10.1071/CH17215_AC

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SUPPLEMENTARY MATERIAL

Photoactive and physical properties of an azobenzene-containing coordination framework

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Details of the single crystal structure determination of $[Zn_4(tbazip)_3(bpe)_2(OH)_2]\cdot bpe\cdot\{solvent\}$

Experimental: Single crystals of $[Zn_4(tbazip)_3(bpe)_2(OH)_2]\cdot bpe\cdot\{solvent\}$ (formula: $C_{90}H_{80}N_{12}O_{14}Zn_4$, CCDC 1538659) were obtained directly from the solvothermal reaction. A suitable crystal was selected and mounted on a glass capilary with oil on a Bruker APEX2 microfocus rotating anode diffractometer. The crystal was kept at 90.0 K during data collection. Using Olex2,[1] the structure was solved with the ShelXS-1997[2] structure solution program using Direct Methods and refined with the XL[2] refinement package using least squares minimisation.

All hydrogen atom positions were assigned using idealised geometries (riding) with the exception of the hydroxyl protons. The positions of the hydroxide protons were initially located using peaks from the electron density difference maps. For refinement, the OH distances and thermal parameters were restrained, however, no geometric restraints were used. The *tert*-butyl group of one tbazip linker and all three unique bpe molecule were refined using disorder models. Restraints were applied to the thermal parameters and in the case of the unbound bpe, soft geometric restraints were applied to ensure a chemically reasonable geometry was obtained. Electron density associated with strongly disordered solvent molecules was removed from the structure using SQUEEZE. The electron count for each of the two equivalent voids in the unit cell (calculated volume 297 $Å^3$, giving total porosity 13.0%) was determined to be 78 e^-.

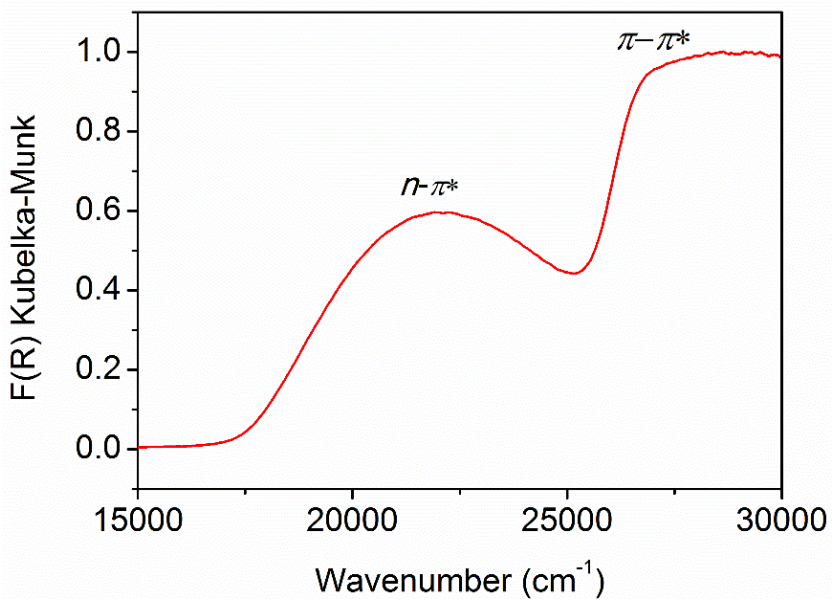

Figure S1: UV-Vis-NIR of tbazip

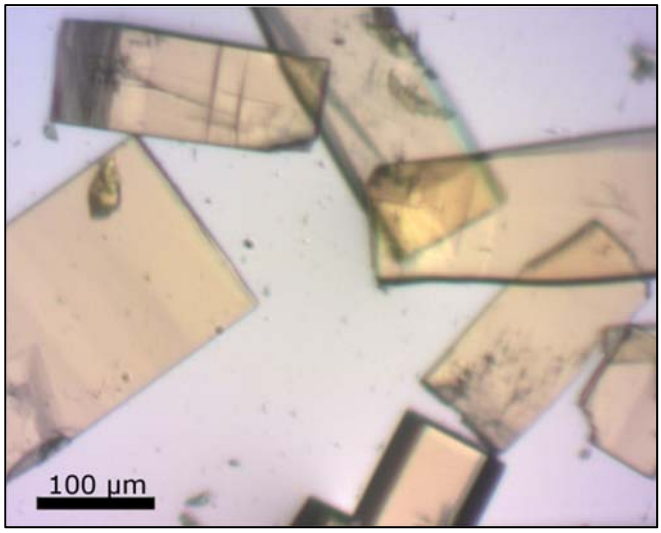

Figure S2: Image of crystals of $[Zn_4(tbazip)_3(bpe)_2(OH)_2]\cdot bpe\cdot\{solvent\}$ in oil that were obtained from the solvothermal reaction

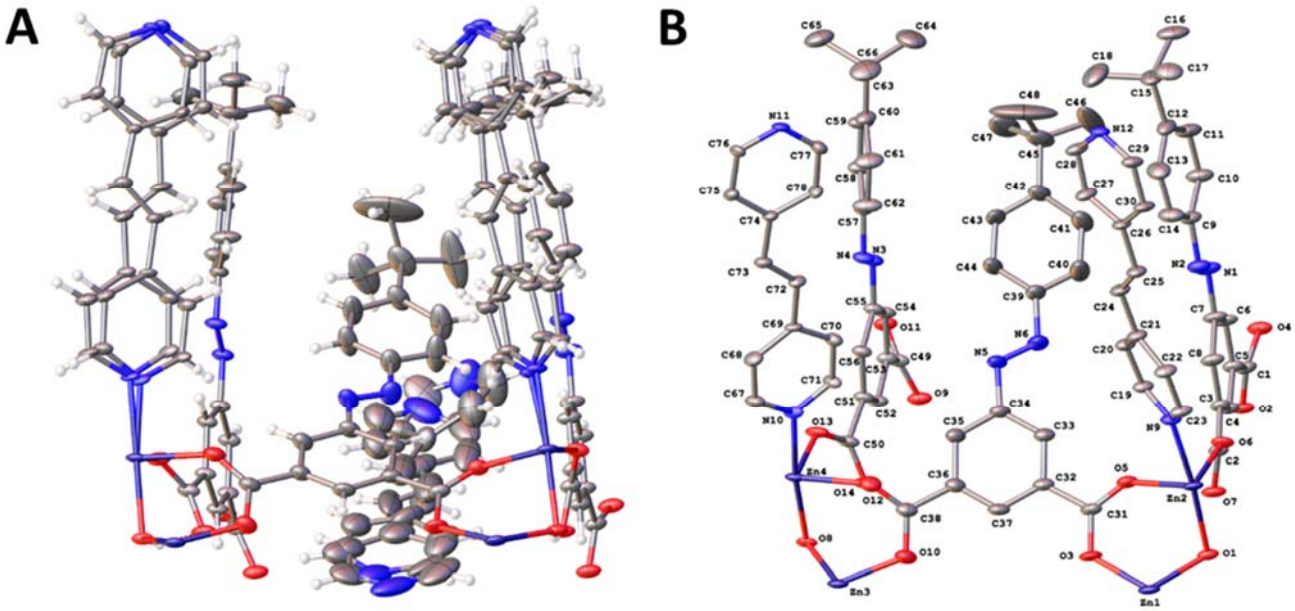

*Figure S3: **A** Asymmetric unit of $[Zn_4(tbazip)_3(bpe)_2(OH)_2].bpe\cdot\{solvent\}$ showing refined disorder. **B** Labelled asymmetric unit in which hydrogen atoms and minor disordered species have been omitted for clarity.*

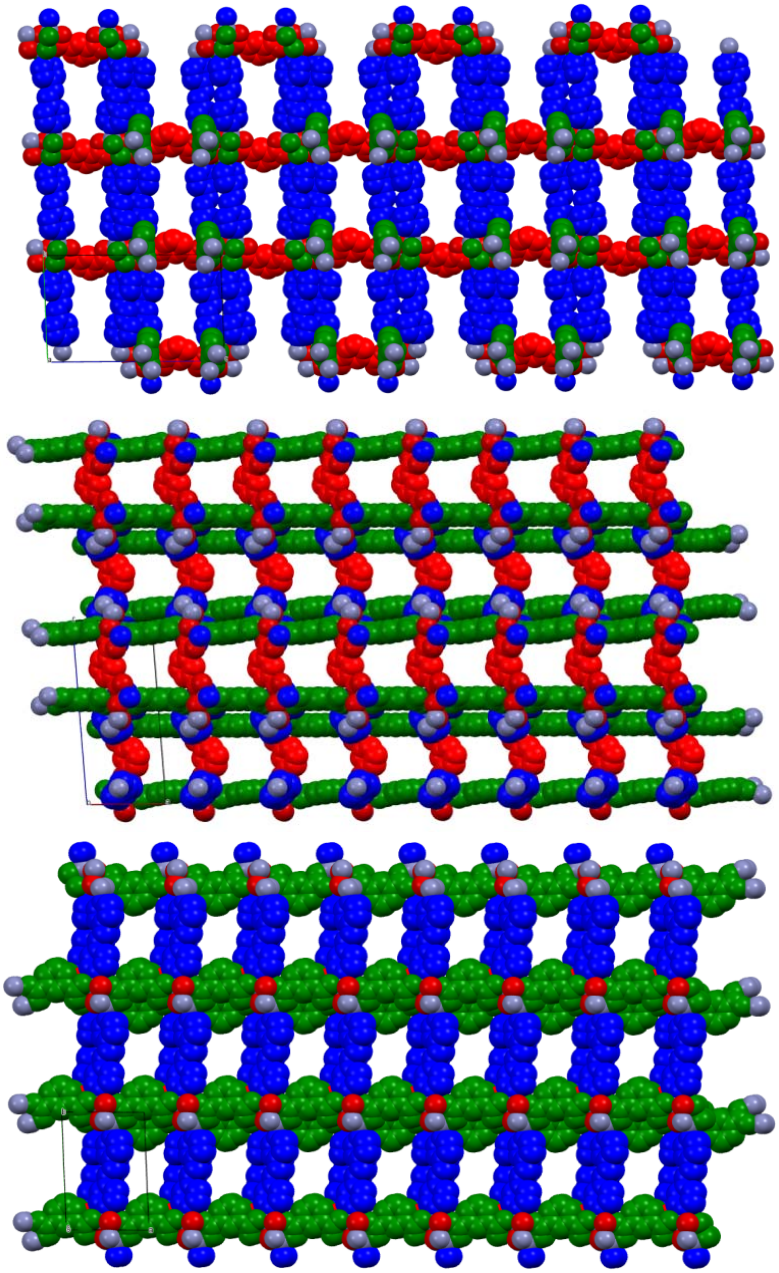

Figure S4: Packing diagrams highlighting the unique directional connectivity of the framework [$Zn_4(tbazip)_3(bpe)_2(OH)_2$].bpe·{solvent} in the bc-plane (upper), ac-plane (middle) and ab-plane (lower). The bpe linkage along the b-axis is shown in blue, and the isophthalate linkage along the a and c axes are shown in green and red, respectively. The zinc atoms are grey. All tert-butyl phenyl azo groups, non-coordinated bpe and hydrogen atoms have been omitted for clarity.

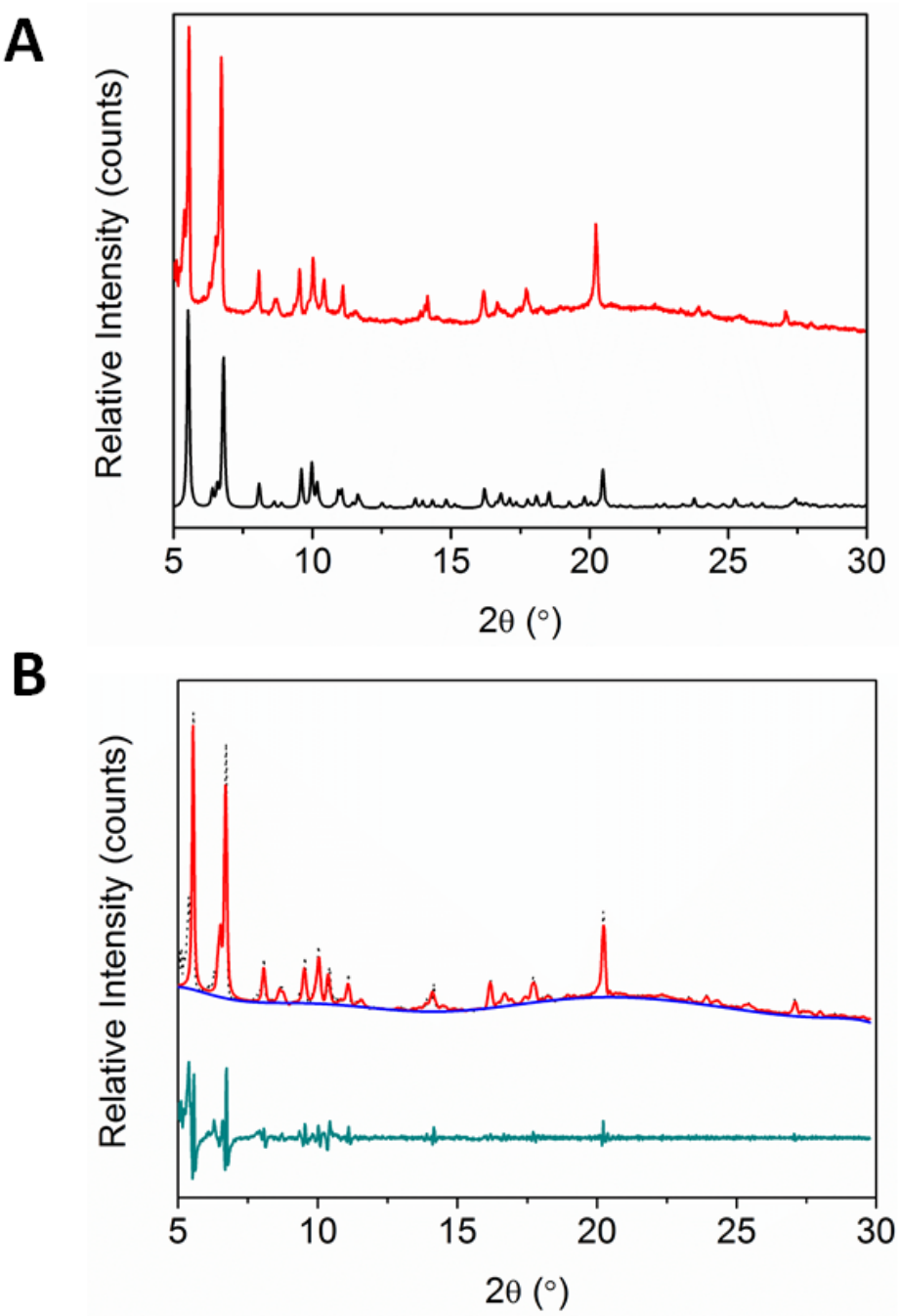

*Figure S5: **A**: PXRD patterns (λ=1.5418 Å) of the framework calculated from the crystal structure of [Zn_4(tbazip)$_3$(bpe)$_2$($OH)_2$].bpe·{solvent} (black) and the bulk-synthesised sample [Zn_4(tbazip)$_3$(bpe)$_2$($OH)_2$].bpe·2H_2O (red). **B**: Le Bail refinement of the observed bulk synthesised sample [Zn_4(tbazip)$_3$(bpe)$_2$($OH)_2$].bpe·2H_2O (black). The red pattern indicates the calculated powder pattern. The calculated background (blue) and difference pattern (green) are also provided.*

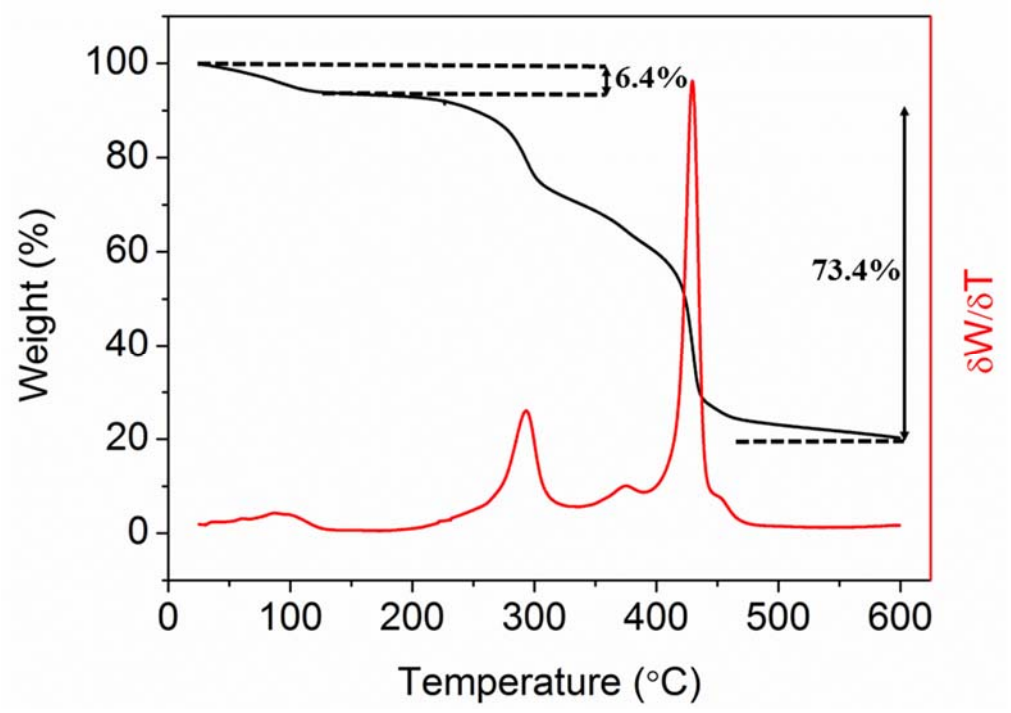

Figure S6: TGA plot of $[Zn_4(tbazip)_3(bpe)_2(OH)_2]\cdot bpe\cdot 2H_2O$. The black curve shows the mass fraction of the framework, and the red curve shows the derivative profile.

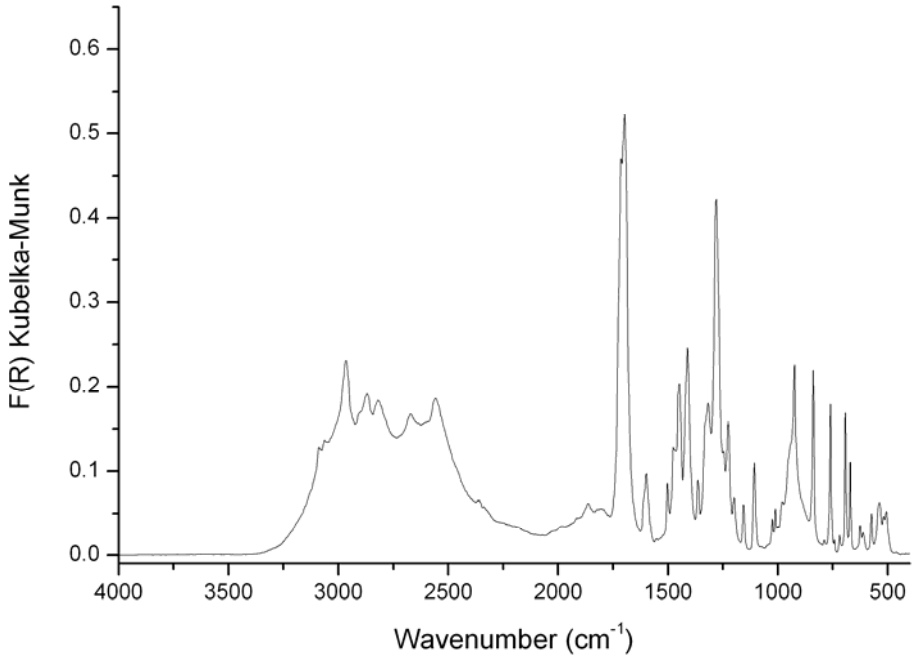

Figure S7: FTIR spectrum of tbazip

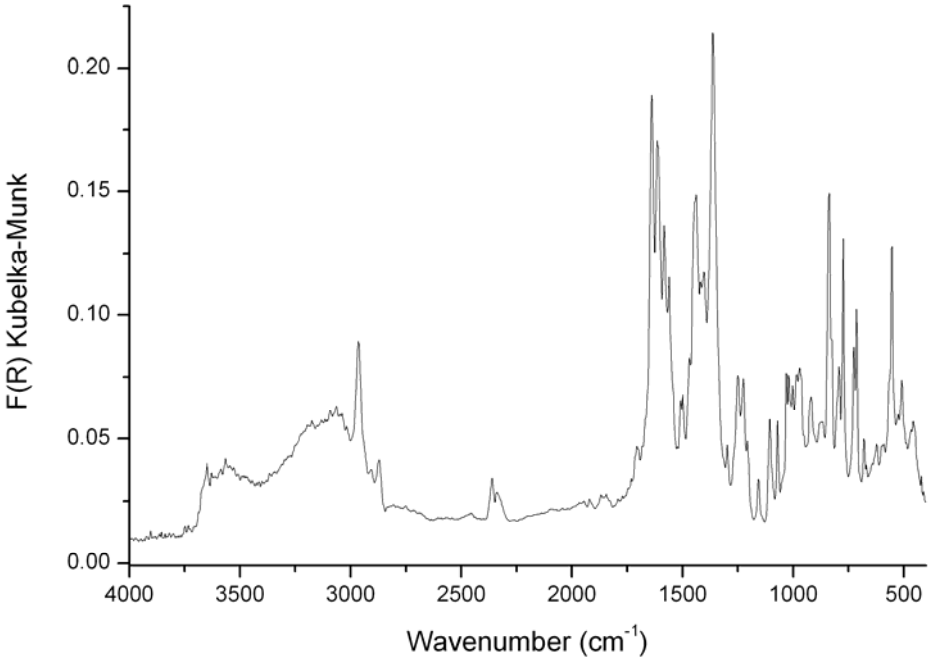

Figure S8: FTIR spectrum of $[Zn_4(tbazip)_3(bpe)_2(OH)_2]\cdot bpe\cdot 2H_2O$

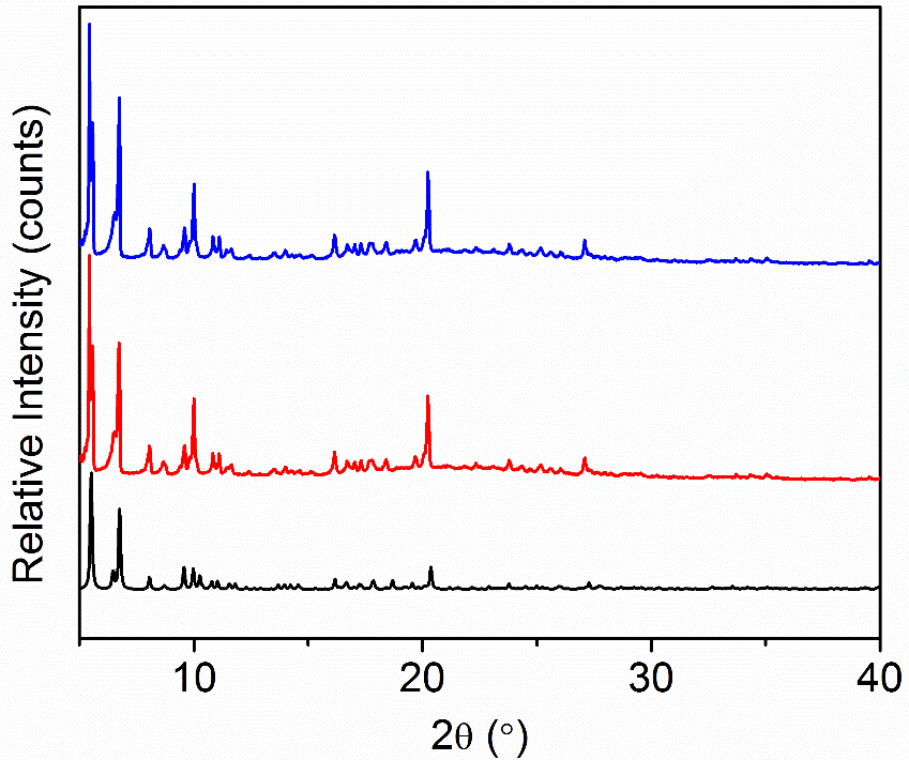

Figure S9: PXRD patterns (λ=1.5418 Å) of $[Zn_4(tbazip)_3(bpe)_2(OH)_2]\cdot bpe\cdot${solvent} (simulated, black), under vacuum (blue) and under 750 mbar CO_2 (red).

Table S1: Crystal data and structure refinement for $[Zn_4(tbazip)_3(bpe)_2(OH)_2]\cdot bpe[Zn_4(tbazip)_3(bpe)_2(OH)_2].bpe\cdot\{solvent\}$

Empirical formula	$C_{90}H_{80}N_{12}O_{14}Zn_4$
Formula weight	1815.14
Temperature /K	90.0
Crystal system	triclinic
Space group	*P*-1
***a* /Å**	10.9673(7)
***b* /Å**	16.0053(11)
***c* /Å**	26.0812(18)
***α* /°**	91.5674(18)
***β* /°**	94.1464(17)
***γ* /°**	92.2275(17)
Volume /Å^3	4560.6(5)
Z	2
ρ_{calc} mg/mm^3	1.322
μ /mm^{-1}	1.106
F(000)	1872.0
Crystal size /mm^3	0.1 × 0.1 × 0.05
Radiation	MoKα (λ = 0.71073 Å)
2Θ range for data collection	3.726 to 69.974°
Index ranges	$-17 \leq h \leq 16$, $-24 \leq k \leq 25$, $-41 \leq l \leq 41$
Reflections collected	75190
Independent reflections	36791 [R_{int} = 0.0398, R_{sigma} = 0.0750]
Data/restraints/parameters	36791/1064/1484
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0560, wR_2 = 0.1377
Final R indexes [all data]	R_1 = 0.0986, wR_2 = 0.1485
Largest diff. peak/hole / e Å^{-3}	1.21/-0.80

Table S2: Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[Zn_4(tbazip)_3(bpe)_2(OH)_2]$.bpe·{solvent}. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	*x*	*y*	*z*	U(eq)
Zn1	4197.4(2)	10944.3(2)	868.1(2)	19.67(6)
Zn2	5184.2(2)	9318.6(2)	417.6(2)	16.95(6)
Zn3	3715.9(2)	10831.8(2)	4128.3(2)	18.15(6)
Zn4	4813.6(2)	9243.2(2)	4616.9(2)	16.44(6)
O1	5317.2(13)	10666.7(9)	352.9(6)	19.2(3)
O3	4844.9(15)	10585.3(9)	1545.3(7)	25.4(4)
O5	5782.6(14)	9500.8(9)	1200.5(7)	22.4(3)
O6	6949.3(13)	9132.4(9)	296.0(7)	21.6(3)
O7	7809.3(14)	10386.8(9)	562.1(7)	24.3(4)
O8	5078.1(13)	10575.8(9)	4603.7(6)	17.9(3)
O10	4288.7(16)	10502(1)	3450.5(7)	28.7(4)
O12	4616.9(16)	9255.2(10)	3791.7(7)	28.5(4)
O13	6616.0(14)	9049.5(9)	4579.0(7)	23.8(4)
O14	7293.4(14)	10225.0(9)	4211.0(7)	24.7(4)
N1	10223.8(17)	7031.9(12)	709.8(9)	29.0(5)
N2	9210.8(18)	6625.2(12)	661.9(9)	25.8(4)
N3	9832.1(16)	6923.0(11)	4234.3(8)	20.8(4)
N4	8828.7(16)	6512.7(11)	4190.5(8)	21.3(4)
N5	7741(2)	8009.7(13)	2726.9(8)	30.3(5)
N6	8368(2)	7857.4(15)	2355.4(9)	36.9(5)
C2	7841.5(18)	9619.6(13)	470.3(9)	19.7(4)
C3	9036.3(18)	9193.4(13)	567.2(9)	19.4(4)
C4	10149.5(18)	9656.9(13)	625.2(9)	19.8(4)
C5	11250.4(19)	9248.6(13)	688.0(9)	20.6(4)
C6	11232.2(19)	8382.5(13)	717.4(10)	25.2(5)
C7	10128.7(19)	7915.2(13)	673.7(10)	24.4(5)
C8	9027.8(19)	8323.6(13)	595.4(10)	23.6(5)
C9	9313(2)	5742.3(13)	711.9(10)	24.0(5)
C10	10388(2)	5318.7(15)	712.0(12)	34.0(6)
C11	10368(3)	4459.5(16)	781.8(12)	36.3(6)
C12	9292(3)	4011.9(14)	864.1(10)	30.4(6)
C13	8219(3)	4446.5(15)	849.1(12)	36.9(6)
C14	8225(2)	5301.9(14)	768.3(11)	32.2(6)
C15	9272(3)	3067.4(15)	966.6(12)	40.0(7)
C16	10607(5)	2697(3)	870(2)	46.9(14)
C17	8357(4)	2603(2)	646(2)	38.0(12)
C18	9163(7)	3012(3)	1549(2)	60.8(18)
C21	4693(3)	6306.7(17)	782.8(15)	21.9(6)
C20	5610(3)	6819.3(18)	1041.4(14)	22.4(6)
C19	5739(4)	7656(3)	916.9(18)	20.9(7)
N9	5010(6)	8008(4)	556(2)	20.3(8)
C23	4110(3)	7518(2)	314.8(15)	23.3(7)
C22	3921(3)	6674.5(18)	411.2(15)	24.0(6)
C24	4600(3)	5417.6(16)	900.5(13)	24.4(6)
C25	3969(3)	4826.1(16)	617.1(13)	23.5(6)

C26	3958(3)	3932.0(17)	722.5(14)	21.0(6)
C27	4576(3)	3606(2)	1152.1(15)	25.8(7)
C28	4602(4)	2747(2)	1205.9(17)	25.8(8)
N12	4029(7)	2194(4)	862(2)	19.6(8)
C29	3378(3)	2511(2)	456.8(17)	23.8(7)
C30	3336(3)	3355.0(17)	377.2(14)	25.0(6)
C31	5447(2)	9917.8(13)	1570.5(10)	22.8(5)
C32	5764(2)	9589.7(13)	2096.4(10)	23.2(5)
C33	6624(2)	8977.4(14)	2151.4(10)	26.1(5)
C34	6879(2)	8642.0(14)	2632.6(10)	27.2(5)
C35	6250(2)	8901.5(15)	3050.3(10)	28.6(5)
C36	5398(2)	9520.0(14)	2992.3(10)	26.1(5)
C37	5161(2)	9867.3(13)	2520.9(10)	26.0(5)
C38	4726(2)	9769.6(14)	3446.1(10)	25.6(5)
C39	9217(3)	7215.7(18)	2440.2(11)	35.0(6)
C40	9885(4)	7026(3)	2037.0(13)	65.2(12)
C41	10739(4)	6401(3)	2070.1(13)	60.4(11)
C42	10903(3)	5942.5(19)	2520.1(11)	39.8(7)
C43	10279(3)	6203(2)	2929.8(11)	46.2(8)
C44	9436(3)	6822(2)	2898.9(11)	46.3(8)
C45	11773(3)	5212(2)	2570.2(14)	55.9(10)
C46	12553(5)	5139(4)	2112.5(16)	133(3)
C47	12608(4)	5312(3)	3051.9(15)	85.7(17)
C48	10983(6)	4431(3)	2611(3)	169(4)
C50	7413.2(18)	9503.6(13)	4366.2(10)	21.4(5)
C51	8616.1(18)	9080.8(12)	4315.3(9)	18.6(4)
C52	9710.6(18)	9551.6(12)	4320.3(9)	18.6(4)
C53	10821.0(18)	9148.1(12)	4323.3(9)	18.8(4)
C54	10820.7(18)	8272.7(13)	4296.1(9)	20.8(4)
C55	9725.0(18)	7807.9(12)	4263.8(9)	18.4(4)
C56	8613.1(18)	8209.6(12)	4284.6(9)	18.8(4)
C57	8933.3(19)	5628.4(12)	4155.9(9)	19.1(4)
C58	9994(2)	5210.8(14)	4288.5(10)	27.8(5)
C59	9992(2)	4349.8(14)	4229.7(11)	32.3(6)
C60	8951(2)	3880.6(14)	4029.3(10)	27.1(5)
C61	7915(3)	4313.5(15)	3897.6(12)	36.7(7)
C62	7899(2)	5174.8(14)	3965.2(12)	34.4(6)
C63	8988(3)	2922.6(15)	3966.7(12)	39.1(7)
C64	9881(4)	2698.0(19)	3582.6(15)	59.5(10)
C65	9398(3)	2559.7(18)	4498.2(14)	48.6(8)
C66	7707(3)	2520.2(18)	3807.6(15)	52.9(9)
C69	4253(5)	6180(3)	4390(2)	16.3(9)
C70	4962(5)	6653(4)	4074(2)	19.8(10)
C71	5115(8)	7512(5)	4156(3)	19.6(12)
N10	4590(12)	7934(10)	4531(5)	18.5(16)
C67	3876(10)	7472(7)	4834(3)	21.1(15)
C68	3701(6)	6600(4)	4778(3)	22.7(12)
C72	4135(4)	5270(2)	4283.9(19)	18.7(9)

C73	3539(3)	4707(2)	4543.3(16)	18.9(9)
C74	3498(4)	3803(2)	4412(2)	15.5(8)
C78	4000(4)	3493(3)	3969(2)	18.9(9)
C77	3988(6)	2636(4)	3882(3)	21.4(12)
N11	3505(13)	2093(10)	4198(5)	16.4(15)
C76	2989(6)	2385(4)	4619(3)	17.3(11)
C75	2982(4)	3231(3)	4734(2)	17.6(9)
C81	9390(4)	10111(3)	2441(2)	80.0(18)
C82	8795(5)	10400(3)	2860.0(14)	64.3(14)
C83	7869(4)	10963(3)	2789.1(16)	78.6(18)
N7	7538(4)	11238(2)	2299(2)	92.2(17)
C79	8133(6)	10949(3)	1880.6(15)	111(2)
C80	9060(6)	10385(4)	1951.5(16)	91(2)
C84	10475(8)	9475(4)	2616(3)	111(3)
C85	10967(11)	9179(6)	2267(4)	127(3)
C86	12026(8)	8678(5)	2465(3)	75(2)
C87	12860(9)	8420(6)	2063(3)	102(3)
C88	13730(8)	7854(6)	2185(4)	100(3)
N8	13915(8)	7502(5)	2625(5)	83(3)
C89	13155(11)	7698(7)	2993(4)	85(3)
C90	12299(6)	8254(4)	2933(2)	69.4(17)
C16A	9448(7)	2630(4)	444(3)	30.2(17)
C18A	9998(10)	2795(5)	1399(4)	45(2)
C17A	7844(8)	2690(4)	1048(3)	39(2)
C74A	3870(6)	3825(3)	4195(3)	17(1)
C75A	4299(6)	3380(4)	3779(3)	21.4(12)
C76A	4173(9)	2526(5)	3755(4)	20.1(14)
N11A	3633(18)	2068(14)	4111(7)	18.1(19)
C77A	3218(9)	2496(6)	4511(4)	21.0(15)
C78A	3300(6)	3366(4)	4564(3)	18.0(11)
C73A	4091(5)	4742(3)	4214(2)	22.4(13)
C72A	3759(5)	5261(3)	4570(3)	21.9(13)
C69A	4009(6)	6175(4)	4585(3)	17.4(12)
C68A	4701(7)	6560(5)	4226(3)	22.4(14)
C67A	4912(9)	7429(7)	4266(5)	20.2(16)
N10A	4448(14)	7890(11)	4623(6)	13.7(17)
C71A	3787(13)	7534(8)	4969(5)	21.5(17)
C70A	3545(8)	6673(6)	4953(4)	24.0(15)
C27A	3746(14)	3504(9)	517(7)	23.5(13)
C28A	3669(17)	2590(13)	537(9)	23.2(13)
N12A	4100(40)	2250(20)	943(13)	22.1(14)
C29A	4700(20)	2645(13)	1337(9)	24.3(14)
C30A	4785(17)	3505(11)	1313(7)	25.4(15)
C26A	4313(14)	3929(9)	921(7)	21.8(14)
C25A	4504(13)	4866(7)	917(6)	24(2)
C24A	4164(12)	5328(8)	563(6)	25(2)
C21A	4437(13)	6286(8)	554(7)	20.0(14)
C20A	3816(14)	6708(9)	174(7)	23.5(15)

C19A	4027(18)	7581(11)	141(7)	23.0(14)
N9A	4890(30)	7960(20)	478(12)	20.6(14)
C23A	5539(19)	7555(13)	825(9)	20.4(13)
C22A	5328(14)	6683(8)	880(7)	19.8(13)
C81A	9848(11)	9793(7)	2372(4)	69(3)
C82A	9323(14)	10226(9)	1963(3)	77(3)
C83A	8440(12)	10803(7)	2048(4)	78(3)
N7A	8081(10)	10948(6)	2542(4)	69(2)
C79A	8605(12)	10515(7)	2951(3)	73(3)
C80A	9488(11)	9937(6)	2866(3)	68(3)
C84A	11058(18)	9368(15)	2323(8)	125(4)
C85A	11440(20)	8802(12)	2587(9)	122(4)
C88A	14170(20)	7165(18)	2647(14)	81(7)
N8A	14110(10)	6958(10)	2190(5)	74(4)
C89A	13240(17)	7166(14)	1823(7)	98(6)
C90A	12303(16)	7700(13)	1940(6)	81(5)
C87A	12399(10)	8186(9)	2447(5)	41(3)
C86A	13351(16)	7883(10)	2794(8)	43(4)
C1	12457.8(19)	9717.8(13)	714.7(10)	21.3(4)
O2	12482.2(13)	10505.2(9)	803.1(7)	23.9(4)
O4	13378.3(14)	9302.2(10)	651.1(7)	26.5(4)
C49	12029.0(18)	9620.7(13)	4374.1(10)	21.0(5)
O11	12902.3(13)	9259.4(9)	4589.5(7)	23.6(3)
O9	12081.4(14)	10354.1(9)	4194.6(7)	24.7(4)

Table S3: Atomic occupancy for [Zn_4(tbazip)$_3$(bpe)$_2$(OH)$_2$].bpe·{solvent}

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
C16	0.634(5)	**H16A**	0.634(5)	**H16B**	0.634(5)
H16C	0.634(5)	**C17**	0.634(5)	**H17A**	0.634(5)
H17B	0.634(5)	**H17C**	0.634(5)	**C18**	0.634(5)
H18A	0.634(5)	**H18B**	0.634(5)	**H18C**	0.634(5)
C21	0.816(4)	**C20**	0.816(4)	**H20**	0.816(4)
C19	0.816(4)	**H19**	0.816(4)	**N9**	0.816(4)
C23	0.816(4)	**H23**	0.816(4)	**C22**	0.816(4)
H22	0.816(4)	**C24**	0.816(4)	**H24**	0.816(4)
C25	0.816(4)	**H25**	0.816(4)	**C26**	0.816(4)
C27	0.816(4)	**H27**	0.816(4)	**C28**	0.816(4)
H28	0.816(4)	**N12**	0.816(4)	**C29**	0.816(4)
H29	0.816(4)	**C30**	0.816(4)	**H30**	0.816(4)
C69	0.564(6)	**C70**	0.564(6)	**H70**	0.564(6)
C71	0.564(6)	**H71**	0.564(6)	**N10**	0.564(6)
C67	0.564(6)	**H67**	0.564(6)	**C68**	0.564(6)
H68	0.564(6)	**C72**	0.564(6)	**H72**	0.564(6)
C73	0.564(6)	**H73**	0.564(6)	**C74**	0.564(6)
C78	0.564(6)	**H78**	0.564(6)	**C77**	0.564(6)
H77	0.564(6)	**N11**	0.564(6)	**C76**	0.564(6)
H76	0.564(6)	**C75**	0.564(6)	**H75**	0.564(6)
C81	0.721(4)	**C82**	0.721(4)	**H82**	0.721(4)
C83	0.721(4)	**H83**	0.721(4)	**N7**	0.721(4)
C79	0.721(4)	**H79**	0.721(4)	**C80**	0.721(4)
H80	0.721(4)	**C84**	0.721(4)	**H84**	0.721(4)
C85	0.721(4)	**H85**	0.721(4)	**C86**	0.721(4)
C87	0.721(4)	**H87**	0.721(4)	**C88**	0.721(4)
H88	0.721(4)	**N8**	0.721(4)	**C89**	0.721(4)
H89	0.721(4)	**C90**	0.721(4)	**H90**	0.721(4)
C16A	0.366(5)	**H16D**	0.366(5)	**H16E**	0.366(5)
H16F	0.366(5)	**C18A**	0.366(5)	**H18D**	0.366(5)
H18E	0.366(5)	**H18F**	0.366(5)	**C17A**	0.366(5)
H17D	0.366(5)	**H17E**	0.366(5)	**H17F**	0.366(5)
C74A	0.436(6)	**C75A**	0.436(6)	**H75A**	0.436(6)
C76A	0.436(6)	**H76A**	0.436(6)	**N11A**	0.436(6)
C77A	0.436(6)	**H77A**	0.436(6)	**C78A**	0.436(6)
H78A	0.436(6)	**C73A**	0.436(6)	**H73A**	0.436(6)
C72A	0.436(6)	**H72A**	0.436(6)	**C69A**	0.436(6)
C68A	0.436(6)	**H68A**	0.436(6)	**C67A**	0.436(6)
H67A	0.436(6)	**N10A**	0.436(6)	**C71A**	0.436(6)
H71A	0.436(6)	**C70A**	0.436(6)	**H70A**	0.436(6)
C27A	0.184(4)	**H27A**	0.184(4)	**C28A**	0.184(4)
H28A	0.184(4)	**N12A**	0.184(4)	**C29A**	0.184(4)
H29A	0.184(4)	**C30A**	0.184(4)	**H30A**	0.184(4)
C26A	0.184(4)	**C25A**	0.184(4)	**H25A**	0.184(4)
C24A	0.184(4)	**H24A**	0.184(4)	**C21A**	0.184(4)
C20A	0.184(4)	**H20A**	0.184(4)	**C19A**	0.184(4)

H19A	0.184(4)	**N9A**	0.184(4)	**C23A**	0.184(4)
H23A	0.184(4)	**C22A**	0.184(4)	**H22A**	0.184(4)
C81A	0.279(4)	**C82A**	0.279(4)	**H82A**	0.279(4)
C83A	0.279(4)	**H83A**	0.279(4)	**N7A**	0.279(4)
C79A	0.279(4)	**H79A**	0.279(4)	**C80A**	0.279(4)
H80A	0.279(4)	**C84A**	0.279(4)	**H84A**	0.279(4)
C85A	0.279(4)	**H85A**	0.279(4)	**C88A**	0.279(4)
H88A	0.279(4)	**N8A**	0.279(4)	**C89A**	0.279(4)
H89A	0.279(4)	**C90A**	0.279(4)	**H90A**	0.279(4)
C87A	0.279(4)	**C86A**	0.279(4)	**H86A**	0.279(4)

Table S4: Solvent masks information for $[Zn_4(tbazip)_3(bpe)_2(OH)_2].bpe\cdot\{solvent\}$

Number	**x**	**y**	**z**	**Volume /Å^3**	**Electron count**	**Content**
1	-0.148	0.348	0.249	297.4	78.3	ethanol and/or water
2	-0.431	0.652	0.751	297.4	78.1	ethanol and/or water

References

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Journal of Applied Crystallography*, 2009, **42**, 339-341.
2. G. Sheldrick, *Acta Crystallographica Section A*, 2008, **64**, 112-122.