Supplementary Materials :

The "Periodic Table" of 1-methylbenzotriazole: Zinc(II) Complexes

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Table S1. Selected bond lengths (Å) and angles (°) for complex **5**, obtained experimentally (X-Ray) and computationally (BSI and BSII).

	X-Ray	BSI	BSII
Distances (Å)			
Zn-O(4)	1.992(2)	2.00	2.00
Zn-N(13)	1.995(2)	2.05	2.06
Zn-N(3)	1.996(2)	2.03	2.04
Zn-O(1)	2.016(2)	1.98	1.99
Zn···O(2)	2.588(5)	2.60	2.51
Zn···O(6)	2.722(6)	2.66	2.66
Angles (°)			
O(4)-Zn-N(13)	105.0(1)	100.3	100.8
O(4)-Zn-N(3)	117.4(1)	118.2	114.0
N(13)-Zn-N(3)	118.2(1)	114.8	118.1
O(4)-Zn-O(1)	87.9(1)	100.6	98.8
N(13)-Zn-O(1)	108.2(1)	110.7	111.2
N(3)-Zn-O(1)	115.7(1)	111.0	111.8
O(2)···Zn···O(6)	164.3(1)	152.0	152.2

Table S2. Selected bond lengths (Å) and angles (°) for complex **6**, obtained experimentally (X-Ray) and computationally (BSI and BSII).

	X-Ray	BSI	BSII
Distances (Å)			
Zn-N(3)	2.040(2)	2.14	2.15
Zn-N(3')	2.040(2)	2.14	2.15
Zn-O(1)	2.061(2)	2.10	2.08
Zn-O(1')	2.061(2)	2.10	2.08
Zn-O(2)	2.388(2)	2.20	2.19
Zn-O(2')	2.388(2)	2.20	2.19
Angles (°)			
N(3)-Zn-N(3')	101.7(1)	87.5	90.0
N(3')-Zn-O(1')	105.9(1)	95.3	95.3
N(3)-Zn-O(1')	97.6(1)	97.9	98.7
N(3')-Zn-O(1)	97.6(1)	97.9	98.7
N(3)-Zn-O(1)	105.9(1)	95.1	95.3
O(1)-Zn-O(1')	142.5(1)	161.9	160.1
N(3')-Zn-O(2)	153.7(1)	154.8	155.5
N(3)-Zn-O(2')	153.7(1)	155.0	155.5

Table S3. Liquid-phase Cartesian coordinates of Mebta, calculated by the MP2/6-31+G(d) computational protocol, in ethanol with the PCM model.

C	-2.56372900	-0.02864900	0.00083600
C	-2.01502000	1.28482300	0.00203900
C	-0.64526800	1.50988200	-0.01721700
C	0.16529600	0.35966400	0.01116400
C	-0.36546400	-0.95088100	-0.01095400
C	-1.76051900	-1.15929200	0.01637000
N	0.67140400	-1.84957200	-0.00662300
N	1.81177400	-1.15324400	-0.00525800
N	1.51402000	0.17002800	-0.00433700
C	2.57466500	1.16859800	0.01265600
H	-3.64541100	-0.14149500	0.01485300
H	-2.69174600	2.13633400	-0.01101500
H	-0.23023200	2.51488100	-0.01637200
H	-2.18026100	-2.16270600	0.01316600
H	2.51140100	1.75597300	0.93076500
H	2.47543500	1.82029300	-0.85747700
H	3.52275400	0.63282500	-0.02618500

Table S4. Gas-phase Cartesian coordinates of **5** and **6**, calculated by the wB97XD/6-311+G** computational protocol (BSI).

		5	
Zn	0.01348900	-1.00486700	0.42845400
N	3.97659600	-0.57032300	-0.25627200
N	2.84897300	-1.21795700	-0.02008400
N	1.93014400	-0.35545500	0.26363100
C	1.88068100	2.17116200	0.43330200
C	2.71451300	3.25537900	0.28876300
C	4.07876500	3.11134000	-0.05921300
C	4.65119100	1.87753200	-0.27264100
C	2.45372700	0.91191000	0.21493200
C	3.79882100	0.77694200	-0.12751900
C	5.18086500	-1.29680600	-0.60264600
N	-2.24381800	1.74645700	-1.62391900
N	-1.11321300	1.16035300	-1.25469000
N	-1.39086600	0.24297600	-0.39252200
C	-3.52843200	-0.59346200	0.67057500
C	-4.88325000	-0.35791600	0.64446700
C	-5.45412300	0.63761900	-0.18398900
C	-4.68917100	1.43155600	-1.00926200
C	-2.74374700	0.20767900	-0.17001000
C	-3.31093400	1.19072500	-0.97988700
C	-2.23257400	2.81177800	-2.60382900
N	0.11478300	-2.82084900	-1.55642200
O	-0.16799200	-2.84716700	-0.28677900
O	0.38561300	-1.71423800	-2.04716200
O	0.09778800	-3.85476200	-2.18121600
N	-0.72411100	-0.11336000	2.90127600
O	-0.74786500	-1.24462500	2.26399300
O	-1.26587700	-0.03615200	3.97833500
O	-0.14274100	0.83325400	2.34744800
H	0.84303500	2.26502300	0.72155100
H	2.32258200	4.25173600	0.45458400
H	4.68965500	4.00142100	-0.15470200
H	5.69619300	1.76662100	-0.53342500
H	4.91739600	-2.34882300	-0.68676000
H	5.56300200	-0.93629700	-1.55865300
H	5.93448400	-1.16340100	0.17507700
H	-3.07632600	-1.34233700	1.30987500
H	-5.53586500	-0.94700800	1.27707400
H	-6.52831800	0.77954200	-0.16280300
H	-5.12903200	2.19348000	-1.64045800
H	-1.19477500	3.00129100	-2.86927200
H	-2.67655600	3.71216700	-2.17647300
H	-2.78899500	2.50659200	-3.49141900

		6	
Zn	-1.14325000	2.60393900	3.74622700
N	0.11880400	-0.31423300	6.48840700
N	0.26280800	0.76158200	5.72206500
N	-0.87631300	1.04886400	5.19294000
C	-3.18408800	0.01650400	5.32034900
C	-3.84173100	-1.03488200	5.91737700
C	-3.17915000	-1.94131100	6.77869800
C	-1.83826000	-1.82441200	7.07148900
C	-1.81767600	0.13972800	5.60926500
C	-1.17109600	-0.75675000	6.46026500
C	1.24313400	-0.84097500	7.23221300
N	-3.02575600	3.77410800	4.99836500
O	-3.19670200	2.92806600	4.04620400
O	-1.82126400	4.04035600	5.26361300
O	-3.95672300	4.25635400	5.58768700
H	-3.68114200	0.73349400	4.67750100
H	-4.90101900	-1.17114300	5.73527700
H	-3.74841100	-2.74796500	7.22581000
H	-1.33473000	-2.51460800	7.73684800
H	1.06335700	-0.73888400	8.30371500
H	2.12123100	-0.26285300	6.95203600
H	1.39585600	-1.89131700	6.97942900
N	-2.37671300	-0.26985600	0.94241800
N	-2.53060700	0.79276100	1.72516500
N	-1.39962900	1.06740200	2.27774300
C	0.90762800	0.03219600	2.16906200
C	1.57266000	-1.00995400	1.56410900
C	0.92206000	-1.89966300	0.67660000
C	-0.41378200	-1.77472600	0.36462200
C	-0.45376600	0.16333200	1.86068300
C	-1.08850200	-0.71636500	0.98371300
C	-3.49021900	-0.78040000	0.17150400
N	0.73564400	3.79757000	2.51111800
O	0.90982900	2.94149200	3.45338200
O	-0.47007000	4.06083000	2.24761700
O	1.66457700	4.29173900	1.92850200
H	1.39567200	0.73711500	2.83180400
H	2.62885200	-1.15140000	1.75983500
H	1.49691300	-2.69949100	0.22437800
H	-0.90775300	-2.45212700	-0.32074900
H	-3.29383200	-0.65907000	-0.89507700
H	-4.37152000	-0.20573500	0.44869600
H	-3.64877900	-1.83486000	0.40262700

Table S5. Gas-phase Cartesian coordinates of **5** and **6**, calculated by the wB97XD/Def2tzvp computational protocol (BSII).

		5	
Zn	0.01769300	-0.96553100	0.33758100
N	4.01377100	-0.60978400	-0.20447800
N	2.86038200	-1.21985400	-0.01571400
N	1.94714200	-0.33038800	0.17053500
C	1.95122600	2.19640800	0.23927900
C	2.81781500	3.25237600	0.10914400
C	4.19364700	3.06397600	-0.14526600
C	4.74524700	1.81322000	-0.27654000
C	2.50247900	0.91924200	0.10468900
C	3.85989200	0.74144700	-0.14454200
C	5.21554700	-1.37299700	-0.44558300
N	-2.41596300	1.71554700	-1.61171600
N	-1.25974300	1.14065100	-1.32520600
N	-1.46422300	0.22208200	-0.44877800
C	-3.51016800	-0.63251100	0.75833000
C	-4.86158000	-0.40775100	0.83156100
C	-5.49660500	0.58517800	0.05368100
C	-4.80065700	1.38365800	-0.82097300
C	-2.79433500	0.17528300	-0.13056800
C	-3.42548600	1.15271600	-0.89314200
C	-2.48594500	2.78132900	-2.58202400
N	0.06457900	-2.85517600	-1.51419200
O	-0.19067400	-2.85917600	-0.24437200
O	0.32912100	-1.75387600	-2.02253700
O	0.03275200	-3.89071000	-2.12810000
N	-0.58800600	-0.00288300	2.82007200
O	-0.61702000	-1.15474700	2.22971100
O	-1.02586000	0.09221900	3.93930400
O	-0.10906500	0.94631100	2.18379500
H	0.90173900	2.32694500	0.45654900
H	2.44250400	4.26172100	0.21399400
H	4.83108600	3.93411400	-0.23398900
H	5.79971000	1.66887600	-0.46743200
H	4.95226700	-2.42584800	-0.39989600
H	5.61486800	-1.13653400	-1.43146000
H	5.95884100	-1.14459200	0.31766300
H	-3.00976500	-1.37983900	1.35981600
H	-5.46255700	-1.00341800	1.50530900
H	-6.56538000	0.72068900	0.15553600
H	-5.28994200	2.14475200	-1.41321100
H	-1.48623700	2.93357900	-2.97871500
H	-2.84031000	3.69642600	-2.10788900
H	-3.16128900	2.50156000	-3.39015000

		6	
Zn	-1.12613100	2.46461400	3.74170900
N	0.10635800	-0.28632700	6.66605900
N	0.26050300	0.69643100	5.79108900
N	-0.87403000	0.94482700	5.24023400
C	-3.19250500	-0.02734400	5.49400400
C	-3.86057300	-0.99560600	6.20215200
C	-3.20616900	-1.81463900	7.14767600
C	-1.86428100	-1.69029000	7.41495600
C	-1.82481900	0.10334200	5.75597500
C	-1.18710200	-0.70678800	6.69133800
C	1.22645500	-0.75507400	7.44578000
N	-2.99448500	3.68138800	4.93728400
O	-3.16057400	2.82363300	3.99815500
O	-1.79534500	3.92350500	5.23236200
O	-3.92785400	4.19667800	5.48805700
H	-3.68575700	0.62351600	4.78386400
H	-4.92165800	-1.13311200	6.04220000
H	-3.78382400	-2.55821900	7.68136400
H	-1.36648000	-2.31475300	8.14425200
H	1.03893200	-0.58938400	8.50647700
H	2.10134200	-0.18979200	7.13698200
H	1.39009200	-1.81706400	7.26371400
N	-2.35860800	-0.28632500	0.81735300
N	-2.51275900	0.69642100	1.69233600
N	-1.37822700	0.94482300	2.24318800
C	0.94024800	-0.02735200	1.98943000
C	1.60831700	-0.99561500	1.28128600
C	0.95391800	-1.81464700	0.33575800
C	-0.38796900	-1.69029500	0.06847000
C	-0.42743700	0.10333600	1.72745200
C	-1.06515000	-0.70679200	0.79208500
C	-3.47869900	-0.75506100	0.03761800
N	0.74222100	3.68139100	2.54613300
O	0.90831200	2.82363900	3.48526400
O	-0.45692100	3.92350500	2.25105400
O	1.67558900	4.19668200	1.99535900
H	1.43349700	0.62350600	2.69957300
H	2.66940200	-1.13312300	1.44124200
H	1.53157500	-2.55822600	-0.19792900
H	-0.88576700	-2.31475500	-0.66083100
H	-3.29116800	-0.58936300	-1.02307600
H	-4.35358800	-0.18978100	0.34641300
H	-3.64233900	-1.81705300	0.21967300

Table S6. Sum of electronic and thermal free energies (a.u.) of complexes **5** and **6** (BSI and BSII).

Complex	BSI	BSII
5	-3210.109391	-3210.378632
6	-3210.110223	-3210.379412

Table S7. Crystallographic data and structural refinement parameters for complexes **3** and **4**.

Parameter	**[$ZnBr_2(Mebta)_2$] (3)**	**[$ZnI_2(Mebta)_2$] (4)**
Empirical formula	$C_{14}H_{14}ZnBr_2N_6$	$C_{14}H_{14}ZnI_2N_6$
Formula weight	491.50	585.48
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Color, habit	colorless, parallelepiped	colorless, parallelepiped
Crystal size, mm	0.32x0.42x0.52	0.17x0.24x0.75
a, Å	7.6642(1)	15.9969(2)
b, Å	8.1402(1)	8.4320(1)
c, Å	14.2671(2)	13.6229(2)
α, °	78.230(1)	90.00(1)
β, °	83.206(1)	95.904(1)
γ, °	71.356(1)	90.00(1)
Volume, $Å^3$	824.30(2)	1827.79(4)
Z	2	4
Temperature, K	160(2)	160(2)
Radiation, Å	Cu Kα, 1.54178	Cu Kα, 1.54178
Calculated density, g cm^{-3}	1.980	2.128
Absorption coefficient, mm^{-1}	7.812	28.449
No. of measured, independent and observed [$I>2\sigma(I)$] reflections	9958, 2582, 2453	26131, 3203, 3129
R_{int}	0.0432	0.1378
Number of parameters	264	210
Final *R* indices [$I>2\sigma(I)$][a,b]	R_1 = 0.0347, wR_2 = 0.0880	R_1 = 0.0443, wR_2 = 0.1190
Goodness-of-fit on F^2	1.10	1.07
Largest differences peak and hole (e $Å^{-3}$)	0.66/-0.91	1.42/-1.58

[a] $R_1 = (\Sigma(|Fo|-|Fc|)/\Sigma(|Fo|)$, $wR_2 = \{\Sigma[w(Fo^2-Fc^2)^2]/\Sigma[w(Fo^2)^2]\}^{1/2}$, $w = 1/\sigma^2(F_o^2)+(aP)^2+bP]$, where $P = [\max(F_o^2, 0)+2F_c^2]/3$.

[b] For **3**, a = 0.0431, b = 1.7397; for **4**, a = 0.0730, b = 2.4599.

Table S8. Crystallographic data and structural refinement parameters for complexes **5**-**7**.

Parameter	**tet-[Zn(NO$_3$)$_2$(Mebta)$_2$] (5)**	**oct-[Zn(NO$_3$)$_2$(Mebta)$_2$] (6)**	**[Zn(Mebta)$_4$] (ClO$_4$)$_2$ (7)**
Empirical formula	$C_{14}H_{14}ZnN_8O_6$	$C_{14}H_{14}ZnN_8O_6$	$C_{28}H_{28}ZnCl_2N_{12}O_8$
Formula weight	455.70	455.70	796.89
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$	$I2/a$
Color, habit	colorless, parallelepiped	colorless, parallelepiped	colorless, parallelepiped
Crystal size, mm	0.20x0.25x0.30	0.20x0.20x0.50	0.64x0.68x0.70
a, Å	8.4531(12)	12.726(7)	18.5986(3)
b, Å	15.844(2)	10.067(5)	15.4065(2)
c, Å	7.2484(11)	15.630(9)	23.2569(5)
α, °	82.018(6)	90.00(1)	90.00(1)
β, °	70.404(5)	106.75(2)	92.193(1)
γ, °	83.908(5)	90.00(1)	90.00(1)
Volume, Å^3	903.9(2)	1917.4(18)	6659.1(2)
Z	2	4	8
Temperature, K	293(2)	293(2)	160(2)
Radiation, Å	Cu Kα, 1.54178	Mo Kα, 0.71078	Cu Kα, 1.54178
Calculated density, g cm^{-3}	1.674	1.579	1.590
Absorption coefficient, mm^{-1}	2.382	1.331	3.101
No. of measured, independent and observed [$I>2\sigma(I)$] reflections	3259, 3000, 2870	1950, 1878, 1703	40357, 5643, 5394
R_{int}	0.076	0.0238	0.0338
Number of parameters	318	160	578
Final R indices [$I>2\sigma(I)$][a,b]	R_1 = 0.0326, wR_2 = 0.0900	R_1 = 0.0311, wR_2 = 0.0819	R_1 = 0.0400, wR_2 = 0.0937
Goodness-of-fit on F^2	1.12	1.08	1.06
Largest differences peak and hole (e Å^{-3})	0.51/-0.40	0.27/-0.29	0.58/-0.72

[a] $R_1 = (\Sigma(|Fo|-|Fc|)/\Sigma(|Fo|)$, $wR_2 = \{\Sigma[w(Fo^2-Fc^2)^2]/\Sigma[w(Fo^2)^2]\}^{1/2}$, $w = 1/\sigma^2(F_o^2)+(aP)^2+bP]$, where $P = [\max(F_o^2, 0)+2F_c^2]/3$.

[b] For **5**, a = 0.0320, b = 0.5254; for **6**, a = 0.0266, b = 1.9740; for **7**, a = 0.0361, b = 20.5559.

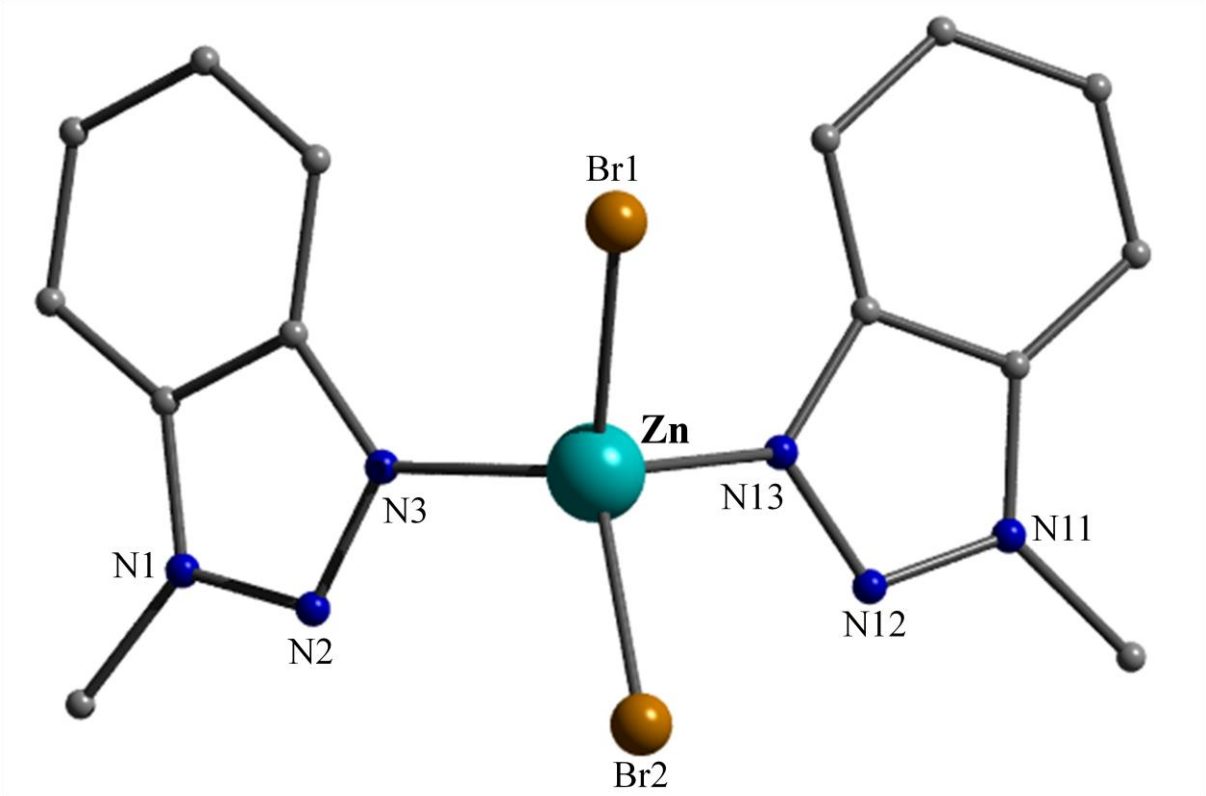


Figure S1. Partially labelled ball and stick representation of the structure of the molecule [$ZnBr_2(Mebta)_2$] that is present in **3**. The H atoms have not been drawn.

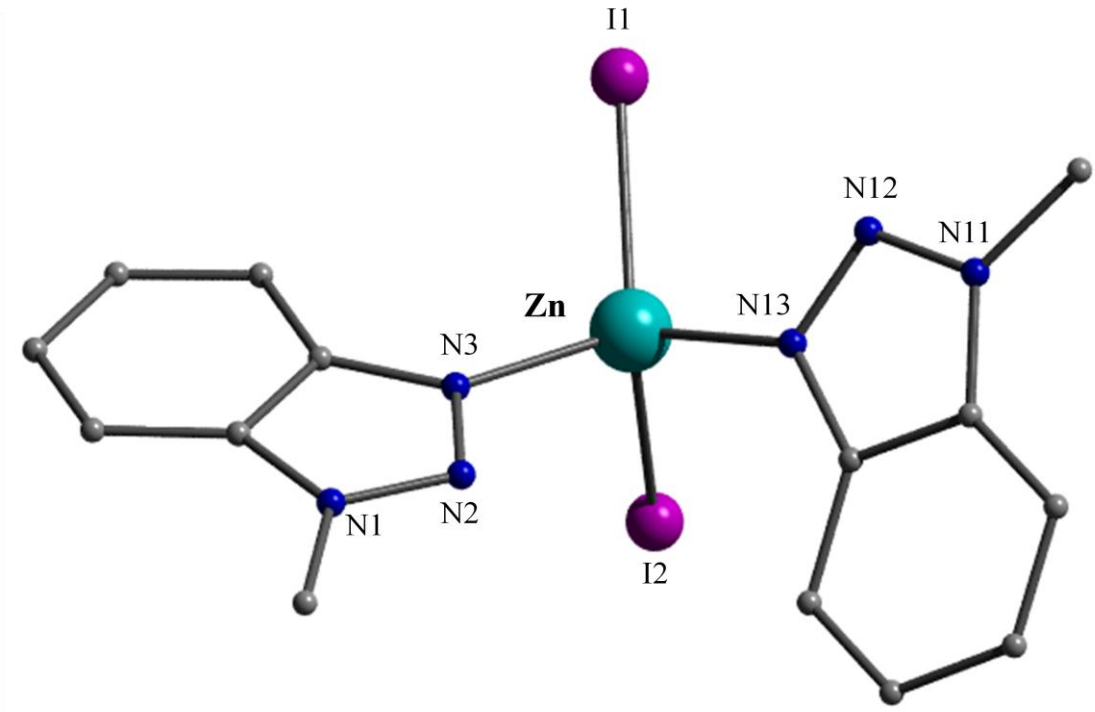
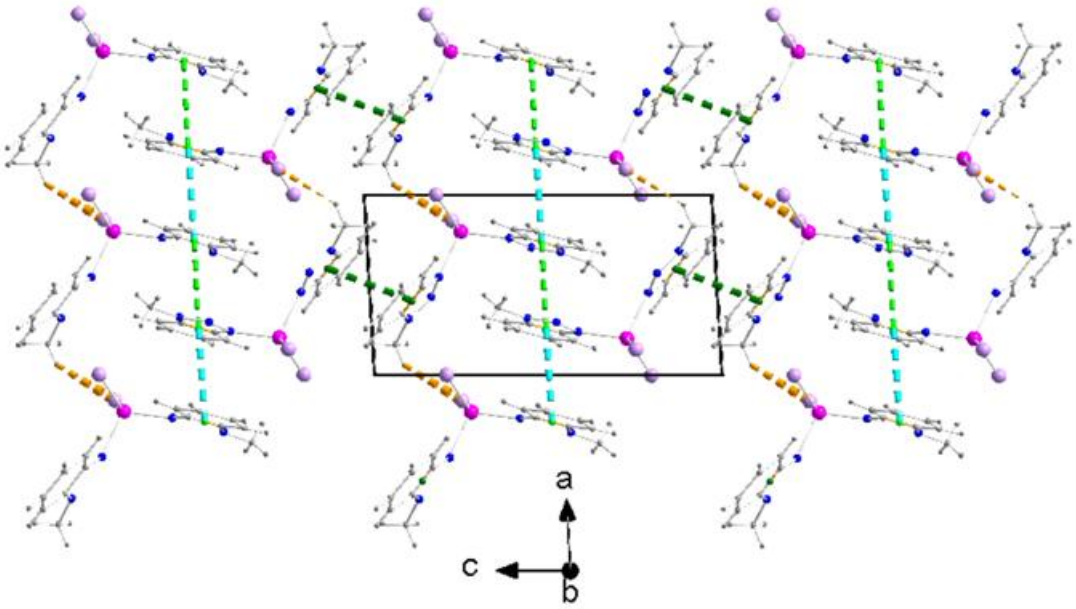
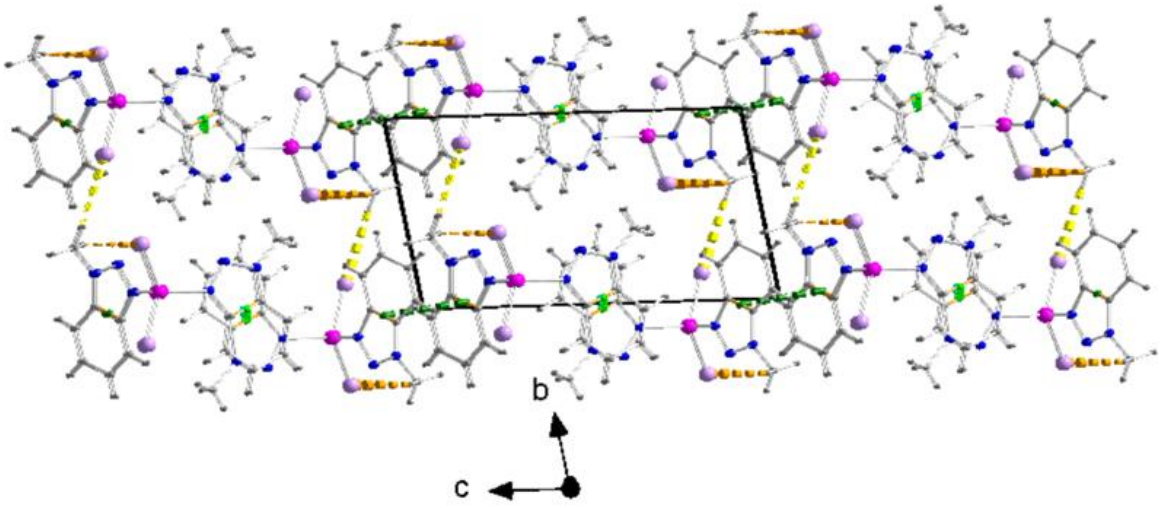


Figure S2. Partially labelled ball and stick representation of the structure of the molecule [$ZnI_2(Mebta)_2$] that is present in **4**. The H atoms have not been drawn.



a)



b)

Figure S3. (a) Layers of [$ZnBr_2(Mebta)_2$] molecules parallel to the (010) plane in **3**. **(b)** Side view parallel to the *a* axis of the stacks of layers developed along the *b* axis in the structure of **3**. Light green, cyan and dark green dashed lines indicate π-π stacking interactions. Orange and yellow dashed lines denote the C20-H_B(C20)···Br2 and C20-H_C(C20)···Br1 H bonds, respectively. For more details, see the text of the paper.

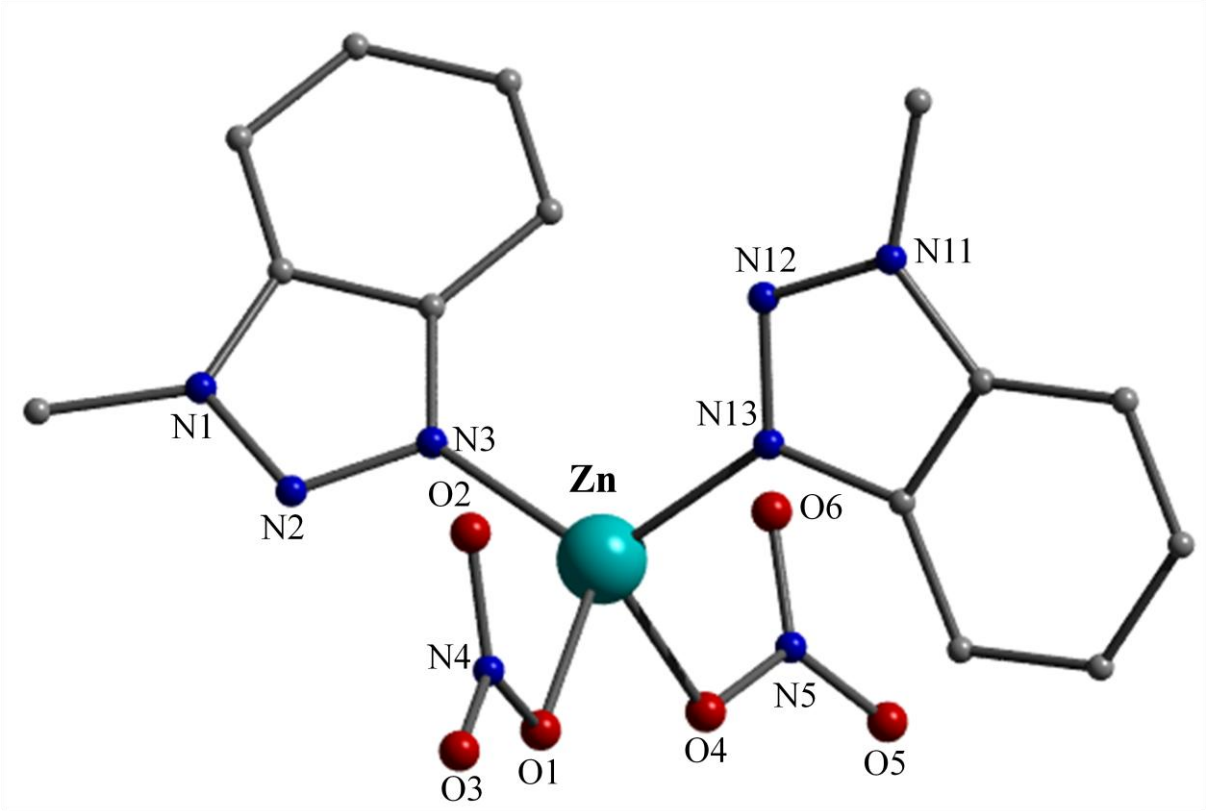
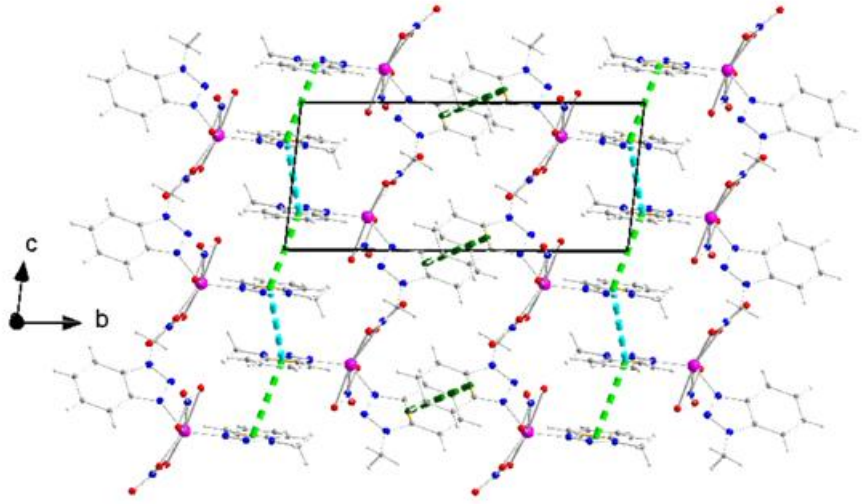
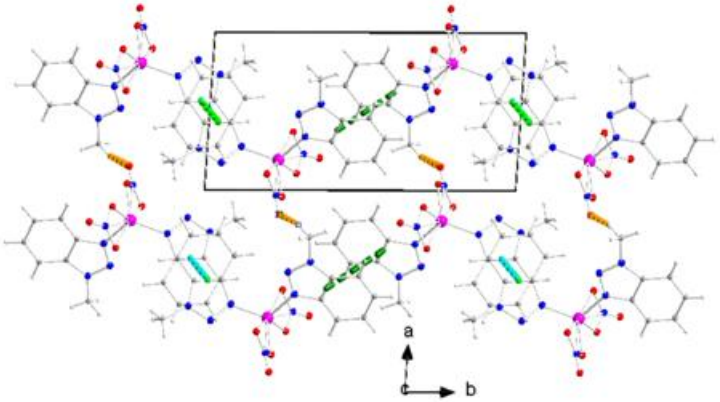


Figure S4. Partially labelled ball and stick representation of the structure of the molecule tet-$[Zn(NO_3)_2(Mebta)_2]$ that is present in **5**. The long Zn···O2 and Zn···O6, weakly bonding interactions are not shown. The H atoms have not been drawn.



a)



b)

Figure S5. (a) Layers of tet-[$Zn(NO_3)_2(Mebta)_2$] molecules parallel to the (100) plane in **5**. (b) Side view parallel to the *c* axis of the stacks of layers developed along the *a* axis in the crystal structure of **5**. Light green, cyan and dark green dashed lines indicate π-π stacking interactions. Orange dashed lines denote the C20-H_A(C20)···O3 H bonds.

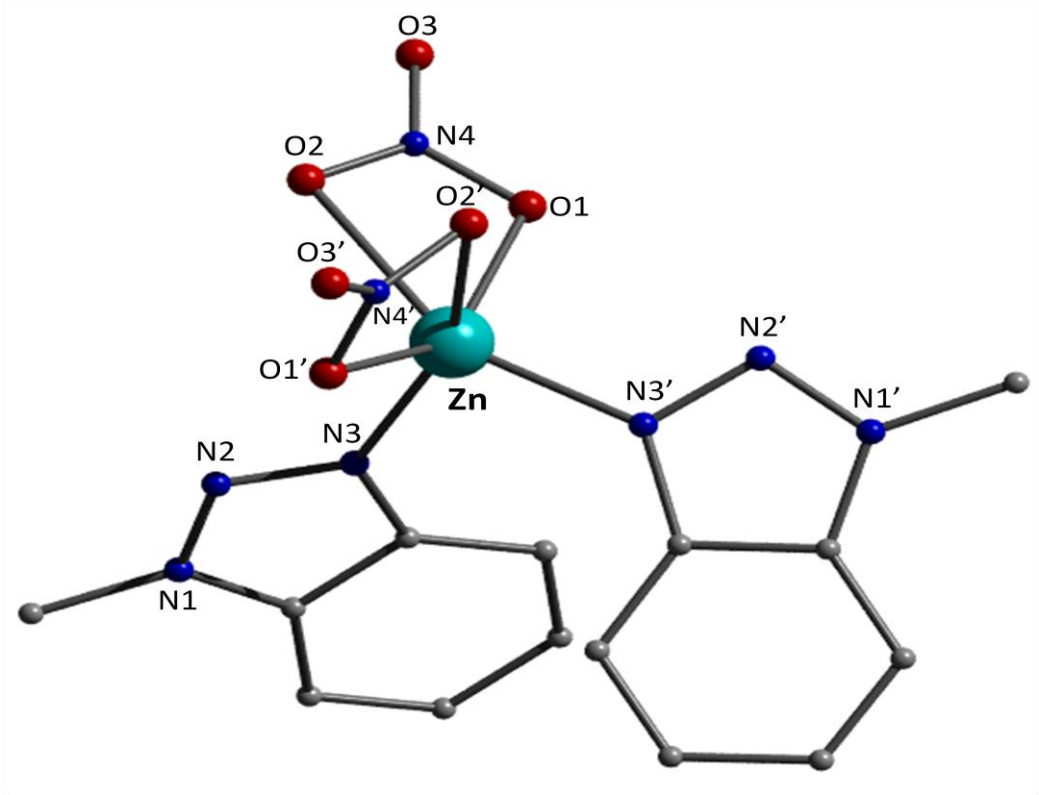
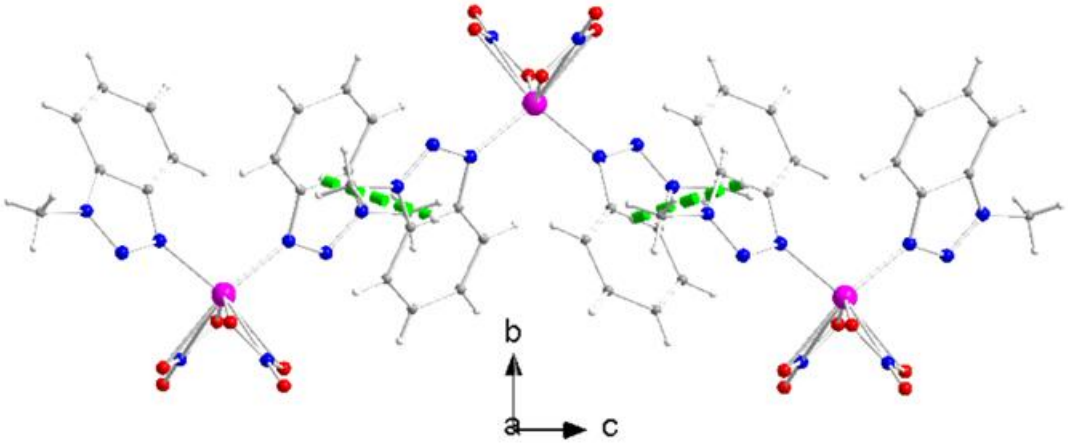
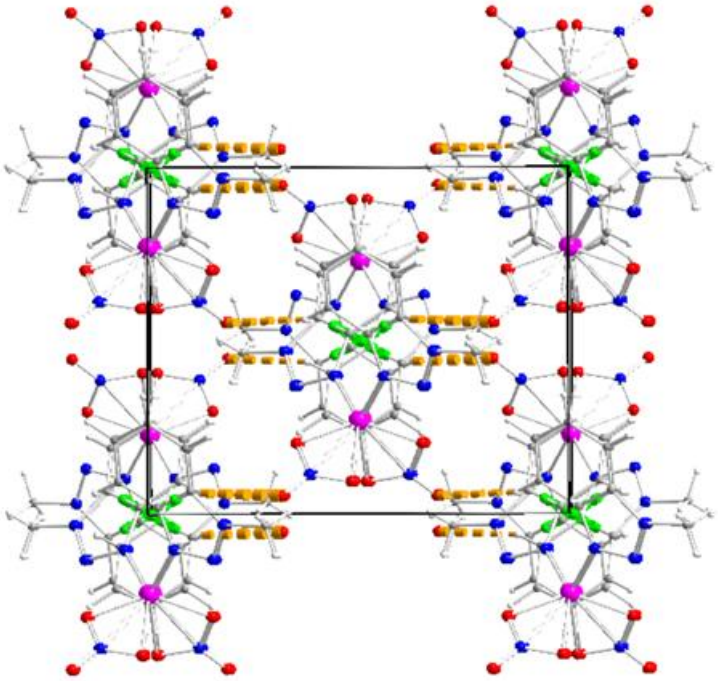


Figure S6. Partially labelled ball and stick representation of the structure of the molecule oct-$[Zn(NO_3)_2(Mebta)_2]$ that is present in **6**. The H atoms have not been drawn. Primed atoms are generated by the symmetry operation *–x, y, -z*+1/2.



a)



b)

Figure S7. (a) A small portion of the zig-zag chains along the *c* axis due to π-π stacking interactions in **6**. (b) A small part of the 3D framework due to C4-H(C4)···O3 H-bonding interactions. Light green and orange dashed lines indicate π-π and H-bonding interactions, respectively.

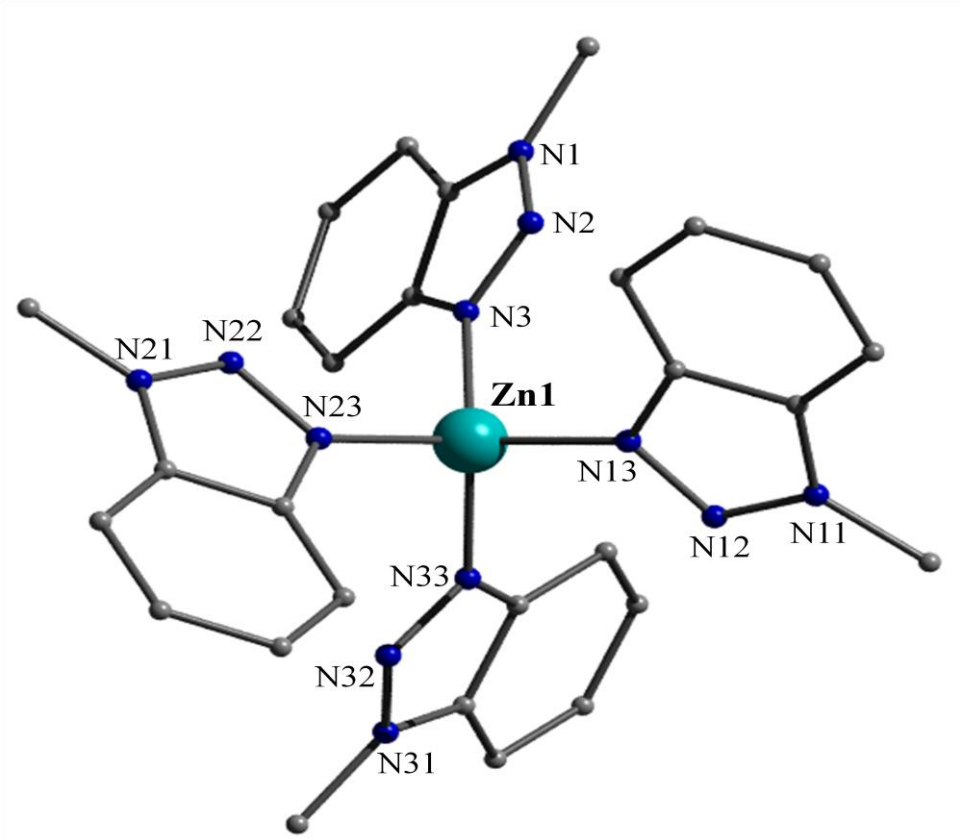


Figure S8. Partially labelled ball and stick representation of the structure of the cation $[Zn(Mebta)_4]^{2+}$ that is present in **7**. The H atoms have not been drawn.

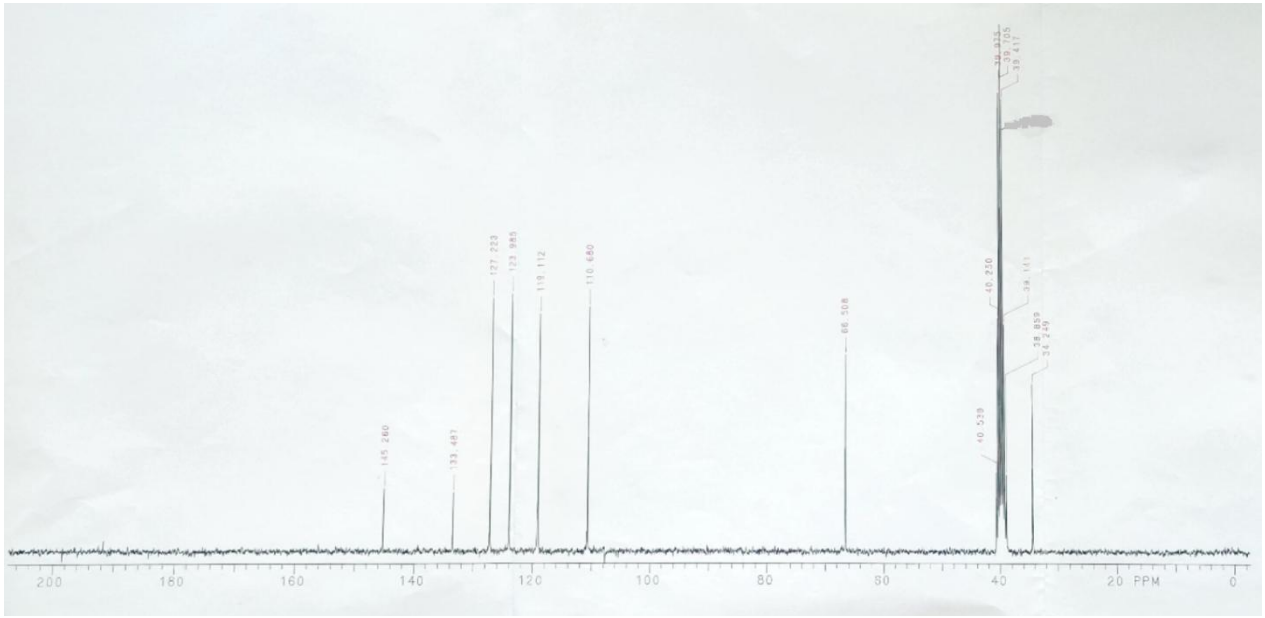


Figure S9. The $^{13}C[^{1}H]$ NMR spectrum of Mebta in a mixture of deuteriated DMSO and dioxane (reference). The signals at δ ca. 39.8 and 66.6 ppm are due to DMSO and dioxane, respectively.

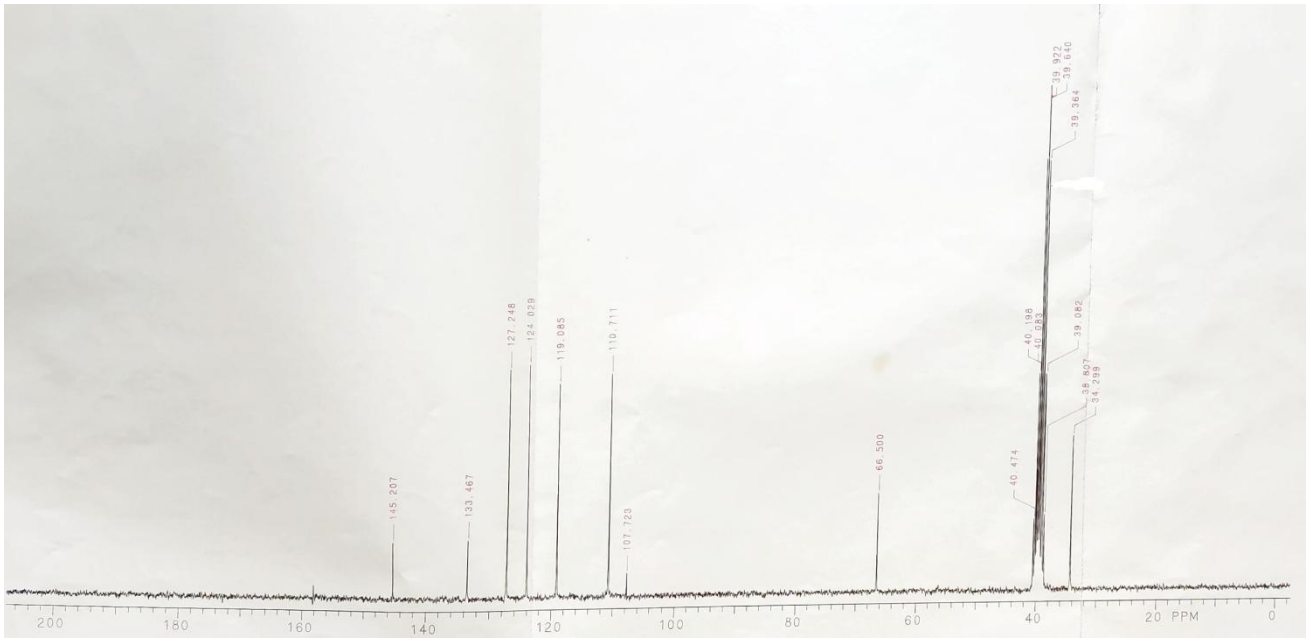


Figure S10. The $^{13}C[^{1}H]$ NMR spectrum of $[ZnCl_2(Mebta)_2]$ (**1**) in a mixture of deuteriated DMSO and dioxane (reference). The signals at δ ca. 39.8 and 66.6 ppm are due to DMSO and dioxane, respectively.

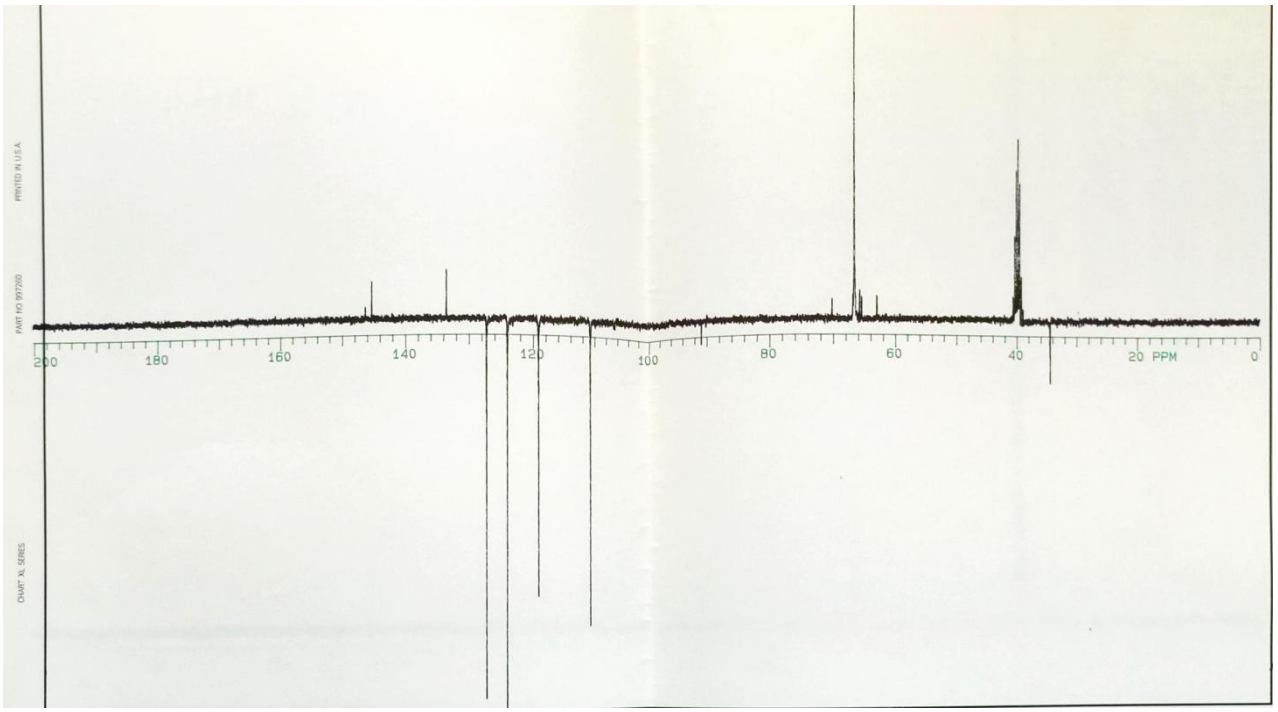


Figure S11. The APT ^{13}C NMR spectrum of $[ZnI_2(Mebta)_2]$ (**4**) in a mixture of deuteriated DMSO and dioxane (reference). The signals at δ ca. 39.8 and 66.6 ppm are due to DMSO and dioxane, respectively.

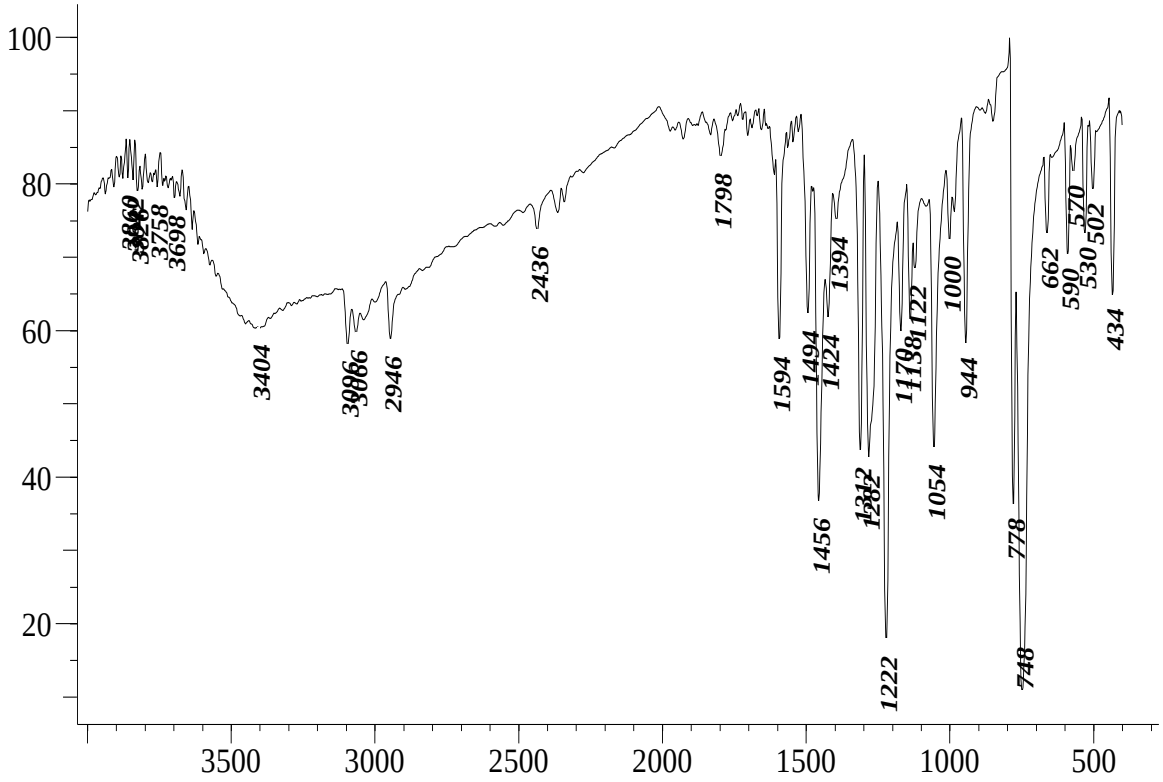


Figure S12. The IR spectrum (KBr, cm^{-1}) of $[ZnCl_2(Mebta)_2]$ (**1**).

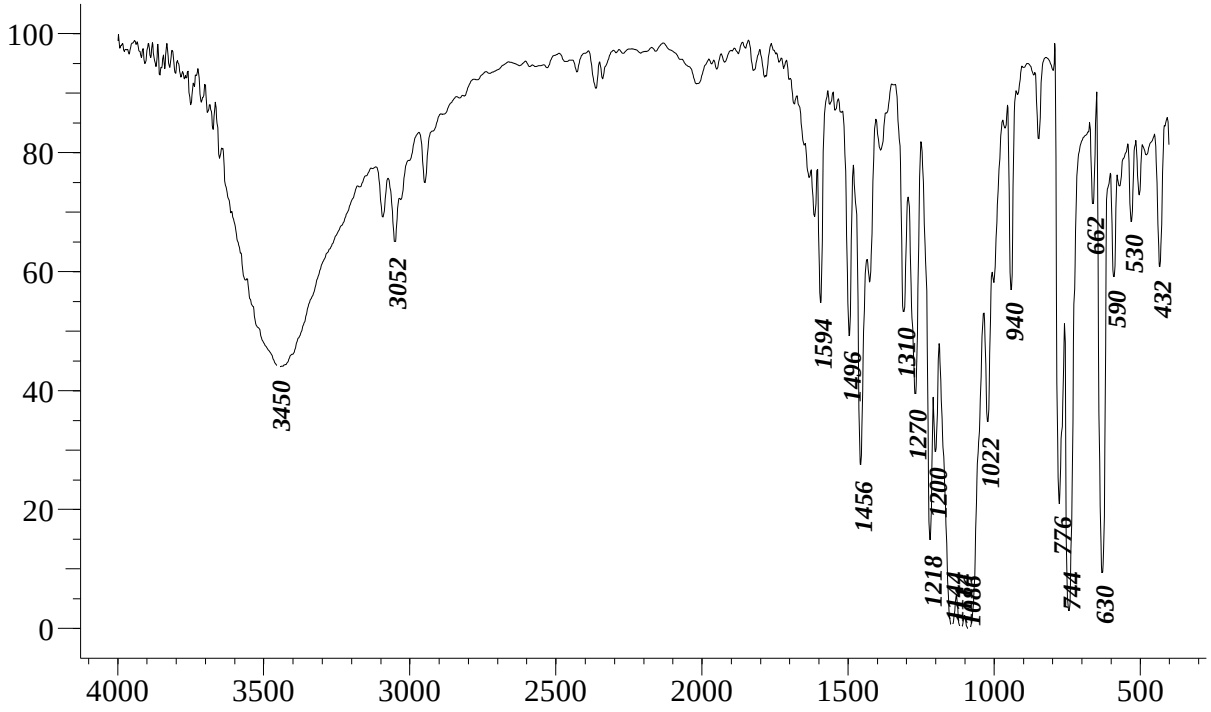


Figure S13. The IR spectrum (KBr, cm^{-1}) of $[Zn(Mebta)_4](ClO_4)_2$ (**7**).

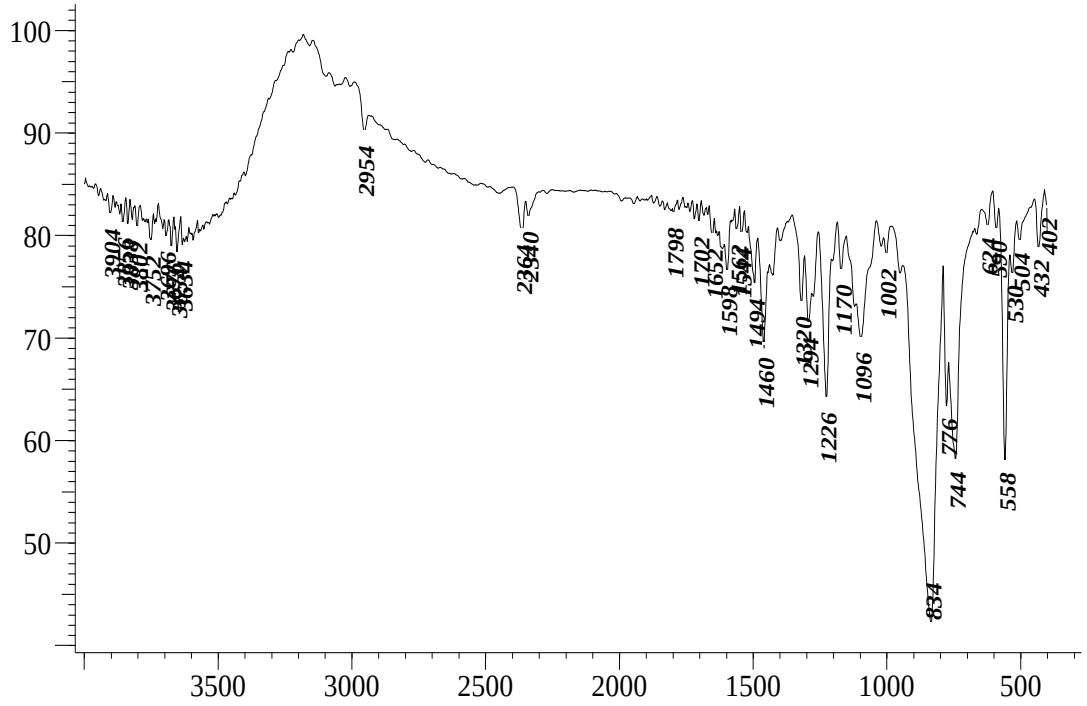


Figure S14. The IR spectrum (KBr, cm^{-1}) of $[Zn(Mebta)_4](PF_6)_2$ (**8**).

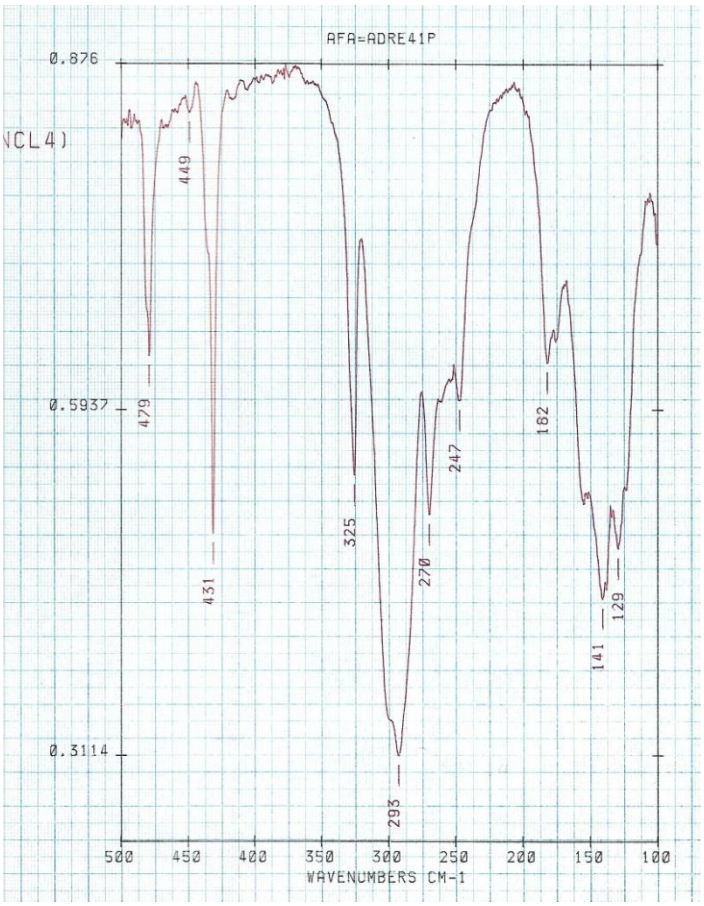


Figure S15. The FT far-IR spectrum (polyethylene, cm^{-1}) of $(MebtaH)_2[ZnCl_4]$ (**2**).

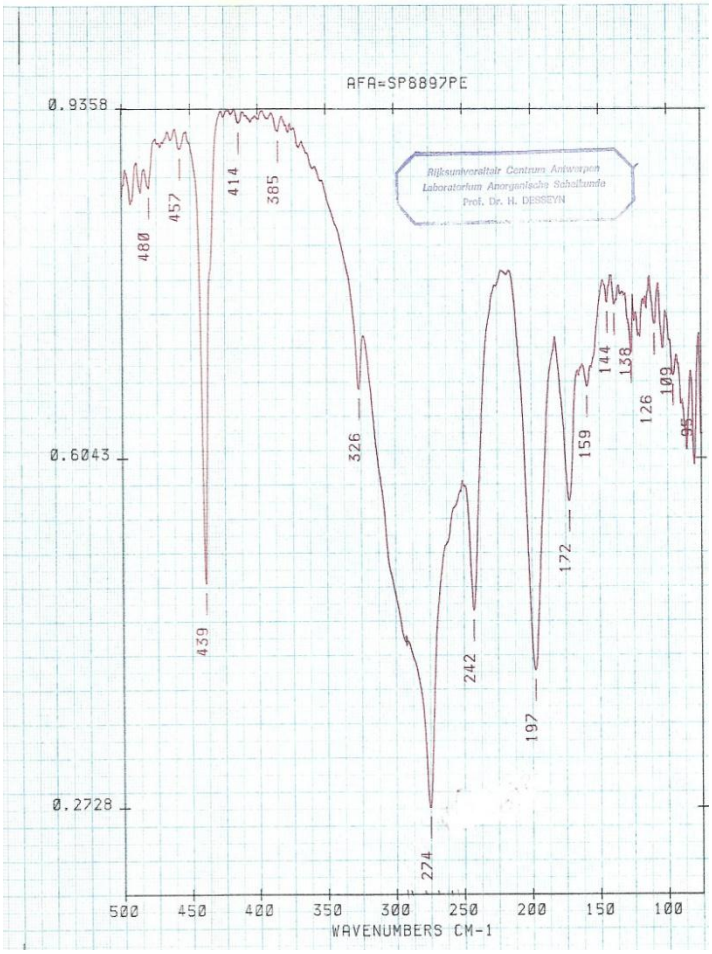


Figure S16. The FT far-IR spectrum (polyethylene, cm^{-1}) of oct-[$Zn(NO_3)_2(Mebta)_2$] (**6**).

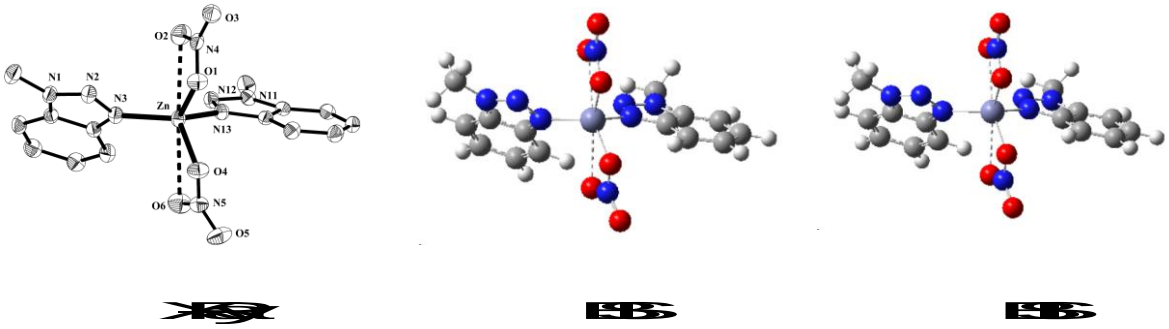


Figure S17. The X-ray structure of **5** (left) along with the DFT calculated gas-phase ones (BSI and BSII). The dashed lines indicate long Zn-$O_{nitrato}$ interactions (see also Figure 5).

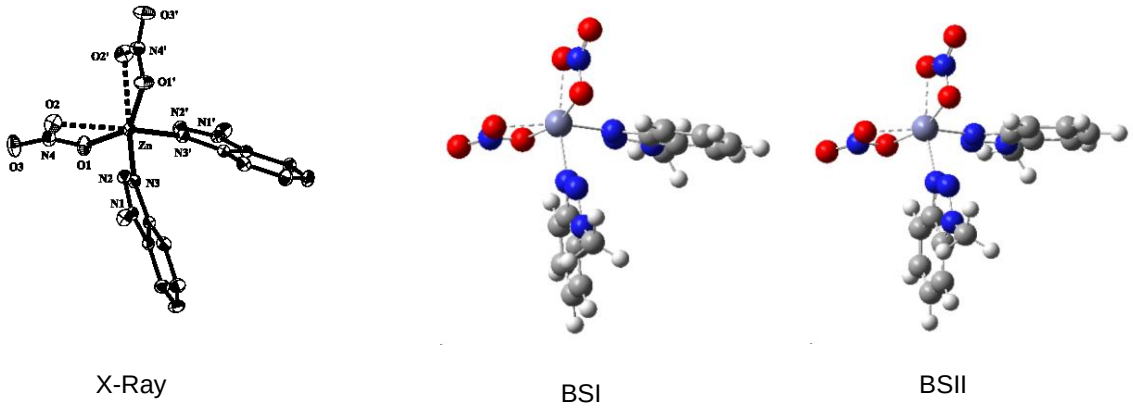


Figure S18. The X-ray structure of **6** (left) along with the DFT calculated gas-phase ones (BSI and BSII). The dashed lines indicate long Zn-O bonds. Note that these bonds have been drawn with solid lines in Figure S6.