3)
C(36)-C(40)	1.511(3)
C(37)-C(38)	1.379(3)
C(37)-C(39)	1.508(3)
C(41)-C(42)	1.389(3)
C(41)-C(46)	1.410(3)
C(42)-C(43)	1.403(3)
C(43)-C(44)	1.378(3)
C(44)-C(45)	1.433(3)
C(44)-C(47)	1.503(3)
C(45)-C(46)	1.379(3)
C(45)-C(48)	1.517(3)
C(49)-C(50)	1.531(3)
C(51)-C(52)	1.531(3)
C(53)-C(54)	1.533(3)
C(55)-C(56)	1.531(2)
C(57)-C(58)#1	1.377(3)
C(57)-C(59)	1.3933
C(58)-C(59)	1.3633
C(58)-C(57)#1	1.377(4)
C(60A)-C(61A)	1.366(7)
C(60A)-C(62A)#2	1.378(10)
C(61A)-C(62A)	1.385(8)
C(62A)-C(60A)#2	1.378(10)
C(60B)-C(61B)	1.365(14)
C(60B)-C(62B)#2	1.38(3)
C(61B)-C(62B)	1.367(16)
C(62B)-C(60B)#2	1.38(3)
N(8)-Zn(1)-N(14)	92.18(6)
N(8)-Zn(1)-N(5)	89.78(6)

N(14)-Zn(1)-N(5)	91.18(6)
N(8)-Zn(1)-N(11)	177.91(6)
N(14)-Zn(1)-N(11)	89.63(6)
N(5)-Zn(1)-N(11)	91.23(6)
N(8)-Zn(1)-N(2)	90.16(6)
N(14)-Zn(1)-N(2)	176.46(6)
N(5)-Zn(1)-N(2)	91.48(6)
N(11)-Zn(1)-N(2)	87.98(6)
N(8)-Zn(1)-N(17)	88.68(6)
N(14)-Zn(1)-N(17)	88.39(6)
N(5)-Zn(1)-N(17)	178.39(6)
N(11)-Zn(1)-N(17)	90.32(6)
N(2)-Zn(1)-N(17)	89.01(6)
C(55)-Zn(2)-N(10)	124.58(8)
C(55)-Zn(2)-N(18)	118.54(8)
N(10)-Zn(2)-N(18)	97.05(6)
C(55)-Zn(2)-N(3)	121.90(9)
N(10)-Zn(2)-N(3)	95.42(6)
N(18)-Zn(2)-N(3)	91.99(6)
C(49)-Zn(3)-N(4)	125.39(8)
C(49)-Zn(3)-N(1)	121.86(9)
N(4)-Zn(3)-N(1)	97.46(6)
C(49)-Zn(3)-N(7)	116.95(8)
N(4)-Zn(3)-N(7)	93.28(6)
N(1)-Zn(3)-N(7)	94.58(6)
C(51)-Zn(4)-N(16)	122.78(8)
C(51)-Zn(4)-N(9)	122.37(9)
N(16)-Zn(4)-N(9)	93.85(6)
C(51)-Zn(4)-N(15)	118.17(8)
N(16)-Zn(4)-N(15)	93.79(6)
N(9)-Zn(4)-N(15)	99.48(6)
C(53)-Zn(5)-N(6)	125.47(8)
C(53)-Zn(5)-N(13)	118.79(8)
N(6)-Zn(5)-N(13)	95.80(6)
C(53)-Zn(5)-N(12)	120.35(8)
N(6)-Zn(5)-N(12)	95.58(6)
N(13)-Zn(5)-N(12)	93.72(6)
N(2)-N(1)-C(1)	107.05(15)

N(2)-N(1)-Zn(3)	120.67(12)
C(1)-N(1)-Zn(3)	131.64(13)
N(1)-N(2)-N(3)	111.06(15)
N(1)-N(2)-Zn(1)	125.25(12)
N(3)-N(2)-Zn(1)	123.56(12)
N(2)-N(3)-C(6)	107.37(16)
N(2)-N(3)-Zn(2)	123.64(12)
C(6)-N(3)-Zn(2)	128.40(13)
N(5)-N(4)-C(17)	107.16(15)
N(5)-N(4)-Zn(3)	122.05(12)
C(17)-N(4)-Zn(3)	130.72(13)
N(4)-N(5)-N(6)	111.02(14)
N(4)-N(5)-Zn(1)	124.80(12)
N(6)-N(5)-Zn(1)	124.14(12)
N(5)-N(6)-C(18)	107.21(16)
N(5)-N(6)-Zn(5)	122.46(12)
C(18)-N(6)-Zn(5)	130.15(13)
N(8)-N(7)-C(9)	107.14(16)
N(8)-N(7)-Zn(3)	123.00(12)
C(9)-N(7)-Zn(3)	129.85(13)
N(7)-N(8)-N(9)	111.61(15)
N(7)-N(8)-Zn(1)	123.32(12)
N(9)-N(8)-Zn(1)	125.04(12)
N(8)-N(9)-C(10)	106.77(16)
N(8)-N(9)-Zn(4)	122.03(12)
C(10)-N(9)-Zn(4)	131.18(13)
N(11)-N(10)-C(25)	107.20(15)
N(11)-N(10)-Zn(2)	123.31(12)
C(25)-N(10)-Zn(2)	129.35(13)
N(12)-N(11)-N(10)	110.99(15)
N(12)-N(11)-Zn(1)	124.07(12)
N(10)-N(11)-Zn(1)	124.88(12)
N(11)-N(12)-C(26)	107.19(15)
N(11)-N(12)-Zn(5)	121.29(12)
C(26)-N(12)-Zn(5)	131.17(13)
N(14)-N(13)-C(34)	107.20(15)
N(14)-N(13)-Zn(5)	122.65(12)
C(34)-N(13)-Zn(5)	130.13(13)

N(13)-N(14)-N(15)	111.19(15)
N(13)-N(14)-Zn(1)	123.31(12)
N(15)-N(14)-Zn(1)	125.11(12)
N(14)-N(15)-C(33)	107.07(16)
N(14)-N(15)-Zn(4)	121.33(12)
C(33)-N(15)-Zn(4)	131.55(13)
N(17)-N(16)-C(41)	106.90(16)
N(17)-N(16)-Zn(4)	120.92(12)
C(41)-N(16)-Zn(4)	132.12(13)
N(18)-N(17)-N(16)	111.39(15)
N(18)-N(17)-Zn(1)	124.33(12)
N(16)-N(17)-Zn(1)	124.26(12)
N(17)-N(18)-C(42)	107.03(15)
N(17)-N(18)-Zn(2)	122.29(12)
C(42)-N(18)-Zn(2)	130.66(13)
N(1)-C(1)-C(6)	107.32(17)
N(1)-C(1)-C(2)	131.88(19)
C(6)-C(1)-C(2)	120.76(18)
C(3)-C(2)-C(1)	117.31(19)
C(2)-C(3)-C(4)	121.61(19)
C(2)-C(3)-C(7)	118.9(2)
C(4)-C(3)-C(7)	119.5(2)
C(5)-C(4)-C(3)	120.75(19)
C(5)-C(4)-C(8)	119.7(2)
C(3)-C(4)-C(8)	119.6(2)
C(4)-C(5)-C(6)	117.79(19)
N(3)-C(6)-C(1)	107.19(17)
N(3)-C(6)-C(5)	131.20(19)
C(1)-C(6)-C(5)	121.60(18)
N(7)-C(9)-C(10)	107.03(17)
N(7)-C(9)-C(14)	131.70(19)
C(10)-C(9)-C(14)	121.27(18)
N(9)-C(10)-C(9)	107.45(17)
N(9)-C(10)-C(11)	131.67(19)
C(9)-C(10)-C(11)	120.88(19)
C(12)-C(11)-C(10)	118.1(2)
C(11)-C(12)-C(13)	121.0(2)
C(11)-C(12)-C(16)	119.5(2)

C(13)-C(12)-C(16)	119.5(2)
C(14)-C(13)-C(12)	120.8(2)
C(14)-C(13)-C(15)	119.6(2)
C(12)-C(13)-C(15)	119.6(2)
C(13)-C(14)-C(9)	118.0(2)
N(4)-C(17)-C(18)	107.27(17)
N(4)-C(17)-C(22)	131.52(19)
C(18)-C(17)-C(22)	121.20(18)
N(6)-C(18)-C(17)	107.35(17)
N(6)-C(18)-C(19)	131.50(19)
C(17)-C(18)-C(19)	121.10(18)
C(20)-C(19)-C(18)	117.89(19)
C(19)-C(20)-C(21)	121.17(18)
C(19)-C(20)-C(24)	119.1(2)
C(21)-C(20)-C(24)	119.55(19)
C(22)-C(21)-C(20)	120.86(19)
C(22)-C(21)-C(23)	119.5(2)
C(20)-C(21)-C(23)	119.55(19)
C(21)-C(22)-C(17)	117.69(19)
N(10)-C(25)-C(26)	107.55(17)
N(10)-C(25)-C(30)	131.32(18)
C(26)-C(25)-C(30)	121.13(18)
N(12)-C(26)-C(25)	107.07(16)
N(12)-C(26)-C(27)	131.66(18)
C(25)-C(26)-C(27)	121.27(18)
C(28)-C(27)-C(26)	117.77(18)
C(27)-C(28)-C(29)	121.15(18)
C(27)-C(28)-C(32)	119.95(19)
C(29)-C(28)-C(32)	118.86(18)
C(30)-C(29)-C(28)	120.71(18)
C(30)-C(29)-C(31)	119.82(18)
C(28)-C(29)-C(31)	119.46(18)
C(29)-C(30)-C(25)	117.96(18)
N(15)-C(33)-C(34)	107.10(17)
N(15)-C(33)-C(38)	131.98(19)
C(34)-C(33)-C(38)	120.92(19)
N(13)-C(34)-C(33)	107.44(17)
N(13)-C(34)-C(35)	131.17(18)

C(33)-C(34)-C(35)	121.39(18)
C(36)-C(35)-C(34)	118.00(19)
C(35)-C(36)-C(37)	120.76(19)
C(35)-C(36)-C(40)	119.8(2)
C(37)-C(36)-C(40)	119.40(19)
C(38)-C(37)-C(36)	120.88(19)
C(38)-C(37)-C(39)	119.8(2)
C(36)-C(37)-C(39)	119.4(2)
C(37)-C(38)-C(33)	118.0(2)
N(16)-C(41)-C(42)	107.40(16)
N(16)-C(41)-C(46)	131.41(19)
C(42)-C(41)-C(46)	121.18(18)
N(18)-C(42)-C(41)	107.28(16)
N(18)-C(42)-C(43)	131.24(19)
C(41)-C(42)-C(43)	121.48(18)
C(44)-C(43)-C(42)	117.82(19)
C(43)-C(44)-C(45)	120.87(18)
C(43)-C(44)-C(47)	119.6(2)
C(45)-C(44)-C(47)	119.55(19)
C(46)-C(45)-C(44)	121.03(18)
C(46)-C(45)-C(48)	119.5(2)
C(44)-C(45)-C(48)	119.46(19)
C(45)-C(46)-C(41)	117.61(19)
C(50)-C(49)-Zn(3)	119.55(17)
C(52)-C(51)-Zn(4)	119.83(16)
C(54)-C(53)-Zn(5)	119.00(16)
C(56)-C(55)-Zn(2)	120.46(13)
C(58)#1-C(57)-C(59)	119.05(15)
C(59)-C(58)-C(57)#1	121.00(13)
C(61A)-C(60A)-C(62A)#2	120.4(7)
C(60A)-C(61A)-C(62A)	119.0(9)
C(60A)#2-C(62A)-C(61A)	120.6(8)
C(61B)-C(60B)-C(62B)#2	128.1(16)
C(60B)-C(61B)-C(62B)	119(3)
C(61B)-C(62B)-C(60B)#2	113(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+2 #2 -x+2,-y+1,-z+2

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for compound **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zn(1)	12(1)	12(1)	9(1)	-1(1)	2(1)	0(1)
Zn(2)	14(1)	17(1)	9(1)	-1(1)	0(1)	1(1)
Zn(3)	17(1)	12(1)	13(1)	1(1)	5(1)	1(1)
Zn(4)	13(1)	18(1)	14(1)	-2(1)	5(1)	0(1)
Zn(5)	16(1)	13(1)	11(1)	-3(1)	2(1)	1(1)
N(1)	16(1)	13(1)	13(1)	-1(1)	5(1)	-1(1)
N(2)	15(1)	14(1)	11(1)	-1(1)	3(1)	1(1)
N(3)	12(1)	16(1)	11(1)	-2(1)	1(1)	0(1)
N(4)	15(1)	15(1)	10(1)	1(1)	3(1)	1(1)
N(5)	15(1)	14(1)	10(1)	-1(1)	3(1)	1(1)
N(6)	14(1)	16(1)	10(1)	-2(1)	2(1)	2(1)
N(7)	16(1)	13(1)	12(1)	0(1)	3(1)	2(1)
N(8)	13(1)	15(1)	12(1)	-1(1)	3(1)	1(1)
N(9)	12(1)	19(1)	14(1)	0(1)	4(1)	2(1)
N(10)	16(1)	15(1)	10(1)	1(1)	2(1)	1(1)
N(11)	15(1)	14(1)	10(1)	-1(1)	2(1)	1(1)
N(12)	15(1)	13(1)	12(1)	-1(1)	4(1)	1(1)
N(13)	16(1)	13(1)	12(1)	-2(1)	2(1)	-1(1)
N(14)	14(1)	15(1)	12(1)	-1(1)	3(1)	0(1)
N(15)	14(1)	18(1)	13(1)	-1(1)	4(1)	-2(1)
N(16)	16(1)	17(1)	11(1)	-1(1)	5(1)	-1(1)
N(17)	14(1)	14(1)	12(1)	0(1)	3(1)	-1(1)
N(18)	15(1)	16(1)	10(1)	0(1)	2(1)	-1(1)
C(1)	15(1)	14(1)	15(1)	-5(1)	7(1)	0(1)
C(2)	23(1)	13(1)	21(1)	-2(1)	11(1)	0(1)
C(3)	20(1)	14(1)	31(1)	-10(1)	14(1)	-4(1)
C(4)	16(1)	22(1)	24(1)	-13(1)	8(1)	-3(1)
C(5)	17(1)	22(1)	16(1)	-6(1)	5(1)	-1(1)
C(6)	14(1)	15(1)	15(1)	-5(1)	6(1)	0(1)
C(7)	29(1)	20(1)	45(1)	-9(1)	16(1)	-8(1)
C(8)	19(1)	34(1)	34(1)	-16(1)	5(1)	-8(1)
C(9)	16(1)	18(1)	12(1)	-2(1)	1(1)	3(1)
C(10)	16(1)	18(1)	15(1)	0(1)	3(1)	3(1)

C(11)	20(1)	27(1)	28(1)	5(1)	11(1)	7(1)
C(12)	24(1)	31(1)	29(1)	1(1)	10(1)	13(1)
C(13)	32(1)	22(1)	24(1)	4(1)	7(1)	12(1)
C(14)	24(1)	19(1)	20(1)	2(1)	7(1)	5(1)
C(15)	52(2)	27(1)	43(2)	10(1)	22(1)	21(1)
C(16)	38(2)	40(2)	53(2)	10(1)	24(1)	20(1)
C(17)	13(1)	20(1)	12(1)	-1(1)	4(1)	2(1)
C(18)	13(1)	18(1)	11(1)	1(1)	2(1)	5(1)
C(19)	18(1)	20(1)	15(1)	-4(1)	4(1)	4(1)
C(20)	15(1)	30(1)	11(1)	-2(1)	2(1)	6(1)
C(21)	17(1)	28(1)	14(1)	3(1)	5(1)	2(1)
C(22)	19(1)	19(1)	15(1)	3(1)	6(1)	1(1)
C(23)	38(1)	38(1)	17(1)	5(1)	14(1)	0(1)
C(24)	26(1)	41(1)	14(1)	-4(1)	7(1)	9(1)
C(25)	15(1)	13(1)	12(1)	2(1)	5(1)	0(1)
C(26)	15(1)	14(1)	12(1)	3(1)	5(1)	0(1)
C(27)	20(1)	15(1)	14(1)	0(1)	4(1)	1(1)
C(28)	20(1)	12(1)	19(1)	3(1)	7(1)	1(1)
C(29)	14(1)	16(1)	16(1)	8(1)	6(1)	1(1)
C(30)	15(1)	18(1)	11(1)	3(1)	2(1)	0(1)
C(31)	17(1)	22(1)	24(1)	9(1)	5(1)	6(1)
C(32)	32(1)	18(1)	26(1)	1(1)	6(1)	11(1)
C(33)	16(1)	15(1)	14(1)	1(1)	1(1)	-2(1)
C(34)	16(1)	14(1)	13(1)	2(1)	0(1)	-1(1)
C(35)	20(1)	16(1)	16(1)	-1(1)	2(1)	0(1)
C(36)	22(1)	15(1)	21(1)	1(1)	0(1)	-4(1)
C(37)	19(1)	22(1)	28(1)	3(1)	6(1)	-5(1)
C(38)	21(1)	24(1)	22(1)	-1(1)	9(1)	-3(1)
C(39)	32(1)	27(1)	50(2)	-5(1)	20(1)	-12(1)
C(40)	30(1)	20(1)	30(1)	-2(1)	3(1)	-8(1)
C(41)	20(1)	11(1)	12(1)	-1(1)	4(1)	-1(1)
C(42)	21(1)	9(1)	13(1)	-1(1)	4(1)	-3(1)
C(43)	21(1)	17(1)	13(1)	0(1)	0(1)	-4(1)
C(44)	31(1)	15(1)	12(1)	0(1)	3(1)	-4(1)
C(45)	32(1)	15(1)	14(1)	-2(1)	10(1)	-4(1)
C(46)	22(1)	15(1)	17(1)	-1(1)	8(1)	-1(1)
C(47)	37(1)	42(2)	12(1)	1(1)	4(1)	-6(1)
C(48)	38(1)	31(1)	18(1)	-1(1)	13(1)	-2(1)

C(49)	36(1)	18(1)	27(1)	6(1)	10(1)	1(1)
C(50)	49(2)	37(2)	30(1)	8(1)	14(1)	-13(1)
C(51)	17(1)	39(1)	24(1)	-10(1)	10(1)	-4(1)
C(52)	25(1)	41(1)	24(1)	-5(1)	9(1)	7(1)
C(53)	29(1)	19(1)	21(1)	-8(1)	4(1)	-1(1)
C(54)	47(2)	26(1)	21(1)	-3(1)	8(1)	13(1)
C(55)	23(1)	35(1)	14(1)	-2(1)	-1(1)	4(1)
C(56)	21(1)	37(1)	32(1)	-7(1)	-5(1)	4(1)
C(57)	18(1)	89(2)	23(1)	4(1)	8(1)	12(1)
C(58)	19(1)	78(2)	35(1)	-10(1)	9(1)	6(1)
C(59)	21(1)	72(2)	41(2)	9(2)	14(1)	10(1)
C(60A)	25(3)	79(10)	19(3)	-3(5)	-1(2)	24(6)
C(61A)	23(4)	39(7)	49(6)	13(5)	-13(3)	0(4)
C(62A)	42(9)	60(10)	36(6)	-13(5)	-21(4)	24(7)
C(60B)	15(6)	16(13)	12(11)	3(8)	4(7)	3(10)
C(61B)	15(14)	37(11)	60(30)	-10(20)	-2(13)	17(10)
C(62B)	34(15)	30(20)	42(17)	-23(15)	-12(10)	9(14)

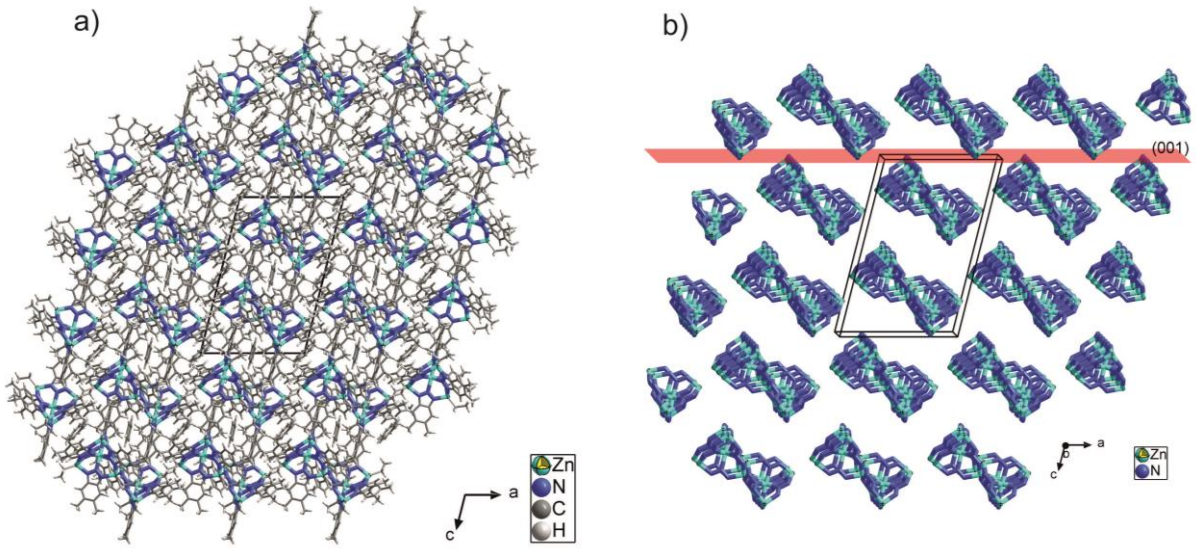

Figure S27. Packing diagram of **1** (a) - view in a *b*-direction, and simplified packing diagram of **1** (b) with C- and H- atoms omitted for clarity, view in a *b*-direction.

References

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