Electronic Supporting Information

Clathrate directed structural changes in novel tetrapyridyltetraphenylethylene metal organic frameworks

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Supplemental data: Tables S1-S20

Supplemental data: Figures S1-S30

Gas isotherms

Table S1: Optimised virial coefficients and R^2 value for the least squares fitting of the modelled ln(P) as a function of the amount of surface excess of CO_2 and CH_4 sorbed over the measurement temperatures for [($MnCl_2$)tppe].

Gas	CO_2	CH_4
Temps (K)	258, 273	258, 273, 298.2
a0	-3283.69	-1549.29
a1	203.8899	321.9999
a2	255.6273	578.7002
a3	-177.186	-85.691
a4	42.20766	-394.63
a5	-3.55909	85.80318
b	16.19187	12.27671
R^2	0.91314737	0.98725542

Table S2: Optimised virial coefficients and R^2 value for the least squares fitting of the modelled ln(P) as a function of the amount of surface excess of CO_2 and CH_4 sorbed over the measurement temperatures for [($NiCl_2$)tppe].

Gas	CO_2	CH_4
Temps (K)	258, 273	258, 273
a0	-3283.69	-2369.12
a1	203.8899	340.3052
a2	255.6273	242.5437
a3	-177.186	1.679216
a4	42.20766	-125.666
a5	-3.55909	168.004
b	16.19187	14.76754
R^2	0.99771945	0.99850225

SCXRD

[($MnCl_2$)tppe●4TCE

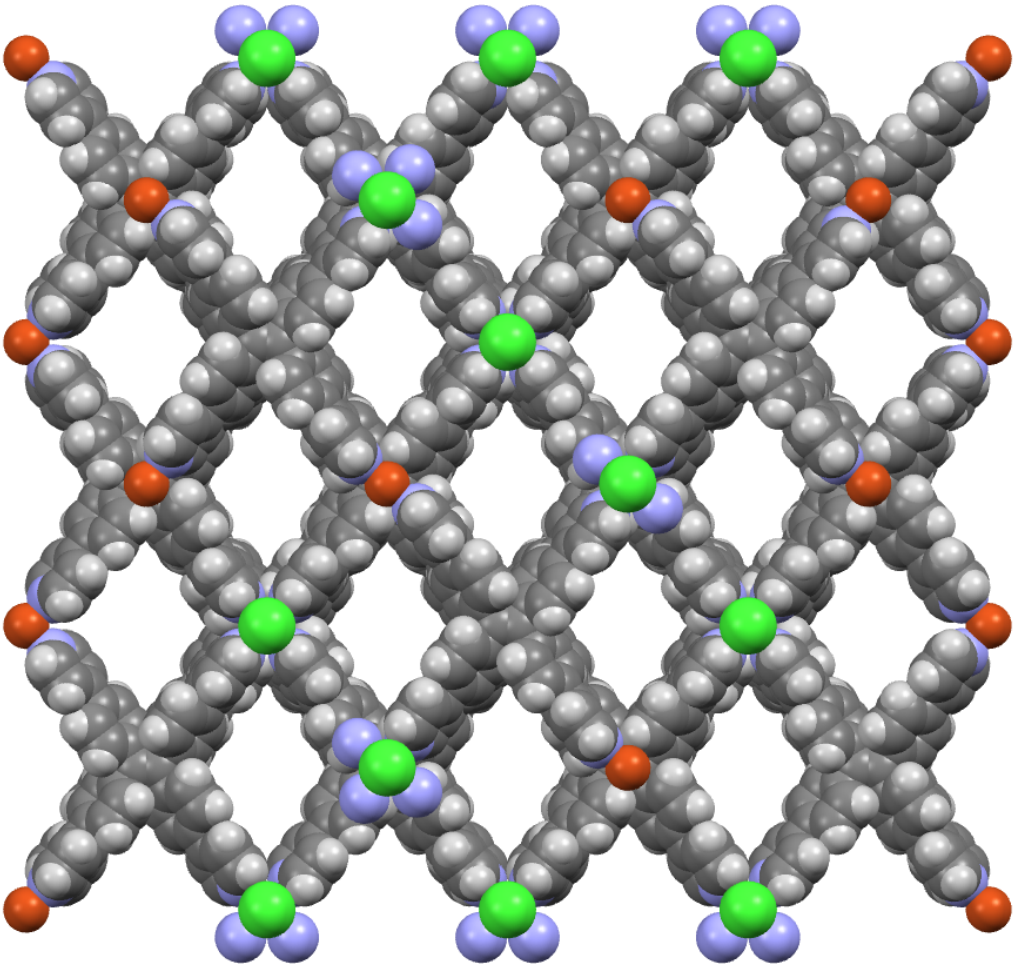

Figure S1. Spacefill image of [($MnCl_2$)tppe].

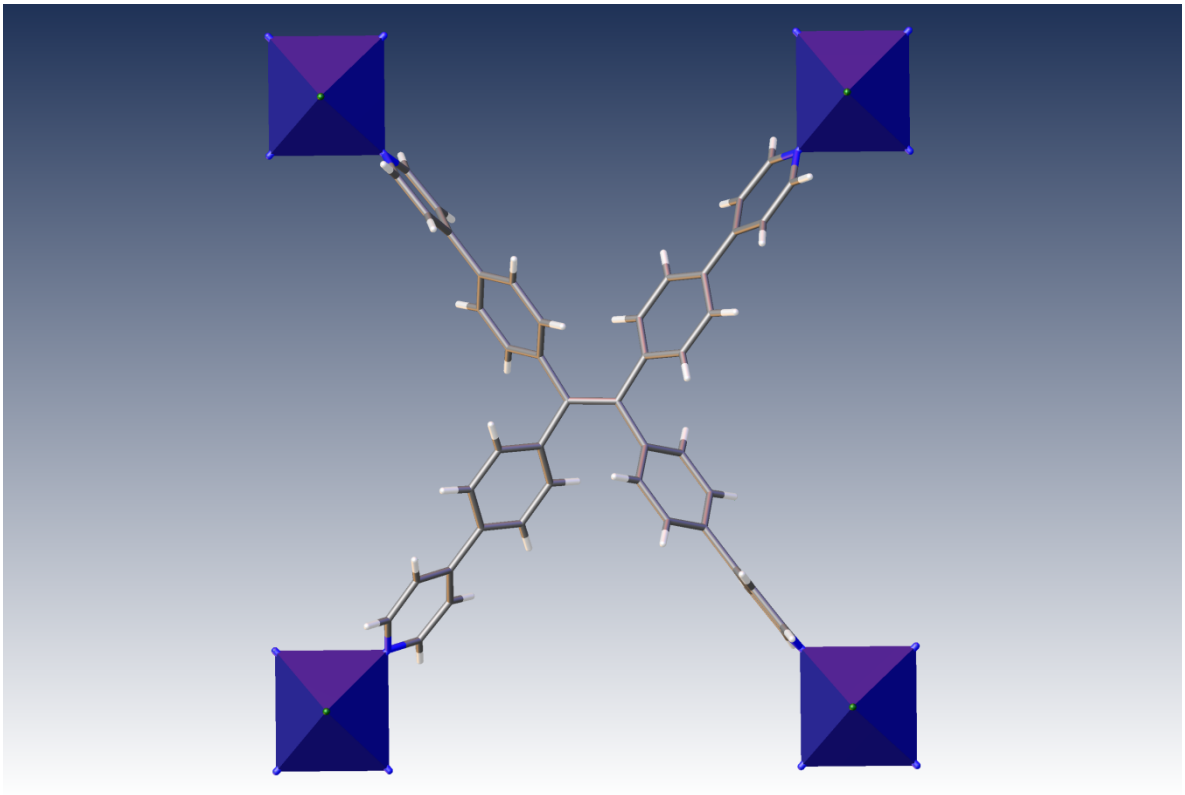

Figure S2. [($MnCl_2$)tppe] with Mn^{2+} polyhedral displayed.

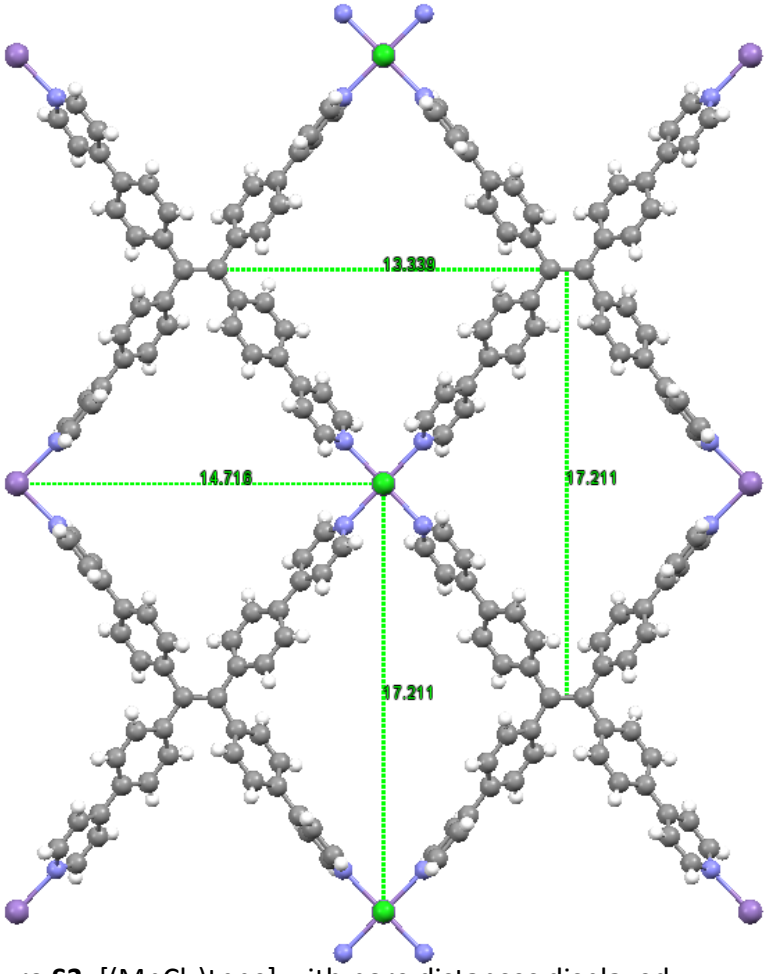

Figure S3. [($MnCl_2$)tppe] with pore distances displayed.

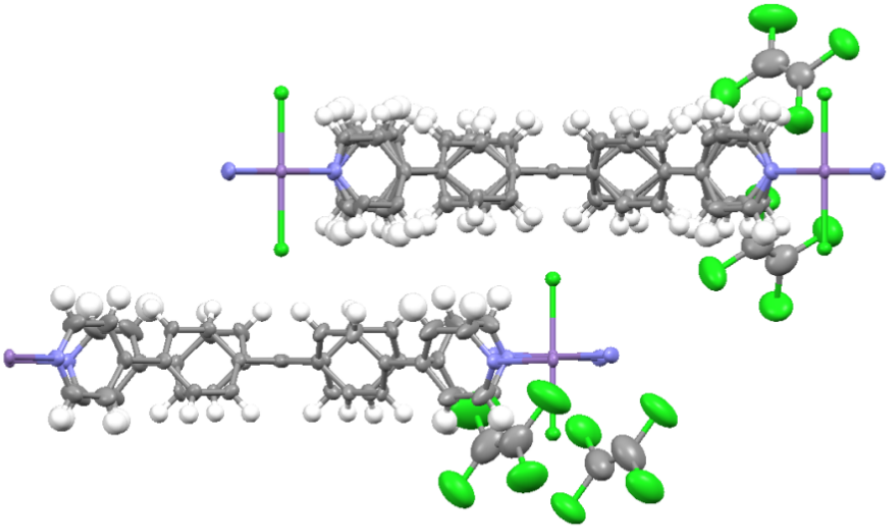

Figure S4. [($MnCl_2$)tppe]●4TCE displayed along the b axis.

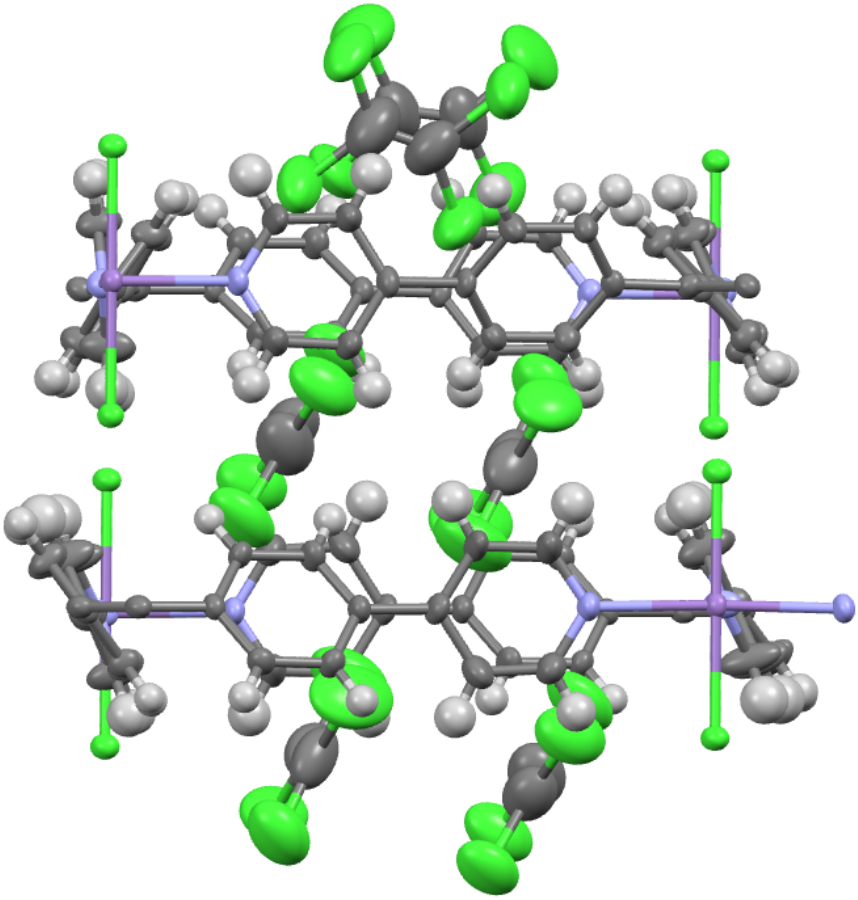

Figure S5. [($MnCl_2$)tppe]●4TCE to show alternating TCE molecules.

Table S3. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for [($MnCl_2$)tppe]. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C24	10377(4)	9505(4)	8284(3)	71(3)
C25	10377(4)	9242(4)	8617(3)	72(4)
C26	9934(3)	8956(3)	8696(2)	35.4(18)
C27	9486(4)	8994(3)	8449(3)	58(3)
C28	9514(4)	9276(3)	8136(3)	62(3)

C29	9937(3)	8641(3)	9038(2)	31.1(17)
C30	10337(3)	8672(3)	9326(2)	40(2)
C31	10347(3)	8373(3)	9633(2)	34.5(18)
C32	9951(3)	8028(2)	9662.9(19)	26.0(16)
C33	9544(3)	7995(2)	9375(2)	28.6(17)
C34	9539(3)	8294(3)	9066(2)	31.3(18)
C35	10477(4)	9223(3)	6923(3)	47(2)
C36	10512(4)	8925(3)	6618(3)	53(2)
C37	10022(3)	8768(3)	6438(2)	35.7(18)
C38	9531(4)	8924(3)	6597(3)	53(3)
C39	9539(4)	9218(3)	6903(3)	55(3)
C40	10033(3)	8481(2)	6081(2)	31.1(17)
C41	10458(3)	8533(3)	5806(2)	32.7(18)
C42	10450(3)	8287(2)	5467(2)	30.6(17)
C43	10026(3)	7971(2)	5393.4(19)	24.6(15)
C44	9617(3)	7906(2)	5672(2)	28.5(16)
C45	9619(3)	8166(3)	6010(2)	33.4(18)
C46	10034(3)	7726(2)	5013(2)	26.2(15)
N3	9957(3)	9526(2)	8036.1(17)	34.0(15)
N4	9995(3)	9384(2)	7066.3(17)	33.6(15)
Cl2	11011.4(10)	10000	7500	28.0(6)
Cl3	8939.2(10)	10000	7500	27.8(6)
Mn2	9976.9(6)	10000	7500	19.6(3)
C1	7960(3)	8232(3)	5620(2)	42(2)
C2	7981(3)	8524(3)	5934(2)	43(2)
C3	7488(3)	8654(2)	6123(2)	31.2(17)
C4	6992(4)	8474(3)	5973(3)	53(3)
C5	7009(4)	8187(3)	5658(3)	57(3)
C6	7490(3)	8952(2)	6464.5(19)	27.8(16)
C7	7904(3)	8914(3)	6741(2)	35.8(19)
C8	7901(3)	9186(3)	7067(2)	34.3(18)
C9	7483(3)	9504(2)	7126.3(19)	23.6(15)
C10	7056(3)	9547(3)	6852(2)	34.4(18)
C11	7062(3)	9275(3)	6524(2)	38.1(19)
C12	7496(3)	9766(2)	7497(2)	25.4(15)
C13	7503(3)	9495(2)	7861.7(19)	24.9(16)
C14	7867(3)	9570(3)	8167(2)	35.5(18)
C15	7873(3)	9291(3)	8493(2)	34.9(18)
C16	7504(3)	8931(2)	8522.0(19)	25.3(16)
C17	7134(3)	8848(3)	8206(2)	33.5(18)
C18	7140(3)	9126(3)	7888(2)	34.1(18)
C19	7495(3)	8629(2)	8864.0(19)	25.5(16)
C20	7947(3)	8605(3)	9121(2)	33.7(18)
C21	7927(3)	8308(3)	9435(2)	32.8(18)
C22	7057(3)	8060(3)	9262(2)	43(2)
C23	7046(3)	8340(3)	8943(2)	39(2)
N1	7493(3)	8051(2)	5486.6(16)	29.6(14)

N2	7498(3)	8038(2)	9508.8(16)	29.4(14)
Cl1	8545.2(10)	7500	5000	25.9(6)
Mn1	7500	7500	5000	19.8(5)
C51	11273(8)	7850(5)	8198(5)	127(6)
C52	11424(7)	8067(5)	7924(4)	110(5)
Cl13	12006.8(17)	8005.9(14)	7640.5(13)	115.5(14)
Cl14	11716.1(19)	7396.9(13)	8344.1(14)	128.2(16)
Cl15	10978.5(18)	8536.2(14)	7779.4(13)	126.4(15)
Cl16	10695.3(18)	7926.0(14)	8476.5(13)	129.3(17)
C53	11112(6)	7026(4)	7162(4)	105(5)
C54	11169(7)	7309(4)	6901(4)	108(5)
Cl17	11755(2)	7305.7(16)	6614.9(14)	138.9(17)
Cl18	11588.3(18)	6622.0(14)	7264.4(15)	132.5(16)
Cl19	10698(2)	7728.2(17)	6780(2)	186(3)
Cl20	10521(2)	7032(2)	7464.0(18)	169(2)
C47	6218(5)	9409(4)	9774(4)	76(3)
C48	6057(6)	9678(4)	9510(4)	99(4)
Cl9	6466.2(18)	9746.1(15)	9089.6(11)	118.0(14)
Cl10	6815.7(15)	9108.8(13)	9757.4(11)	102.2(11)
Cl11	5457.9(18)	9994.4(16)	9524.0(19)	157(2)
Cl12	5797.3(16)	9315.8(13)	10179.1(11)	104.1(12)
C49	8475(6)	10307(5)	9386(4)	100(4)
C50	8685(6)	10586(4)	9610(4)	95(4)
Cl5	8866.9(18)	10144.7(15)	8970.9(11)	116.8(14)
Cl6	9303.2(16)	10861.8(13)	9554.2(12)	111.1(13)
Cl7	7856.8(16)	10027.9(15)	9431.9(13)	120.9(15)
Cl8	8303.5(17)	10739.8(13)	10032.7(11)	105.3(12)
Mn3	7500	7500	10000	19.3(5)
Cl4	6465.9(10)	7500	10000	25.9(6)

Table S4. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for [(MnCl2)tppe. 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}**
C24	40(6)	111(9)	63(6)	54(6)	-21(5)	-26(6)
C25	52(6)	100(9)	65(7)	52(6)	-29(5)	-31(6)
C26	37(5)	39(4)	31(4)	13(4)	0(4)	-4(4)
C27	41(5)	74(7)	59(6)	39(5)	-13(5)	-23(5)
C28	54(6)	69(7)	63(6)	37(5)	-26(5)	-26(5)
C29	31(4)	39(4)	23(4)	11(3)	0(3)	0(3)
C30	46(5)	39(5)	35(4)	18(4)	-14(4)	-20(4)
C31	39(5)	35(4)	30(4)	11(3)	-14(4)	-11(4)
C32	28(4)	29(4)	22(4)	2(3)	2(3)	4(3)
C33	30(4)	31(4)	25(4)	9(3)	0(3)	-7(3)
C34	34(4)	43(5)	17(4)	12(3)	-7(3)	-9(3)
C35	38(5)	52(6)	52(5)	-17(5)	-7(4)	-2(4)

C36	42(5)	58(6)	58(6)	-20(5)	0(4)	14(4)
C37	37(4)	44(5)	27(4)	-13(3)	-2(4)	-7(4)
C38	36(5)	73(7)	49(5)	-41(5)	10(4)	-14(4)
C39	40(5)	63(6)	61(6)	-36(5)	13(5)	-13(5)
C40	30(4)	33(4)	30(4)	-12(3)	2(4)	-1(3)
C41	31(4)	37(4)	30(4)	-8(3)	3(3)	-10(3)
C42	28(4)	31(4)	32(4)	-2(3)	7(3)	-4(3)
C43	26(4)	26(4)	22(3)	-5(3)	1(3)	2(3)
C44	28(4)	28(4)	29(4)	-7(3)	0(3)	-6(3)
C45	36(4)	41(5)	24(4)	-9(3)	9(3)	-6(4)
C46	20(4)	34(4)	24(3)	-2(3)	-1(3)	1(3)
N3	29(4)	45(4)	28(3)	17(3)	1(3)	0(3)
N4	31(4)	38(4)	32(3)	-16(3)	0(3)	-2(3)
Cl2	22.0(13)	36.4(14)	25.8(13)	-1.8(11)	0	0
Cl3	24.3(13)	33.6(14)	25.6(13)	1.1(11)	0	0
Mn2	24.2(8)	20.6(7)	14.0(7)	0.3(6)	0	0
C1	33(5)	50(5)	42(5)	-21(4)	7(4)	-5(4)
C2	32(5)	58(6)	40(5)	-23(4)	0(4)	-6(4)
C3	38(5)	31(4)	24(4)	-8(3)	-2(3)	4(3)
C4	32(5)	68(6)	58(6)	-37(5)	4(4)	-2(4)
C5	37(5)	82(7)	50(5)	-43(5)	-2(4)	-1(5)
C6	34(4)	31(4)	19(4)	-8(3)	-1(3)	-1(3)
C7	30(4)	34(4)	44(5)	-13(4)	2(4)	3(3)
C8	35(4)	37(5)	31(4)	-5(4)	-5(4)	5(4)
C9	27(4)	24(4)	20(4)	-1(3)	5(3)	-4(3)
C10	34(4)	35(5)	33(4)	-10(4)	-4(4)	4(3)
C11	36(5)	46(5)	32(4)	-9(4)	-3(4)	9(4)
C12	23(4)	29(4)	24(3)	-2(3)	0(3)	-4(3)
C13	29(4)	23(4)	23(4)	4(3)	0(3)	2(3)
C14	40(5)	35(5)	32(4)	2(4)	-4(4)	-4(4)
C15	39(5)	44(5)	22(4)	5(4)	-6(3)	-6(4)
C16	29(4)	25(4)	22(4)	4(3)	1(3)	1(3)
C17	40(5)	35(4)	26(4)	2(3)	-2(4)	-6(4)
C18	35(4)	41(5)	26(4)	2(4)	-9(3)	-5(4)
C19	34(4)	24(4)	19(4)	2(3)	4(3)	1(3)
C20	32(4)	36(4)	33(4)	12(4)	-4(4)	-7(3)
C21	31(4)	43(5)	24(4)	8(3)	-9(3)	-7(4)
C22	39(5)	55(6)	34(4)	26(4)	-10(4)	-12(4)
C23	36(5)	51(5)	32(4)	13(4)	-11(4)	-7(4)
N1	32(4)	34(4)	23(3)	-11(3)	3(3)	-1(3)
N2	32(4)	33(3)	24(3)	6(3)	-2(3)	-3(3)
Cl1	22.9(13)	31.2(14)	23.6(12)	-2.0(11)	0	0
Mn1	23.8(11)	21.4(11)	14.2(10)	0	0	0
C51	145(14)	107(12)	128(13)	7(9)	46(11)	-21(10)
C52	111(11)	121(12)	98(10)	-1(8)	16(9)	-36(9)
Cl13	108(3)	107(3)	131(3)	25(2)	56(2)	0(2)
Cl14	127(3)	94(3)	163(4)	47(3)	45(3)	30(2)

Cl15	122(3)	114(3)	143(4)	56(3)	30(3)	11(3)
Cl16	129(3)	107(3)	152(4)	32(3)	80(3)	16(2)
C53	121(11)	65(8)	130(12)	14(7)	-34(10)	7(8)
C54	144(13)	59(8)	121(11)	1(7)	-46(10)	-8(8)
Cl17	152(4)	122(3)	143(4)	10(3)	64(3)	3(3)
Cl18	108(3)	103(3)	187(4)	34(3)	-27(3)	37(2)
Cl19	154(4)	107(3)	297(8)	71(4)	-27(5)	47(3)
Cl20	128(4)	168(5)	210(6)	35(4)	78(4)	22(3)
C47	82(8)	51(7)	95(9)	-4(6)	2(7)	-16(6)
C48	96(10)	58(8)	144(12)	6(7)	-19(9)	-9(7)
Cl9	118(3)	139(3)	97(3)	33(2)	0(2)	-32(3)
Cl10	88(2)	115(3)	103(3)	11(2)	0(2)	31(2)
Cl11	95(3)	119(3)	257(7)	70(4)	9(4)	32(2)
Cl12	110(3)	102(3)	101(3)	-7(2)	30(2)	-10(2)
C49	100(10)	83(9)	118(11)	6(8)	-15(9)	-24(8)
C50	108(10)	61(8)	117(11)	15(7)	-23(8)	-11(7)
Cl5	131(3)	133(3)	87(2)	-31(2)	26(2)	-54(3)
Cl6	101(3)	104(3)	128(3)	-23(2)	4(2)	-49(2)
Cl7	84(2)	145(4)	134(3)	-28(3)	16(2)	-51(2)
Cl8	108(3)	107(3)	100(3)	-15(2)	15(2)	-12(2)
Mn3	22.0(11)	22.6(11)	13.3(10)	0	0	0
Cl4	21.0(13)	32.2(14)	24.5(12)	-1.7(11)	0	0

Table S5. Bond Lengths for [(MnCl2)tppe.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C24	C25	1.383(12)	C10	C11	1.386(10)
C24	N3	1.312(10)	C12	C12[4]	1.377(14)
C25	C26	1.375(12)	C12	C13	1.488(10)
C26	C27	1.367(11)	C13	C14	1.379(10)
C26	C29	1.495(10)	C13	C18	1.389(10)
C27	C28	1.361(12)	C14	C15	1.391(10)
C28	N3	1.328(10)	C15	C16	1.376(10)
C29	C30	1.375(10)	C16	C17	1.419(10)
C29	C34	1.394(10)	C16	C19	1.477(9)
C30	C31	1.374(10)	C17	C18	1.366(10)
C31	C32	1.388(10)	C19	C20	1.393(10)
C32	C33	1.389(10)	C19	C23	1.389(10)
C32	C46[1]	1.497(10)	C20	C21	1.391(10)
C33	C34	1.380(10)	C21	N2	1.315(9)
C35	C36	1.369(12)	C22	C23	1.374(10)
C35	N4	1.332(10)	C22	N2	1.349(9)
C36	C37	1.396(11)	N1	Mn1	2.331(5)
C37	C38	1.366(11)	N2	Mn3	2.315(6)
C37	C40	1.494(10)	Cl1	Mn1	2.479(2)
C38	C39	1.366(11)	Mn1	N1[5]	2.331(6)

C39	N4	1.314(10)	Mn1	N1^{6}	2.331(5)
C40	C41	1.389(10)	Mn1	N1^{3}	2.331(5)
C40	C45	1.374(10)	Mn1	Cl1^{6}	2.479(2)
C41	C42	1.375(10)	C51	C52	1.196(14)
C42	C43	1.393(10)	C51	Cl14	1.769(18)
C43	C44	1.377(10)	C51	Cl16	1.687(16)
C43	C46	1.494(9)	C52	Cl13	1.701(15)
C44	C45	1.391(10)	C52	Cl15	1.809(17)
C46	C32^{2}	1.497(10)	C53	C54	1.234(14)
C46	C46^{3}	1.335(14)	C53	Cl18	1.676(14)
N3	Mn2	2.314(6)	C53	Cl20	1.747(17)
N4	Mn2	2.349(6)	C54	Cl17	1.701(17)
Cl2	Mn2	2.454(3)	C54	Cl19	1.715(15)
Cl3	Mn2	2.461(3)	C47	C48	1.263(13)
Mn2	N3^{4}	2.314(6)	C47	Cl10	1.671(13)
Mn2	N4^{4}	2.349(6)	C47	Cl12	1.738(12)
C1	C2	1.383(11)	C48	Cl9	1.753(16)
C1	N1	1.312(10)	C48	Cl11	1.701(14)
C2	C3	1.390(11)	C49	C50	1.231(13)
C3	C4	1.390(11)	C49	Cl5	1.770(16)
C3	C6	1.467(9)	C49	Cl7	1.690(14)
C4	C5	1.375(11)	C50	Cl6	1.687(14)
C5	N1	1.351(10)	C50	Cl8	1.772(15)
C6	C7	1.371(10)	Mn3	N2^{7}	2.315(6)
C6	C11	1.406(10)	Mn3	N2^{8}	2.315(6)
C7	C8	1.379(10)	Mn3	N2^{6}	2.315(6)
C8	C9	1.378(10)	Mn3	Cl4	2.453(2)
C9	C10	1.390(10)	Mn3	Cl4^{6}	2.453(2)
C9	C12	1.491(9)			

Table S6. Bond Angles for [(MnCl2)tppe.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N3	C24	C25	124.4(9)	C14	C13	C12	124.3(7)
C26	C25	C24	120.5(8)	C14	C13	C18	117.7(7)
C25	C26	C29	122.2(7)	C18	C13	C12	117.9(6)
C27	C26	C25	114.8(7)	C13	C14	C15	121.7(7)
C27	C26	C29	123.0(7)	C16	C15	C14	120.4(7)
C28	C27	C26	120.4(8)	C15	C16	C17	118.1(6)
N3	C28	C27	125.5(8)	C15	C16	C19	122.0(6)
C30	C29	C26	122.0(7)	C17	C16	C19	119.9(6)
C30	C29	C34	117.7(6)	C18	C17	C16	120.3(7)
C34	C29	C26	120.4(7)	C17	C18	C13	121.7(7)
C31	C30	C29	121.7(7)	C20	C19	C16	121.7(6)
C30	C31	C32	121.0(7)	C23	C19	C16	122.4(7)
C31	C32	C33	117.9(6)	C23	C19	C20	115.8(6)

C31	C32	C46[1]	118.6(6)	C21	C20	C19	119.8(7)
C33	C32	C46[1]	123.4(6)	N2	C21	C20	124.0(7)
C34	C33	C32	120.8(7)	N2	C22	C23	123.2(7)
C33	C34	C29	121.0(7)	C22	C23	C19	120.6(7)
N4	C35	C36	124.3(8)	C1	N1	C5	116.4(6)
C35	C36	C37	120.1(8)	C1	N1	Mn1	121.8(5)
C36	C37	C40	122.6(7)	C5	N1	Mn1	121.7(5)
C38	C37	C36	115.0(7)	C21	N2	C22	116.6(6)
C38	C37	C40	122.3(7)	C21	N2	Mn3	123.6(5)
C37	C38	C39	120.6(8)	C22	N2	Mn3	119.6(5)
N4	C39	C38	125.2(8)	N1[3]	Mn1	N1	179.2(3)
C41	C40	C37	120.8(7)	N1[5]	Mn1	N1[6]	179.2(3)
C45	C40	C37	121.0(7)	N1[3]	Mn1	N1[5]	88.1(3)
C45	C40	C41	118.2(6)	N1[5]	Mn1	N1	91.9(3)
C42	C41	C40	120.7(7)	N1[3]	Mn1	N1[6]	91.9(3)
C41	C42	C43	121.0(7)	N1[6]	Mn1	N1	88.1(3)
C42	C43	C46	118.1(6)	N1[3]	Mn1	Cl1	90.41(15)
C44	C43	C42	118.3(6)	N1[3]	Mn1	Cl1[6]	89.59(15)
C44	C43	C46	123.6(6)	N1	Mn1	Cl1[6]	89.59(15)
C43	C44	C45	120.4(7)	N1[5]	Mn1	Cl1	89.59(15)
C40	C45	C44	121.3(7)	N1[5]	Mn1	Cl1[6]	90.41(15)
C43	C46	C32[2]	114.8(6)	N1[6]	Mn1	Cl1	89.59(15)
C46[3]	C46	C32[2]	122.5(8)	N1	Mn1	Cl1	90.41(15)
C46[3]	C46	C43	122.7(8)	N1[6]	Mn1	Cl1[6]	90.41(15)
C24	N3	C28	114.0(7)	Cl1	Mn1	Cl1[6]	180.0
C24	N3	Mn2	122.1(6)	C52	C51	Cl14	116.7(15)
C28	N3	Mn2	123.8(5)	C52	C51	Cl16	128.4(17)
C35	N4	Mn2	121.7(5)	Cl16	C51	Cl14	115.0(9)
C39	N4	C35	114.7(7)	C51	C52	Cl13	129.8(16)
C39	N4	Mn2	122.8(5)	C51	C52	Cl15	116.8(15)
N3	Mn2	N3[4]	177.7(3)	Cl13	C52	Cl15	113.4(8)
N3	Mn2	N4	92.4(2)	C54	C53	Cl18	124.0(15)
N3[4]	Mn2	N4[4]	92.4(2)	C54	C53	Cl20	121.0(13)
N3	Mn2	N4[4]	87.6(2)	Cl18	C53	Cl20	115.0(8)
N3[4]	Mn2	N4	87.6(2)	C53	C54	Cl17	120.4(14)
N3	Mn2	Cl2	91.15(16)	C53	C54	Cl19	126.3(15)
N3[4]	Mn2	Cl2	91.15(16)	Cl17	C54	Cl19	113.3(9)
N3	Mn2	Cl3	88.85(16)	C48	C47	Cl10	124.3(11)
N3[4]	Mn2	Cl3	88.85(16)	C48	C47	Cl12	120.2(12)
N4[4]	Mn2	N4	177.9(3)	Cl10	C47	Cl12	115.5(7)
N4[4]	Mn2	Cl2	88.93(16)	C47	C48	Cl9	119.9(12)
N4	Mn2	Cl2	88.93(16)	C47	C48	Cl11	125.1(13)
N4[4]	Mn2	Cl3	91.07(16)	Cl11	C48	Cl9	115.0(8)
N4	Mn2	Cl3	91.07(16)	C50	C49	Cl5	118.3(13)
Cl2	Mn2	Cl3	180.0	C50	C49	Cl7	128.1(14)
N1	C1	C2	123.7(7)	Cl7	C49	Cl5	113.5(8)
C1	C2	C3	120.5(7)	C49	C50	Cl6	126.9(14)

C2	C3	C6	122.4(7)	C49	C50	Cl8	118.6(13)
C4	C3	C2	115.6(7)	Cl6	C50	Cl8	114.5(8)
C4	C3	C6	121.9(7)	N2^{6}	Mn3	N2	86.2(3)
C5	C4	C3	120.2(8)	N2^{7}	Mn3	N2	93.8(3)
N1	C5	C4	123.4(8)	N2^{6}	Mn3	N2^{8}	93.8(3)
C7	C6	C3	120.7(7)	N2^{8}	Mn3	N2	179.8(3)
C7	C6	C11	118.1(6)	N2^{7}	Mn3	N2^{6}	179.8(3)
C11	C6	C3	121.1(7)	N2^{7}	Mn3	N2^{8}	86.2(3)
C6	C7	C8	121.0(7)	N2^{7}	Mn3	Cl4	90.12(15)
C9	C8	C7	121.1(7)	N2^{6}	Mn3	Cl4^{6}	89.88(15)
C8	C9	C10	119.1(6)	N2	Mn3	Cl4^{6}	90.12(15)
C8	C9	C12	117.5(6)	N2^{6}	Mn3	Cl4	90.12(15)
C10	C9	C12	123.3(6)	N2^{8}	Mn3	Cl4^{6}	90.12(15)
C11	C10	C9	119.5(7)	N2^{8}	Mn3	Cl4	89.88(15)
C10	C11	C6	121.1(7)	N2	Mn3	Cl4	89.88(15)
C12^{4}	C12	C9	122.1(8)	N2^{7}	Mn3	Cl4^{6}	89.88(15)
C12^{4}	C12	C13	121.5(8)	Cl4	Mn3	Cl4^{6}	180.0
C13	C12	C9	116.4(6)				

Table S7. Torsion Angles for [(MnCl2)tppe.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C24	C25	C26	C27	-6.8(17)	C4	C3	C6	C7	140.4(9)
C24	C25	C26	C29	175.5(10)	C4	C3	C6	C11	-37.8(12)
C25	C24	N3	C28	1.4(17)	C4	C5	N1	C1	-4.5(14)
C25	C24	N3	Mn2	177.3(10)	C4	C5	N1	Mn1	172.9(8)
C25	C26	C27	C28	4.3(15)	C6	C3	C4	C5	-178.3(9)
C25	C26	C29	C30	11.0(14)	C6	C7	C8	C9	0.2(12)
C25	C26	C29	C34	-166.9(9)	C7	C6	C11	C10	-0.1(12)
C26	C27	C28	N3	1.2(18)	C7	C8	C9	C10	0.3(11)
C26	C29	C30	C31	-178.1(8)	C7	C8	C9	C12	176.9(7)
C26	C29	C34	C33	178.6(7)	C8	C9	C10	C11	-0.6(11)
C27	C26	C29	C30	-166.6(9)	C8	C9	C12	C12^{4}	125.3(5)
C27	C26	C29	C34	15.5(13)	C8	C9	C12	C13	-55.4(9)
C27	C28	N3	C24	-4.1(16)	C9	C10	C11	C6	0.5(12)
C27	C28	N3	Mn2	-179.9(9)	C9	C12	C13	C14	132.3(7)
C29	C26	C27	C28	-177.9(9)	C9	C12	C13	C18	-43.8(9)
C29	C30	C31	C32	0.1(13)	C10	C9	C12	C12^{4}	-58.2(8)
C30	C29	C34	C33	0.6(12)	C10	C9	C12	C13	121.0(8)
C30	C31	C32	C33	-0.4(12)	C11	C6	C7	C8	-0.3(12)
C30	C31	C32	C46^{1}	-177.2(7)	C12	C9	C10	C11	-177.0(7)
C31	C32	C33	C34	0.8(11)	C12^{4}	C12	C13	C14	-48.4(8)
C32	C33	C34	C29	-0.9(12)	C12^{4}	C12	C13	C18	135.4(5)
C34	C29	C30	C31	-0.1(13)	C12	C13	C14	C15	-176.7(7)
C35	C36	C37	C38	-1.7(14)	C12	C13	C18	C17	177.4(7)
C35	C36	C37	C40	173.6(8)	C13	C14	C15	C16	-1.0(12)

C36	C35	N4	C39	3.0(14)	C14	C13	C18	C17	1.0(11)
C36	C35	N4	Mn2	-167.4(8)	C14	C15	C16	C17	2.0(11)
C36	C37	C38	C39	1.2(14)	C14	C15	C16	C19	-179.7(7)
C36	C37	C40	C41	-32.1(12)	C15	C16	C17	C18	-1.5(11)
C36	C37	C40	C45	149.3(9)	C15	C16	C19	C20	-18.4(11)
C37	C38	C39	N4	1.6(17)	C15	C16	C19	C23	163.9(8)
C37	C40	C41	C42	-176.3(7)	C16	C17	C18	C13	0.0(12)
C37	C40	C45	C44	178.1(7)	C16	C19	C20	C21	-178.5(7)
C38	C37	C40	C41	142.9(9)	C16	C19	C23	C22	179.3(8)
C38	C37	C40	C45	-35.7(12)	C17	C16	C19	C20	160.0(7)
C38	C39	N4	C35	-3.6(15)	C17	C16	C19	C23	-17.8(11)
C38	C39	N4	Mn2	166.6(8)	C18	C13	C14	C15	-0.5(11)
C40	C37	C38	C39	-174.1(9)	C19	C16	C17	C18	-179.9(7)
C40	C41	C42	C43	-1.7(12)	C19	C20	C21	N2	0.2(12)
C41	C40	C45	C44	-0.5(12)	C20	C19	C23	C22	1.4(12)
C41	C42	C43	C44	-0.9(11)	C20	C21	N2	C22	-0.5(12)
C41	C42	C43	C46	178.1(7)	C20	C21	N2	Mn3	174.5(6)
C42	C43	C44	C45	2.7(11)	C23	C19	C20	C21	-0.6(11)
C42	C43	C46	C32[2]	-54.5(9)	C23	C22	N2	C21	1.3(13)
C42	C43	C46	C46[3]	124.8(5)	C23	C22	N2	Mn3	-173.8(7)
C43	C44	C45	C40	-2.0(12)	N1	C1	C2	C3	-1.8(14)
C44	C43	C46	C32[2]	124.4(7)	N2	C22	C23	C19	-1.9(14)
C44	C43	C46	C46[3]	-56.3(8)	Cl14	C51	C52	Cl13	1(3)
C45	C40	C41	C42	2.4(12)	Cl14	C51	C52	Cl15	-179.0(8)
C46[1]	C32	C33	C34	177.4(7)	Cl16	C51	C52	Cl13	179.0(10)
C46	C43	C44	C45	-176.2(7)	Cl16	C51	C52	Cl15	-1(3)
N3	C24	C25	C26	4(2)	Cl18	C53	C54	Cl17	0(2)
N4	C35	C36	C37	-0.5(15)	Cl18	C53	C54	Cl19	179.7(9)
C1	C2	C3	C4	-0.5(13)	Cl20	C53	C54	Cl17	178.7(8)
C1	C2	C3	C6	178.0(8)	Cl20	C53	C54	Cl19	-2(2)
C2	C1	N1	C5	4.2(13)	Cl10	C47	C48	Cl9	1.2(17)
C2	C1	N1	Mn1	-173.2(7)	Cl10	C47	C48	Cl11	-178.8(7)
C2	C3	C4	C5	0.2(14)	Cl12	C47	C48	Cl9	-176.5(6)
C2	C3	C6	C7	-37.9(11)	Cl12	C47	C48	Cl11	3.5(18)
C2	C3	C6	C11	143.8(8)	Cl5	C49	C50	Cl6	4(2)
C3	C4	C5	N1	2.4(16)	Cl5	C49	C50	Cl8	-178.4(7)
C3	C6	C7	C8	-178.6(7)	Cl7	C49	C50	Cl6	-179.7(8)
C3	C6	C11	C10	178.2(7)	Cl7	C49	C50	Cl8	-2(2)

Table S8. Hydrogen Atom Coordinates (Å×10[4]) and Isotropic Displacement Parameters (Å[2]×10[3]) for [(MnCl2)tppe.

Atom	***x***	***y***	***z***	**U(eq)**
H24	10696	9679	8232	85
H25	10680	9259	8788	87
H27	9160	8827	8494	69

H28	9197	9295	7978	74
H30	10607	8900	9312	48
H31	10623	8404	9823	41
H33	9271	7769	9390	34
H34	9265	8264	8874	38
H35	10812	9319	7037	57
H36	10863	8827	6531	63
H38	9187	8829	6494	63
H39	9193	9308	7005	66
H41	10750	8736	5852	39
H42	10732	8332	5283	37
H44	9339	7688	5635	34
H45	9333	8125	6192	40
H1	8297	8159	5496	50
H2	8326	8635	6019	52
H4	6648	8548	6085	63
H5	6670	8081	5557	68
H7	8191	8702	6708	43
H8	8187	9155	7251	41
H10	6768	9758	6889	41
H11	6778	9306	6339	46
H14	8116	9814	8155	43
H15	8127	9347	8693	42
H17	6886	8603	8215	40
H18	6894	9066	7683	41
H20	8263	8788	9083	40
H21	8234	8299	9602	39
H22	6745	7877	9311	51
H23	6735	8336	8778	47

[($CuCl_2$)tppe

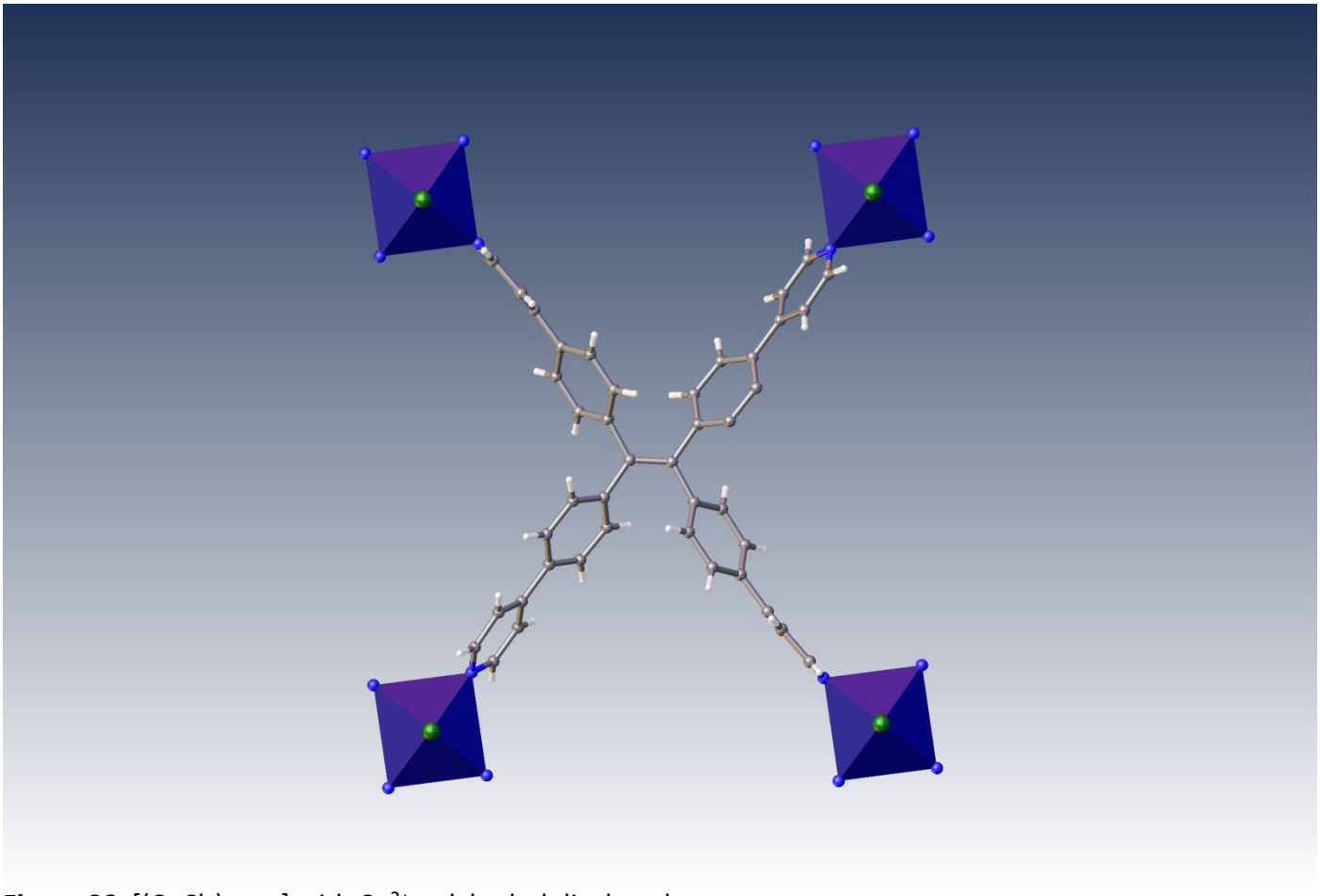

Figure S6. [($CuCl_2$)tppe] with Cu^{2+} polyhedral displayed

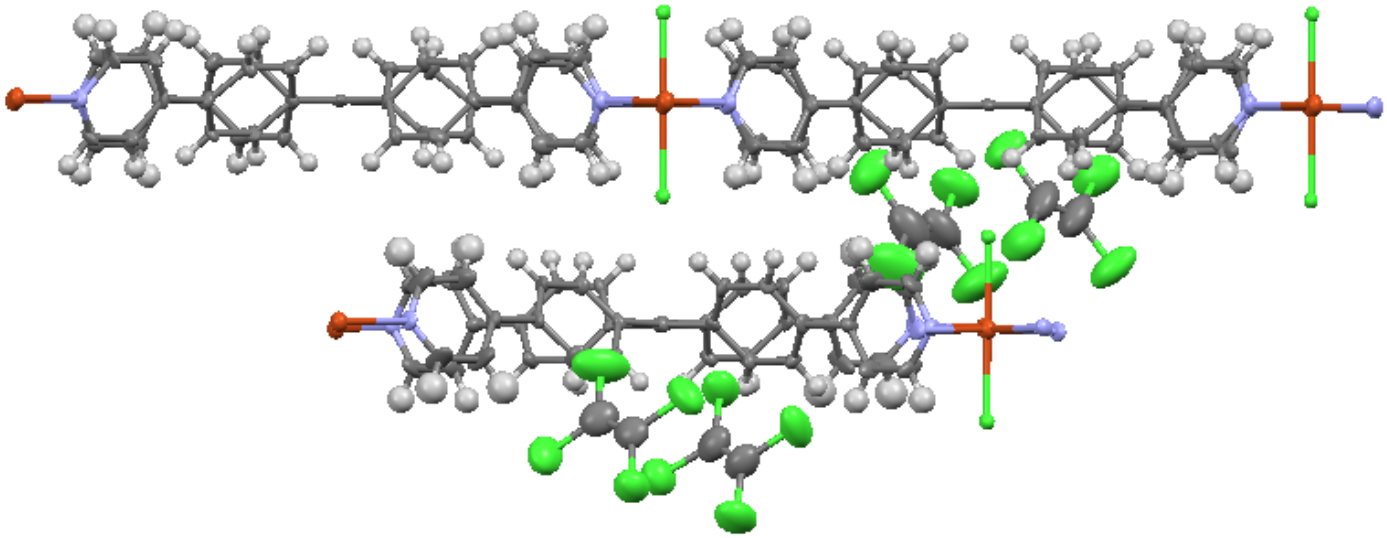

Figure S7. [($CuCl_2$)tppe]●4TCE displayed along the b axis.

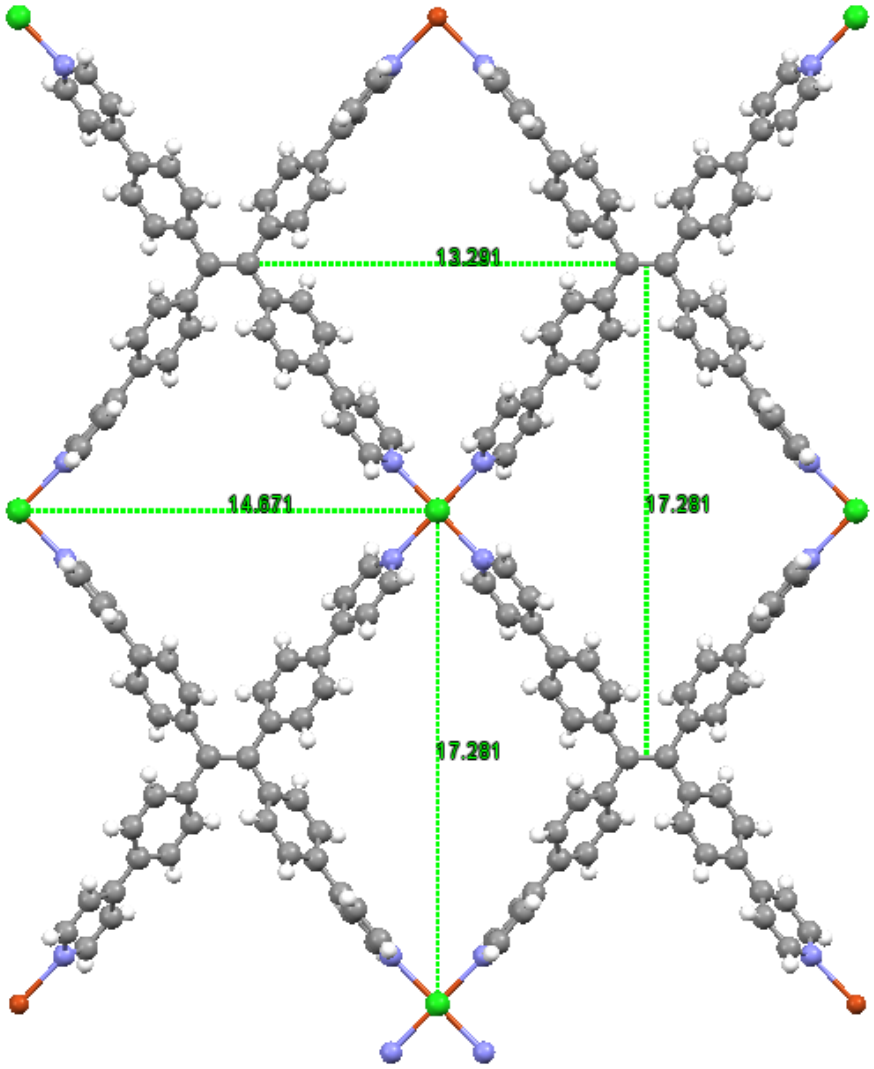

Figure S8. [(CuCl2)tppe] with pore distances displayed

Table S9. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for [$(CuCl_2)$tppe. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C1	7931(3)	3306(3)	5567(2)	26(2)
C2	7944(4)	3602(3)	5880(2)	30(2)
C3	7492(4)	3620(3)	6137(2)	25(2)
C4	7047(4)	3339(3)	6052(3)	33(2)
C5	7055(4)	3059(3)	5731(2)	35(2)
C6	7508(3)	3928(3)	6477(2)	23(2)
C7	7872(3)	4295(3)	6511(2)	24(2)
C8	7869(3)	4570(3)	6838(2)	24(2)
C9	7496(3)	4495(3)	7138(2)	18.6(19)
C10	7136(3)	4119(3)	7114(2)	26(2)
C11	7133(4)	3848(3)	6792(2)	28(2)
C12	7494(3)	4766(3)	7505(2)	19.7(18)
C13	7481(3)	4503(3)	7872(2)	16.1(18)
C14	7898(3)	4183(3)	7927(2)	24(2)
C15	7904(4)	3909(3)	8252(3)	31(2)

C16	7489(3)	3952(3)	8533(2)	22(2)
C17	7071(4)	4279(3)	8473(2)	32(2)
C18	7059(3)	4548(3)	8149(2)	25(2)
C19	7480(4)	3661(3)	8882(2)	28(2)
C20	7987(4)	3523(3)	9061(3)	37(2)
C21	7969(4)	3228(3)	9371(3)	34(2)
C22	7011(4)	3192(3)	9349(3)	39(3)
C23	6988(4)	3477(3)	9033(3)	43(3)
N1	7496(3)	3042(2)	5493.1(19)	25.1(17)
N2	7491(3)	3053(2)	9513.3(19)	27.3(17)
Cl1	6468.0(11)	2500	5000	21.2(7)
Cl2	6454.7(11)	2500	10000	19.5(7)
Cu1	7500	2500	5000	29.2(6)
Cu2	7500	2500	10000	29.4(6)
C24	5383(4)	4489(4)	8278(3)	66(4)
C25	5384(4)	4224(4)	8606(3)	66(4)
C26	4933(3)	3957(3)	8697(2)	26(2)
C27	4484(4)	4003(4)	8456(3)	57(3)
C28	4508(5)	4279(4)	8136(3)	58(3)
C29	4932(3)	3645(3)	9037(2)	26(2)
C30	5338(4)	3673(3)	9330(2)	31(2)
C31	5344(3)	3379(3)	9633(2)	23(2)
C32	4946(3)	3032(3)	9664(2)	18.9(18)
C33	4547(3)	3000(3)	9377(2)	24(2)
C34	4535(3)	3295(3)	9071(2)	27(2)
C35	5030(3)	2723(3)	5015(2)	20.0(18)
C36	5021(3)	2969(3)	5395(2)	20.4(19)
C37	5443(3)	3290(3)	5466(2)	24(2)
C38	5460(3)	3532(3)	5807(2)	24(2)
C39	5033(4)	3475(3)	6083(2)	23.6(19)
C40	4623(3)	3158(3)	6009(2)	26(2)
C41	4616(3)	2903(3)	5677(2)	22.6(19)
C42	5021(3)	3769(3)	6437(2)	26(2)
C43	5513(4)	3926(4)	6611(3)	46(3)
C44	5479(4)	4224(3)	6921(3)	41(3)
C45	4534(4)	4226(4)	6904(3)	47(3)
C46	4524(4)	3920(3)	6596(3)	41(3)
N3	4957(3)	4527(2)	8041.4(19)	27.9(17)
N4	4996(3)	4379(2)	7069.3(19)	24.1(16)
Cl3	3941.8(11)	5000	7500	21.5(7)
Cl4	6013.9(11)	5000	7500	20.8(7)
Cu3	4977.4(6)	5000	7500	29.7(4)
C53	3791(6)	5578(4)	4758(4)	77(4)
C54	3948(6)	5311(5)	4508(5)	92(4)
Cl17	4543.3(19)	5008.3(17)	4519.4(19)	158(2)
Cl18	3530.5(18)	5251.3(16)	4093.5(12)	113.9(15)
Cl19	3188.6(15)	5894.3(14)	4760.5(12)	99.0(13)

Cl20	4205.9(17)	5681.6(14)	5174.8(12)	104.8(14)
C51	3475(6)	4702(5)	5618(4)	89(4)
C52	3676(6)	4421(5)	5401(4)	83(4)
Cl13	4298.7(16)	4135.5(14)	5447.9(12)	101.1(13)
Cl14	3300.2(17)	4261.9(14)	4971.8(12)	99.5(12)
Cl15	2851.9(17)	4971.4(15)	5566.4(14)	117.3(16)
Cl16	3869.7(19)	4853.7(15)	6027.5(12)	113.0(16)
C49	6263(8)	2860(6)	8189(5)	125(6)
C50	6430(7)	3063(6)	7928(5)	122(6)
Cl5	6719(2)	2406.8(15)	8346.5(16)	133.5(18)
Cl6	7007.8(18)	3006.2(15)	7643.0(14)	117.5(16)
Cl7	5975(2)	3538.6(16)	7778.4(15)	130.8(18)
Cl8	5694.5(19)	2930.2(15)	8477.3(15)	131.2(18)
C47	6116(7)	2042(6)	7152(5)	114(6)
C48	6132(8)	2321(6)	6903(5)	122(6)
Cl9	6589.0(19)	1625.5(16)	7257.8(16)	133.6(18)
Cl10	6754(2)	2317.1(17)	6613.7(15)	143.9(19)
Cl11	5690(2)	2726.7(19)	6778(2)	194(3)
Cl12	5524(2)	2036(2)	7451(2)	188(3)

Table S10. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for [(CuCl2)tppe. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	$\mathbf{U_{11}}$	$\mathbf{U_{22}}$	$\mathbf{U_{33}}$	$\mathbf{U_{23}}$	$\mathbf{U_{13}}$	$\mathbf{U_{12}}$
C1	25(5)	30(5)	24(5)	-6(4)	14(4)	-4(4)
C2	27(5)	34(6)	27(5)	-14(5)	1(4)	-5(4)
C3	38(5)	27(5)	9(4)	-4(4)	0(4)	-3(4)
C4	25(5)	40(6)	32(5)	-17(5)	11(4)	-16(4)
C5	33(5)	45(6)	26(5)	-24(5)	13(4)	-5(5)
C6	26(5)	26(5)	16(5)	-1(4)	-4(4)	-4(4)
C7	26(5)	28(5)	17(5)	-1(4)	9(4)	-9(4)
C8	26(5)	23(5)	25(5)	-2(4)	-3(4)	-14(4)
C9	20(5)	22(5)	14(5)	-2(4)	2(4)	-1(4)
C10	21(5)	30(5)	27(5)	5(4)	-1(4)	-7(4)
C11	33(5)	28(5)	22(5)	-5(4)	8(4)	-10(4)
C12	11(4)	29(5)	19(4)	-1(5)	1(3)	3(3)
C13	20(5)	14(5)	15(5)	4(4)	-1(4)	0(4)
C14	31(5)	23(5)	17(5)	-2(4)	3(4)	0(4)
C15	25(5)	29(6)	39(6)	3(5)	7(4)	-5(4)
C16	23(5)	25(5)	19(5)	7(4)	6(4)	-3(4)
C17	31(5)	38(6)	25(5)	10(5)	8(4)	3(5)
C18	31(5)	27(5)	18(5)	8(4)	2(4)	7(4)
C19	32(5)	29(5)	23(5)	8(4)	1(4)	4(4)
C20	31(6)	35(6)	46(6)	21(5)	3(5)	-1(4)
C21	30(6)	40(6)	33(6)	19(5)	-1(4)	1(4)
C22	25(5)	55(7)	37(6)	34(5)	-3(4)	-2(5)

C23	19(5)	62(7)	47(6)	32(6)	-1(4)	-10(5)
N1	30(4)	27(4)	18(4)	-5(3)	-1(3)	-5(3)
N2	30(4)	31(4)	21(4)	9(3)	1(3)	-3(3)
Cl1	20.8(16)	25.4(17)	17.4(15)	3.6(13)	0	0
Cl2	18.6(15)	24.5(17)	15.5(15)	-3.3(13)	0	0
Cu1	33.6(13)	33.2(14)	20.8(12)	0	0	0
Cu2	33.3(13)	30.4(14)	24.4(12)	0	0	0
C24	39(7)	100(10)	59(7)	47(7)	-18(6)	-46(6)
C25	40(6)	101(10)	57(7)	60(7)	-27(6)	-31(7)
C26	26(5)	27(5)	26(5)	15(4)	-2(4)	0(4)
C27	36(6)	70(8)	65(8)	47(7)	-8(5)	-16(5)
C28	54(7)	65(8)	57(7)	42(7)	-28(6)	-20(6)
C29	28(5)	34(5)	16(4)	13(4)	3(4)	5(4)
C30	36(5)	23(5)	33(5)	10(4)	-9(4)	-13(4)
C31	23(5)	25(5)	23(5)	4(4)	-7(4)	-3(4)
C32	24(5)	15(4)	17(4)	3(4)	7(4)	3(4)
C33	29(5)	19(5)	24(5)	4(4)	1(4)	-1(4)
C34	27(5)	39(6)	14(5)	12(4)	-2(4)	-5(4)
C35	20(4)	22(4)	18(4)	-7(4)	-2(4)	-3(3)
C36	16(4)	24(5)	21(4)	-2(4)	-7(4)	6(4)
C37	31(5)	24(5)	17(5)	-4(4)	9(4)	1(4)
C38	23(5)	18(5)	30(5)	-5(4)	-2(4)	-9(4)
C39	33(5)	20(5)	18(4)	-10(4)	0(4)	4(4)
C40	22(5)	34(6)	22(5)	-9(4)	6(4)	-5(4)
C41	28(5)	24(5)	16(4)	-3(4)	-1(4)	-4(4)
C42	19(5)	32(5)	27(5)	-11(4)	-2(4)	0(4)
C43	32(6)	57(7)	49(7)	-24(6)	5(5)	17(5)
C44	32(6)	54(7)	37(6)	-18(5)	-14(5)	-3(5)
C45	30(6)	64(8)	47(6)	-39(6)	17(5)	-13(5)
C46	28(6)	56(7)	39(6)	-34(5)	5(4)	-13(5)
N3	29(4)	32(4)	23(4)	18(3)	-2(4)	0(4)
N4	24(4)	27(4)	22(4)	-8(3)	2(3)	-2(4)
Cl3	21.7(16)	24.4(17)	18.3(15)	0.9(13)	0	0
Cl4	17.3(15)	27.4(17)	17.8(15)	-1.0(13)	0	0
Cu3	32.9(9)	31.6(9)	24.6(8)	1.8(7)	0	0
C53	82(9)	58(9)	92(11)	17(7)	9(8)	-10(7)
C54	97(10)	61(9)	119(12)	1(8)	17(9)	-6(8)
Cl17	93(3)	117(4)	263(7)	-69(4)	-11(4)	33(3)
Cl18	116(3)	132(4)	94(3)	-33(3)	-2(3)	-33(3)
Cl19	86(3)	111(3)	100(3)	-9(2)	-4(2)	29(2)
Cl20	110(3)	102(3)	103(3)	13(3)	-37(2)	-16(2)
C51	95(10)	73(10)	99(11)	7(8)	24(8)	17(8)
C52	98(10)	69(9)	82(10)	19(7)	25(8)	8(8)
Cl13	102(3)	95(3)	106(3)	-14(2)	-5(2)	47(2)
Cl14	107(3)	98(3)	93(3)	-15(2)	-12(2)	6(2)
Cl15	85(3)	130(4)	138(4)	-29(3)	-14(3)	50(2)
Cl16	136(4)	119(3)	84(3)	-37(2)	-28(3)	59(3)

C49	140(13)	139(15)	97(12)	-10(10)	47(10)	-41(11)
C50	129(13)	151(15)	86(11)	-9(10)	32(10)	-53(11)
Cl5	134(4)	93(3)	174(5)	44(3)	44(3)	29(3)
Cl6	115(3)	106(3)	131(4)	17(3)	51(3)	-4(3)
Cl7	127(4)	112(4)	153(4)	61(3)	40(3)	21(3)
Cl8	133(4)	101(3)	159(4)	28(3)	81(3)	14(3)
C47	124(11)	95(13)	124(15)	-14(9)	-51(11)	32(11)
C48	151(13)	85(13)	129(15)	-17(9)	-53(13)	25(11)
Cl9	117(4)	105(3)	179(5)	27(3)	-31(3)	41(3)
Cl10	164(5)	125(4)	143(4)	7(3)	56(4)	-3(4)
Cl11	165(5)	118(4)	300(9)	82(5)	-35(5)	50(4)
Cl12	138(5)	190(6)	237(7)	42(5)	96(5)	31(4)

Table S11. Bond Lengths for [(CuCl2)tppe.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.387(11)	C29	C34	1.395(11)
C1	N1	1.312(10)	C30	C31	1.356(11)
C2	C3	1.392(11)	C31	C32	1.391(11)
C3	C4	1.370(11)	C32	C33	1.372(11)
C3	C6	1.482(11)	C32	$C35^{7}$	1.513(11)
C4	C5	1.379(11)	C33	C34	1.364(11)
C5	N1	1.330(10)	C35	$C32^{8}$	1.513(11)
C6	C7	1.382(11)	C35	$C35^{4}$	1.313(15)
C6	C11	1.424(11)	C35	C36	1.498(11)
C7	C8	1.385(11)	C36	C37	1.392(11)
C8	C9	1.380(11)	C36	C41	1.381(11)
C9	C10	1.395(11)	C37	C38	1.375(11)
C9	C12	1.495(11)	C38	C39	1.401(11)
C10	C11	1.366(11)	C39	C40	1.367(11)
C12	$C12^{1}$	1.369(16)	C39	C42	1.496(11)
C12	C13	1.484(11)	C40	C41	1.369(11)
C13	C14	1.373(11)	C42	C43	1.389(12)
C13	C18	1.390(10)	C42	C46	1.372(11)
C14	C15	1.381(11)	C43	C44	1.386(13)
C15	C16	1.388(11)	C44	N4	1.332(11)
C16	C17	1.394(11)	C45	C46	1.393(12)
C16	C19	1.473(11)	C45	N4	1.313(11)
C17	C18	1.368(11)	N3	Cu3	2.327(6)
C19	C20	1.411(12)	N4	Cu3	2.350(6)
C19	C23	1.386(11)	Cl3	Cu3	2.452(3)
C20	C21	1.377(12)	Cl4	Cu3	2.454(3)
C21	N2	1.335(10)	Cu3	$N3^{1}$	2.327(6)
C22	C23	1.376(12)	Cu3	$N4^{1}$	2.350(6)
C22	N2	1.335(10)	C53	C54	1.225(14)
N1	Cu1	2.328(7)	C53	Cl19	1.701(14)

N2	Cu2	2.334(7)	C53	Cl20	1.769(15)
Cl1	Cu1	2.443(3)	C54	Cl17	1.665(16)
Cl2	Cu2	2.475(3)	C54	Cl18	1.747(17)
Cu1	N1[2]	2.328(7)	C51	C52	1.209(14)
Cu1	N1[3]	2.328(7)	C51	Cl15	1.683(14)
Cu1	N1[4]	2.328(7)	C51	Cl16	1.752(16)
Cu1	Cl1[3]	2.443(3)	C52	Cl13	1.703(14)
Cu2	N2[5]	2.334(7)	C52	Cl14	1.792(15)
Cu2	N2[6]	2.334(7)	C49	C50	1.151(15)
Cu2	N2[3]	2.334(7)	C49	Cl5	1.80(2)
Cu2	Cl2[3]	2.475(3)	C49	Cl8	1.687(17)
C24	C25	1.374(13)	C50	Cl6	1.692(17)
C24	N3	1.302(11)	C50	Cl7	1.83(2)
C25	C26	1.358(12)	C47	C48	1.188(15)
C26	C27	1.357(12)	C47	Cl9	1.695(16)
C26	C29	1.490(11)	C47	Cl12	1.741(19)
C27	C28	1.373(13)	C48	Cl10	1.78(2)
C28	N3	1.330(11)	C48	Cl11	1.642(17)
C29	C30	1.399(11)			

Table S12. Bond Angles for [(CuCl2)tppe.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N1	C1	C2	122.5(8)	C26	C27	C28	121.2(9)
C1	C2	C3	120.3(8)	N3	C28	C27	123.7(9)
C2	C3	C6	120.7(8)	C30	C29	C26	122.2(8)
C4	C3	C2	115.6(8)	C34	C29	C26	121.3(7)
C4	C3	C6	123.8(8)	C34	C29	C30	116.5(7)
C3	C4	C5	121.3(8)	C31	C30	C29	121.9(8)
N1	C5	C4	122.1(8)	C30	C31	C32	121.1(8)
C7	C6	C3	123.8(7)	C31	C32	C35[7]	118.2(7)
C7	C6	C11	116.9(7)	C33	C32	C31	117.5(7)
C11	C6	C3	119.3(7)	C33	C32	C35[7]	124.3(7)
C6	C7	C8	121.2(7)	C34	C33	C32	122.1(8)
C9	C8	C7	121.6(7)	C33	C34	C29	121.0(8)
C8	C9	C10	118.0(7)	C35[2]	C35	C32[8]	122.4(9)
C8	C9	C12	123.7(7)	C35[2]	C35	C36	123.1(9)
C10	C9	C12	118.0(7)	C36	C35	C32[8]	114.5(7)
C11	C10	C9	120.8(8)	C37	C36	C35	118.0(7)
C10	C11	C6	121.4(8)	C41	C36	C35	124.1(7)
C12[1]	C12	C9	120.7(9)	C41	C36	C37	117.9(7)
C12[1]	C12	C13	122.9(9)	C38	C37	C36	121.4(8)

C13	C12	C9	116.5(7)	C37	C38	C39	120.0(7)
C14	C13	C12	117.3(7)	C38	C39	C42	120.1(7)
C14	C13	C18	119.0(7)	C40	C39	C38	117.7(7)
C18	C13	C12	123.6(7)	C40	C39	C42	122.1(8)
C13	C14	C15	121.1(8)	C39	C40	C41	122.4(8)
C14	C15	C16	120.7(8)	C40	C41	C36	120.4(8)
C15	C16	C17	117.3(8)	C43	C42	C39	121.9(8)
C15	C16	C19	122.0(8)	C46	C42	C39	121.8(8)
C17	C16	C19	120.6(7)	C46	C42	C43	116.2(8)
C18	C17	C16	122.2(8)	C44	C43	C42	119.7(8)
C17	C18	C13	119.7(8)	N4	C44	C43	124.1(8)
C20	C19	C16	120.9(8)	N4	C45	C46	124.5(8)
C23	C19	C16	123.0(8)	C42	C46	C45	119.8(8)
C23	C19	C20	115.9(8)	C24	N3	C28	114.7(8)
C21	C20	C19	119.8(8)	C24	N3	Cu3	122.6(6)
N2	C21	C20	123.5(8)	C28	N3	Cu3	122.6(6)
N2	C22	C23	123.9(8)	C44	N4	Cu3	121.5(6)
C22	C23	C19	120.1(8)	C45	N4	C44	115.6(7)
C1	N1	C5	118.3(7)	C45	N4	Cu3	121.6(6)
C1	N1	Cu1	122.7(5)	N3[1]	Cu3	N3	177.7(4)
C5	N1	Cu1	118.8(6)	N3	Cu3	N4[1]	87.3(2)
C21	N2	C22	116.6(7)	N3	Cu3	N4	92.8(2)
C21	N2	Cu2	121.5(6)	N3[1]	Cu3	N4[1]	92.8(2)
C22	N2	Cu2	121.8(6)	N3[1]	Cu3	N4	87.3(2)
N1[2]	Cu1	N1[3]	86.0(3)	N3	Cu3	Cl3	88.83(18)
N1[2]	Cu1	N1[4]	94.0(3)	N3[1]	Cu3	Cl3	88.83(18)
N1	Cu1	N1[4]	86.0(3)	N3	Cu3	Cl4	91.17(18)
N1	Cu1	N1[2]	179.6(3)	N3[1]	Cu3	Cl4	91.17(18)
N1	Cu1	N1[3]	94.0(3)	N4[1]	Cu3	N4	177.8(3)
N1[3]	Cu1	N1[4]	179.6(3)	N4[1]	Cu3	Cl3	91.10(17)
N1	Cu1	Cl1	89.78(17)	N4	Cu3	Cl3	91.09(17)
N1[2]	Cu1	Cl1[4]	90.22(17)	N4[1]	Cu3	Cl4	88.90(17)
N1[4]	Cu1	Cl1[4]	89.78(17)	N4	Cu3	Cl4	88.91(17)
N1[2]	Cu1	Cl1	89.78(17)	Cl3	Cu3	Cl4	180.0
N1[3]	Cu1	Cl1[4]	89.78(17)	C54	C53	Cl19	127.3(13)
N1[4]	Cu1	Cl1	90.22(17)	C54	C53	Cl20	121.1(13)
N1	Cu1	Cl1[4]	90.22(17)	Cl19	C53	Cl20	111.6(8)
N1[3]	Cu1	Cl1	90.22(17)	C53	C54	Cl17	125.4(14)
Cl1	Cu1	Cl1[4]	180.0	C53	C54	Cl18	118.1(13)

N2[5]	Cu2	N2	92.1(3)	Cl17	C54	Cl18	116.5(9)
N2[4]	Cu2	N2[6]	92.1(3)	C52	C51	Cl15	126.7(14)
N2[5]	Cu2	N2[4]	179.0(3)	C52	C51	Cl16	117.6(13)
N2[4]	Cu2	N2	87.9(3)	Cl15	C51	Cl16	115.7(8)
N2[5]	Cu2	N2[6]	87.9(3)	C51	C52	Cl13	128.0(14)
N2[6]	Cu2	N2	179.0(3)	C51	C52	Cl14	119.6(13)
N2[5]	Cu2	Cl2	90.51(17)	Cl13	C52	Cl14	112.3(8)
N2[4]	Cu2	Cl2[4]	89.49(17)	C50	C49	Cl5	114.4(18)
N2	Cu2	Cl2[4]	90.51(17)	C50	C49	Cl8	132(2)
N2[4]	Cu2	Cl2	90.51(17)	Cl8	C49	Cl5	113.0(10)
N2[6]	Cu2	Cl2[4]	90.51(17)	C49	C50	Cl6	133(2)
N2[6]	Cu2	Cl2	89.49(17)	C49	C50	Cl7	114.3(18)
N2[5]	Cu2	Cl2[4]	89.49(17)	Cl6	C50	Cl7	112.7(9)
N2	Cu2	Cl2	89.49(17)	C48	C47	Cl9	129.1(18)
Cl2	Cu2	Cl2[4]	180.0	C48	C47	Cl12	117.5(17)
N3	C24	C25	124.5(9)	Cl9	C47	Cl12	113.4(11)
C26	C25	C24	121.0(9)	C47	C48	Cl10	115.4(17)
C25	C26	C29	122.5(8)	C47	C48	Cl11	132.0(19)
C27	C26	C25	114.7(8)	Cl11	C48	Cl10	112.6(11)
C27	C26	C29	122.7(8)				

Table S13. Torsion Angles for [(CuCl2)tppe.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	C4	-1.1(13)	C25	C26	C29	C34	-163.5(10)
C1	C2	C3	C6	178.7(8)	C26	C27	C28	N3	-2(2)
C2	C1	N1	C5	-0.4(13)	C26	C29	C30	C31	-178.0(8)
C2	C1	N1	Cu1	-174.6(6)	C26	C29	C34	C33	177.8(8)
C2	C3	C4	C5	-0.3(13)	C27	C26	C29	C30	-165.3(10)
C2	C3	C6	C7	18.3(13)	C27	C26	C29	C34	17.3(14)
C2	C3	C6	C11	-161.4(8)	C27	C28	N3	C24	0.2(17)
C3	C4	C5	N1	1.4(15)	C27	C28	N3	Cu3	-179.1(9)
C3	C6	C7	C8	-179.7(8)	C29	C26	C27	C28	-177.2(10)
C3	C6	C11	C10	179.2(8)	C29	C30	C31	C32	0.4(13)
C4	C3	C6	C7	-161.9(9)	C30	C29	C34	C33	0.3(12)
C4	C3	C6	C11	18.4(13)	C30	C31	C32	C33	-0.1(12)
C4	C5	N1	C1	-1.0(14)	C30	C31	C32	C35[2]	-178.6(8)
C4	C5	N1	Cu1	173.4(7)	C31	C32	C33	C34	-0.1(12)
C6	C3	C4	C5	180.0(9)	C32	C33	C34	C29	0.0(13)
C6	C7	C8	C9	-1.4(13)	C32[3]	C35	C36	C37	-52.9(9)
C7	C6	C11	C10	-0.6(12)	C32[3]	C35	C36	C41	125.9(8)
C7	C8	C9	C10	3.2(12)	C34	C29	C30	C31	-0.5(13)

C7	C8	C9	C12	176.9(8)	C35[2]	C32	C33	C34	178.3(8)
C8	C9	C10	C11	-3.6(12)	C35[4]	C35	C36	C37	125.6(6)
C8	C9	C12	C12[1]	50.0(9)	C35[4]	C35	C36	C41	-55.6(9)
C8	C9	C12	C13	-131.2(8)	C35	C36	C37	C38	179.5(7)
C9	C10	C11	C6	2.4(13)	C35	C36	C41	C40	-176.8(8)
C9	C12	C13	C14	55.5(10)	C36	C37	C38	C39	-3.3(13)
C9	C12	C13	C18	-121.5(8)	C37	C36	C41	C40	2.0(12)
C10	C9	C12	C12[1]	-136.3(6)	C37	C38	C39	C40	3.3(12)
C10	C9	C12	C13	42.5(10)	C37	C38	C39	C42	-174.3(8)
C11	C6	C7	C8	0.1(12)	C38	C39	C40	C41	-0.8(13)
C12	C9	C10	C11	-177.7(7)	C38	C39	C42	C43	-33.1(13)
C12[1]	C12	C13	C14	-125.7(6)	C38	C39	C42	C46	143.3(9)
C12[1]	C12	C13	C18	57.2(9)	C39	C40	C41	C36	-1.9(13)
C12	C13	C14	C15	-177.3(8)	C39	C42	C43	C44	175.2(9)
C12	C13	C18	C17	177.8(8)	C39	C42	C46	C45	-174.1(9)
C13	C14	C15	C16	-0.3(13)	C40	C39	C42	C43	149.4(9)
C14	C13	C18	C17	0.8(12)	C40	C39	C42	C46	-34.2(13)
C14	C15	C16	C17	0.0(13)	C41	C36	C37	C38	0.6(12)
C14	C15	C16	C19	179.3(8)	C42	C39	C40	C41	176.7(8)
C15	C16	C17	C18	0.7(13)	C42	C43	C44	N4	-0.2(16)
C15	C16	C19	C20	35.5(13)	C43	C42	C46	C45	2.5(15)
C15	C16	C19	C23	-138.9(10)	C43	C44	N4	C45	0.6(15)
C16	C17	C18	C13	-1.1(13)	C43	C44	N4	Cu3	-166.5(8)
C16	C19	C20	C21	-175.8(9)	C46	C42	C43	C44	-1.4(15)
C16	C19	C23	C22	177.0(9)	C46	C45	N4	C44	0.6(15)
C17	C16	C19	C20	-145.2(9)	C46	C45	N4	Cu3	167.7(8)
C17	C16	C19	C23	40.4(13)	N3	C24	C25	C26	3(2)
C18	C13	C14	C15	-0.1(12)	N4	C45	C46	C42	-2.2(17)
C19	C16	C17	C18	-178.6(8)	Cl19	C53	C54	Cl17	-179.9(8)
C19	C20	C21	N2	1.2(15)	Cl19	C53	C54	Cl18	2(2)
C20	C19	C23	C22	2.4(14)	Cl20	C53	C54	Cl17	1(2)
C20	C21	N2	C22	-2.6(14)	Cl20	C53	C54	Cl18	-176.7(7)
C20	C21	N2	Cu2	173.9(7)	Cl15	C51	C52	Cl13	-178.9(8)
C23	C19	C20	C21	-1.1(14)	Cl15	C51	C52	Cl14	1(2)
C23	C22	N2	C21	4.1(15)	Cl16	C51	C52	Cl13	2(2)
C23	C22	N2	Cu2	-172.4(8)	Cl16	C51	C52	Cl14	-178.5(7)
N1	C1	C2	C3	1.5(14)	Cl5	C49	C50	Cl6	4(3)
N2	C22	C23	C19	-4.2(16)	Cl5	C49	C50	Cl7	-178.0(8)
C24	C25	C26	C27	-4.4(18)	Cl8	C49	C50	Cl6	178.1(11)
C24	C25	C26	C29	176.3(11)	Cl8	C49	C50	Cl7	-4(3)
C25	C24	N3	C28	-1.1(18)	Cl9	C47	C48	Cl10	-3(3)
C25	C24	N3	Cu3	178.2(10)	Cl9	C47	C48	Cl11	178.9(10)
C25	C26	C27	C28	3.5(17)	Cl12	C47	C48	Cl10	178.7(9)
C25	C26	C29	C30	13.9(15)	Cl12	C47	C48	Cl11	1(3)

Table S14. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for [(CuCl2)tppe.

Atom	*x*	*y*	*z*	U(eq)
H1	8249	3294	5399	31
H2	8264	3792	5920	35
H4	6727	3336	6218	39
H5	6735	2873	5678	42
H7	8128	4360	6307	28
H8	8130	4815	6855	29
H10	6891	4051	7324	32
H11	6874	3601	6778	33
H14	8187	4150	7738	28
H15	8196	3690	8284	37
H17	6784	4317	8663	38
H18	6765	4764	8114	30
H20	8339	3632	8969	45
H21	8316	3144	9491	41
H22	6665	3088	9456	47
H23	6634	3548	8918	51
H24	5716	4656	8219	79
H25	5704	4227	8771	80
H27	4146	3840	8511	68
H28	4185	4294	7973	70
H30	5617	3906	9317	37
H31	5626	3410	9828	28
H33	4271	2766	9391	29
H34	4252	3261	8878	32
H37	5724	3343	5275	28
H38	5763	3737	5855	28
H40	4333	3113	6195	32
H41	4330	2680	5640	27
H43	5871	3828	6519	55
H44	5822	4325	7036	49
H45	4182	4332	7001	56
H46	4173	3815	6496	49

[($MnCl_2$)●4DMB

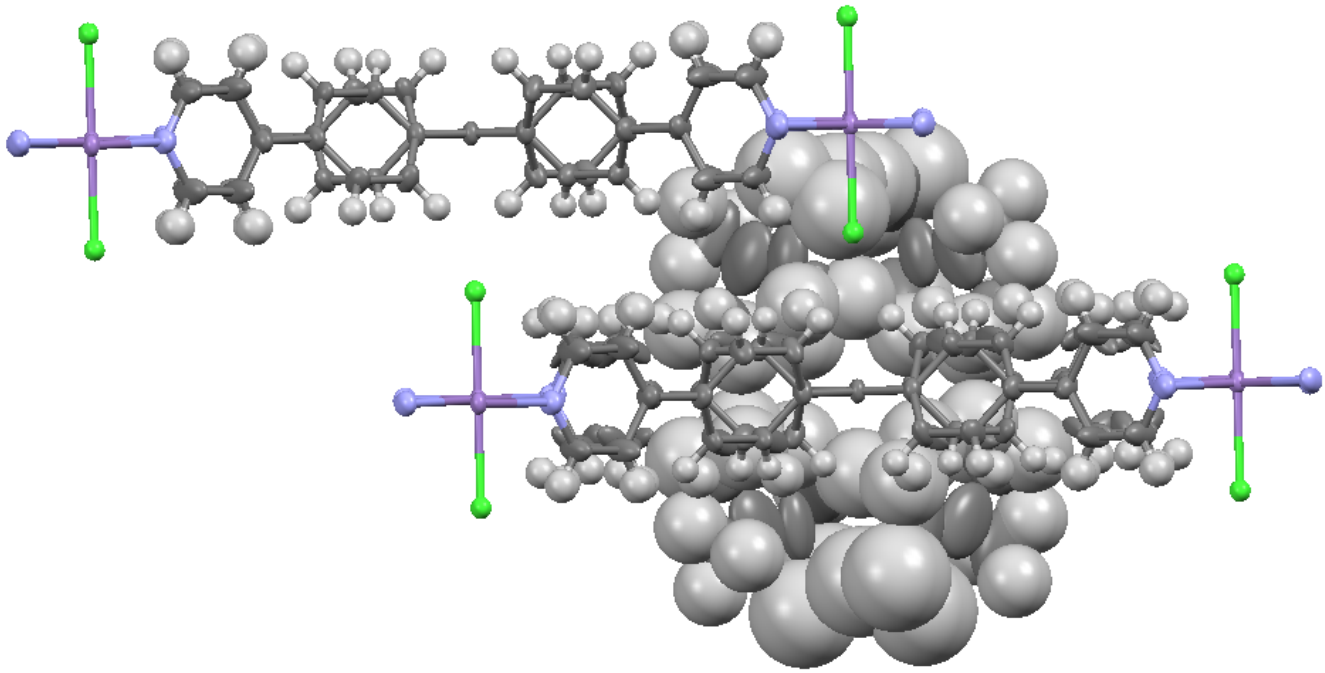

Figure S9. [(MnCl2)●4DMB.displayed along the B axis.

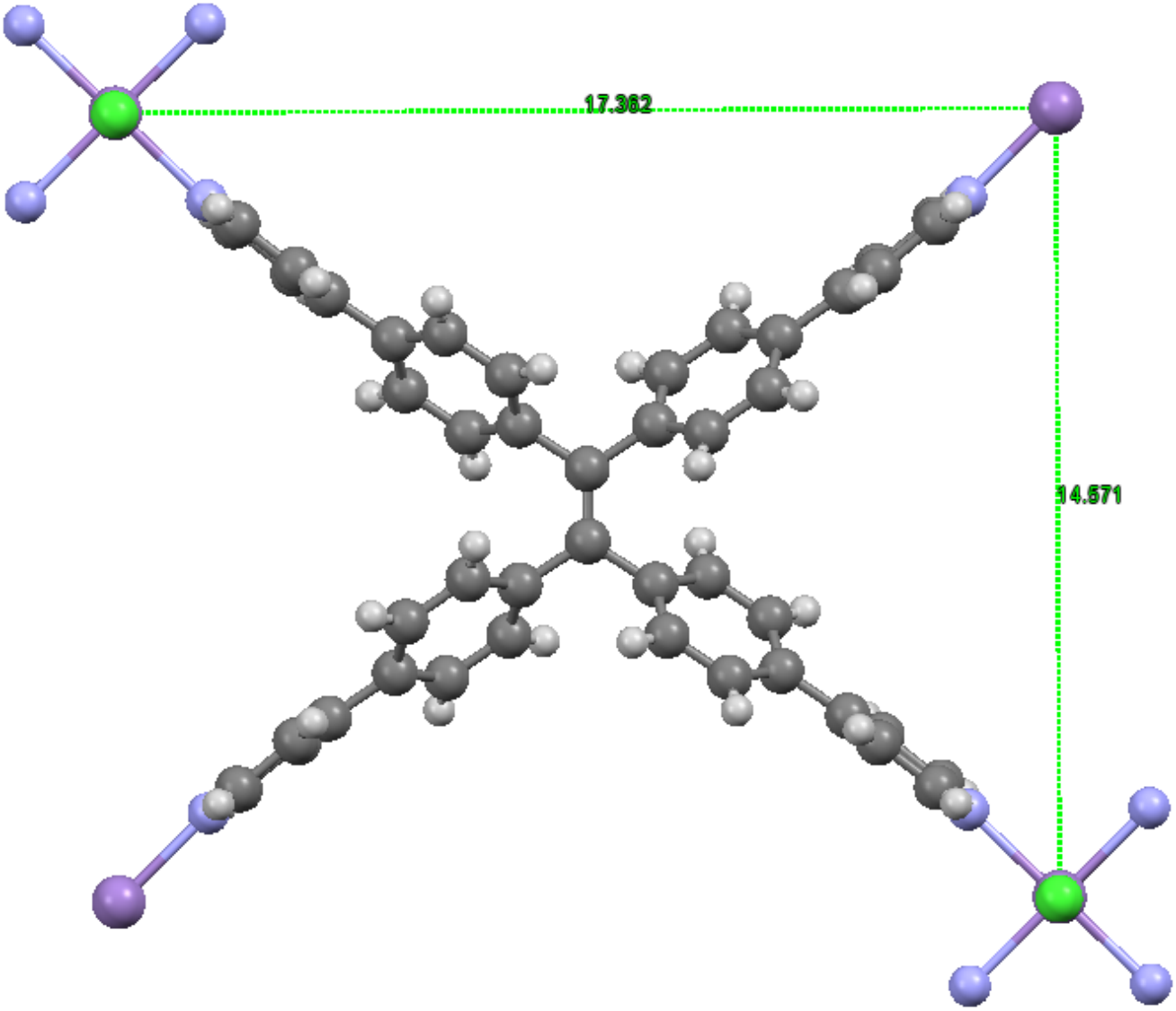

Figure S10. [(MnCl2)●4DMB.with pore distances displayed

Table S15 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for [(MnCl2)●4DMB. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Mn1	7500	7500.3(2)	7500	21.13(12)
Cl1	7500	5472.8(4)	7500	27.63(14)
Cl2	7500	9527.2(4)	7500	27.64(14)
N1	6388(2)	7478(6)	6532.9(19)	35.6(4)
C1	6094(5)	8433(5)	6203(4)	56.7(14)
C2	5521(5)	8459(5)	5585(4)	58.0(16)
C3	5188(3)	7520(9)	5258(2)	33.8(9)
C4	5445(4)	6532(4)	5618(3)	54.3(13)
C5	6045(4)	6563(4)	6246(3)	51.2(12)
N1A	6415(5)	7533(13)	6512(4)	35.6(4)
C1A	5879(5)	8293(9)	6362(5)	46(3)
C2A	5282(6)	8316(10)	5726(7)	53(4)
C3A	5267(7)	7440(20)	5207(5)	33.8(9)
C4A	5828(8)	6673(9)	5381(5)	48(2)
C5A	6390(8)	6698(9)	6008(6)	51(3)
C6	4614.9(11)	7496.6(14)	4553.3(9)	33.3(3)
C7	4687.3(17)	8319(2)	4004.7(15)	38.4(5)
C8	4156.3(16)	8306(2)	3343.0(13)	35.3(5)
C9	3512.5(9)	7490.8(12)	3221.4(8)	25.7(3)
C10	3422.7(16)	6671(2)	3770.9(13)	31.4(5)
C11	3958.0(19)	6683(2)	4432.2(14)	35.3(5)
C6A	4614.9(11)	7496.6(14)	4553.3(9)	33.3(3)
C7A	4157(12)	8401(9)	4330(7)	85(4)
C8A	3646(10)	8387(9)	3671(6)	90(4)
C9A	3512.5(9)	7490.8(12)	3221.4(8)	25.7(3)
C10A	3944(9)	6598(8)	3482(7)	88(4)
C11A	4441(12)	6562(8)	4153(9)	89(4)
N2	8623(3)	7529(6)	6542(2)	34.0(5)
C12	8939(3)	8433(3)	6229(2)	53.5(10)
C13	9545(3)	8465(3)	5610(3)	60.5(12)
C14	9813(4)	7485(12)	5257(3)	34.5(10)
C15	9501(5)	6546(6)	5583(4)	63.0(18)
C16	8911(5)	6582(5)	6208(4)	63.5(16)
N2A	8550(5)	7454(13)	6486(4)	34.0(5)
C12A	8556(4)	8290(7)	5984(4)	44(2)
C13A	9139(5)	8322(7)	5369(4)	39(2)
C14A	9742(10)	7550(30)	5211(7)	34.5(10)
C15A	9702(11)	6699(14)	5754(10)	53(4)
C16A	9117(10)	6696(12)	6354(9)	43(4)
C17	10385.8(11)	7502.4(14)	4552.8(9)	33.2(4)
C18	11040.9(18)	8325(2)	4430.5(13)	34.6(5)
C19	11575.5(17)	8330(2)	3770.5(12)	30.5(4)
C20	11488.1(9)	7510.2(12)	3221.8(8)	25.5(3)
C21	10842.2(16)	6692(2)	3341.5(14)	35.9(5)
C22	10311.3(17)	6683(2)	4006.5(15)	38.2(6)
C17A	10385.8(11)	7502.4(14)	4552.8(9)	33.2(4)
C18A	10512(9)	8407(8)	4127(7)	72(3)
C19A	11057(9)	8406(7)	3471(7)	71(3)
C20A	11488.1(9)	7510.2(12)	3221.8(8)	25.5(3)

C21A	11356(10)	6619(8)	3671(7)	89(4)
C22A	10824(10)	6607(8)	4311(7)	82(4)
C23	2960.0(9)	7498.8(12)	2501.7(7)	23.5(3)
C1B	6569(5)	4973(10)	3366(4)	154(5)
C1C	8436(5)	10041(10)	3355(4)	151(5)
C1D	7189(7)	4991(10)	3895(6)	200(6)
C1E	7820(7)	10018(10)	3868(6)	217(8)
C1G	8874(7)	9158(13)	3048(5)	297(10)
C1I	6118(7)	5846(13)	3059(5)	265(8)
C1J	6224(12)	3939(13)	2998(8)	377(11)
C1L	8779(14)	11049(15)	2978(9)	456(18)
C1M	7412(12)	6285(18)	4217(13)	242(12)
C1H	7860(7)	4557(14)	4345(7)	191(8)
C1F	7121(7)	10474(15)	4315(7)	205(9)
C1K	7477(13)	8720(20)	4204(13)	270(20)

Table S16 Anisotropic Displacement Parameters ($Å^2×10^3$) for [(MnCl2)●4DMB. 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}
Mn1	19.86(16)	28.1(2)	15.44(16)	0	0.92(10)	0
Cl1	30.3(2)	28.0(3)	24.6(2)	0	-0.57(18)	0
Cl2	30.5(2)	27.8(3)	24.6(2)	0	2.56(18)	0
N1	40.1(7)	35.5(11)	31.1(7)	-2.0(6)	-14.1(6)	1.4(6)
C1	77(3)	34(2)	59(3)	1.2(18)	-44(2)	-4(2)
C2	82(4)	28.5(18)	63(3)	5.5(17)	-49(3)	-5(2)
C3	37.7(11)	35.0(19)	28.6(9)	-4.1(11)	-13.2(9)	5.7(13)
C4	66(3)	32.3(18)	64(3)	6.4(17)	-44(2)	-10.1(18)
C5	70(3)	33.4(17)	50(3)	7.0(17)	-36(2)	-6.6(19)
N1A	40.1(7)	35.5(11)	31.1(7)	-2.0(6)	-14.1(6)	1.4(6)
C1A	50(5)	46(6)	43(4)	-25(4)	-25(3)	21(4)
C2A	47(5)	50(7)	63(6)	-23(5)	-36(4)	26(5)
C3A	37.7(11)	35.0(19)	28.6(9)	-4.1(11)	-13.2(9)	5.7(13)
C4A	69(6)	35(4)	41(4)	-15(3)	-34(4)	8(4)
C5A	73(6)	40(5)	38(4)	-7(4)	-27(4)	22(5)
C6	35.5(8)	36.8(9)	27.7(7)	-2.1(7)	-12.9(6)	2.2(7)
C7	36.7(12)	40.6(14)	37.8(12)	3.8(11)	-14.9(9)	-11.2(11)
C8	33.8(11)	44.9(14)	27.1(10)	8.3(10)	-7.2(8)	-12.6(10)
C9	22.1(6)	34.0(8)	21.1(6)	-1.3(6)	-1.6(5)	1.5(6)
C10	34.5(11)	32.6(12)	27.3(10)	3.5(9)	-10.2(8)	-6.5(10)
C11	43.3(13)	34.8(14)	27.8(10)	4.9(10)	-12.5(9)	-5.1(11)
C6A	35.5(8)	36.8(9)	27.7(7)	-2.1(7)	-12.9(6)	2.2(7)
C7A	140(9)	44(5)	69(6)	-18(5)	-77(6)	26(6)
C8A	155(10)	41(5)	74(6)	-15(5)	-86(7)	28(6)
C9A	22.1(6)	34.0(8)	21.1(6)	-1.3(6)	-1.6(5)	1.5(6)
C10A	133(9)	39(5)	92(7)	-30(5)	-88(7)	25(6)
C11A	137(9)	38(5)	93(8)	-26(5)	-92(7)	32(6)
N2	36.6(9)	36.3(12)	29.1(8)	-0.2(7)	11.5(7)	-0.2(8)
C12	72(2)	32.2(16)	57(2)	-4.8(14)	40.9(19)	-2.5(15)
C13	75(3)	33.3(17)	73(3)	-4.6(16)	53(2)	-8.4(17)
C14	38.3(12)	35.7(18)	29.6(9)	2.6(12)	14.3(10)	3.2(15)

C15	93(4)	33.2(19)	63(3)	-2.5(19)	58(3)	-1(2)
C16	84(4)	42(2)	65(3)	1(2)	53(3)	-2(2)
N2A	36.6(9)	36.3(12)	29.1(8)	-0.2(7)	11.5(7)	-0.2(8)
C12A	53(5)	45(5)	35(4)	6(4)	21(4)	15(4)
C13A	51(5)	28(4)	40(4)	12(3)	31(4)	13(4)
C14A	38.3(12)	35.7(18)	29.6(9)	2.6(12)	14.3(10)	3.2(15)
C15A	54(6)	52(9)	52(7)	26(6)	29(5)	33(6)
C16A	44(5)	45(8)	41(5)	34(5)	22(4)	31(5)
C17	34.0(7)	37.8(9)	27.9(7)	3.0(7)	13.9(6)	1.1(6)
C18	41.1(12)	36.1(13)	26.5(10)	-6.9(9)	13.7(9)	-5.3(11)
C19	34.0(11)	31.1(12)	26.5(10)	-3.0(9)	11.7(8)	-6.7(10)
C20	21.4(6)	34.2(8)	21.0(6)	1.1(6)	3.8(5)	0.5(6)
C21	31.6(11)	45.4(14)	30.6(11)	-8.9(10)	9.0(8)	-12.6(11)
C22	35.3(12)	42.1(14)	37.1(12)	-5.4(11)	14.8(9)	-12.9(11)
C17A	34.0(7)	37.8(9)	27.9(7)	3.0(7)	13.9(6)	1.1(6)
C18A	93(6)	43(4)	79(6)	15(4)	62(5)	26(5)
C19A	92(6)	41(4)	81(6)	24(4)	62(5)	14(4)
C20A	21.4(6)	34.2(8)	21.0(6)	1.1(6)	3.8(5)	0.5(6)
C21A	140(9)	41(5)	85(7)	2(5)	87(7)	22(6)
C22A	132(9)	40(5)	74(6)	13(5)	78(7)	7(6)
C23	21.0(6)	33.1(8)	16.3(5)	-0.6(5)	0.9(4)	-0.7(6)
C1B	89(5)	276(11)	98(5)	21(6)	29(4)	9(6)
C1C	76(4)	298(13)	80(5)	-27(5)	-19(3)	17(5)
C1D	122(7)	312(11)	165(8)	63(7)	77(6)	35(7)
C1E	146(10)	326(14)	179(11)	-68(8)	-97(9)	45(8)
C1G	215(10)	460(20)	212(9)	-29(11)	11(7)	204(13)
C1I	202(9)	396(18)	197(9)	19(10)	-23(7)	170(11)
C1J	470(20)	370(20)	295(14)	-133(14)	150(13)	-184(16)
C1L	600(30)	410(30)	360(20)	204(18)	-228(19)	-280(20)
C1M	132(12)	380(30)	216(19)	-78(16)	25(11)	-70(14)
C1H	81(7)	313(19)	178(10)	97(11)	6(6)	-15(8)
C1F	80(6)	350(20)	189(11)	-87(12)	5(6)	-14(9)
C1K	133(14)	450(60)	240(20)	110(20)	41(13)	-19(15)

Table S17 Bond Lengths for [(MnCl2)●4DMB.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Mn1	Cl1	2.4754(6)		C12	C13	1.392(4)
Mn1	Cl2	2.4746(6)		C13	C14	1.400(13)
Mn1	N1[1]	2.3320(14)		C14	C15	1.357(14)
Mn1	N1	2.3321(14)		C14	C17	1.4808(16)
Mn1	N1A[1]	2.3320(15)		C15	C16	1.387(9)
Mn1	N1A	2.3321(15)		N2A	C12A	1.342(16)
Mn1	N2[1]	2.3349(13)		N2A	C16A	1.26(2)
Mn1	N2	2.3349(13)		C12A	C13A	1.366(10)
Mn1	N2A	2.3349(15)		C13A	C14A	1.32(3)
Mn1	N2A[1]	2.3349(15)		C14A	C15A	1.40(4)
N1	C1	1.367(8)		C15A	C16A	1.35(3)
N1	C5	1.322(8)		C17	C18	1.402(3)
C1	C2	1.359(8)		C17	C22	1.382(3)
C2	C3	1.368(9)		C18	C19	1.386(3)

C3	C4	1.410(11)		C19	C20	1.388(3)
C3	C6	1.4807(17)		C20	C21	1.388(3)
C4	C5	1.397(6)		C20	C23^{2}	1.4922(17)
N1A	C1A	1.241(17)		C21	C22	1.391(3)
N1A	C5A	1.343(18)		C18A	C19A	1.390(11)
C1A	C2A	1.406(14)		C21A	C22A	1.356(12)
C2A	C3A	1.40(2)		C23	C20^{2}	1.4923(17)
C3A	C4A	1.28(2)		C23	C20A^{2}	1.4923(17)
C4A	C5A	1.361(12)		C23	C23^{3}	1.341(3)
C6	C7	1.388(3)		C1B	C1D	1.288(13)
C6	C11	1.395(3)		C1B	C1I	1.361(14)
C7	C8	1.385(3)		C1B	C1J	1.501(14)
C8	C9	1.384(3)		C1C	C1E	1.264(13)
C9	C10	1.389(3)		C1C	C1G	1.362(13)
C9	C23	1.4858(18)		C1C	C1L	1.481(15)
C10	C11	1.387(3)		C1D	C1M	1.707(19)
C7A	C8A	1.365(12)		C1D	C1H	1.358(16)
C10A	C11A	1.372(13)		C1E	C1F	1.398(17)
N2	C12	1.314(7)		C1E	C1K	1.77(2)
N2	C16	1.360(8)				

Table S18 Bond Angles for [(MnCl2)●4DMB.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
Cl2	Mn1	Cl1	180.0		C9	C8	C7	120.9(2)
N1	Mn1	Cl1	89.34(18)		C8	C9	C10	118.55(17)
N1^{1}	Mn1	Cl1	89.34(18)		C8	C9	C23	119.35(15)
N1^{1}	Mn1	Cl2	90.66(18)		C10	C9	C23	122.08(15)
N1	Mn1	Cl2	90.66(18)		C11	C10	C9	120.5(2)
N1^{1}	Mn1	N1	178.7(4)		C10	C11	C6	121.2(2)
N1^{1}	Mn1	N2^{1}	88.52(17)		C12	N2	Mn1	123.6(4)
N1^{1}	Mn1	N2	91.50(18)		C12	N2	C16	115.4(3)
N1	Mn1	N2	88.51(17)		C16	N2	Mn1	120.5(4)
N1	Mn1	N2^{1}	91.51(18)		N2	C12	C13	124.4(3)
N1A	Mn1	Cl1	91.0(4)		C12	C13	C14	119.5(4)
N1A^{1}	Mn1	Cl1	91.0(4)		C13	C14	C17	120.5(9)
N1A^{1}	Mn1	Cl2	89.0(4)		C15	C14	C13	116.5(3)
N1A	Mn1	Cl2	89.0(4)		C15	C14	C17	123.0(9)
N1A^{1}	Mn1	N1A	178.1(8)		C14	C15	C16	120.5(6)
N1A	Mn1	N2A^{1}	96.4(4)		N2	C16	C15	123.6(5)
N1A^{1}	Mn1	N2A	96.4(4)		C12A	N2A	Mn1	118.4(8)
N1A^{1}	Mn1	N2A^{1}	83.7(4)		C16A	N2A	Mn1	125.7(11)
N1A	Mn1	N2A	83.7(4)		C16A	N2A	C12A	115.9(8)
N2^{1}	Mn1	Cl1	90.86(18)		N2A	C12A	C13A	122.2(8)
N2	Mn1	Cl1	90.86(18)		C14A	C13A	C12A	123.8(12)
N2^{1}	Mn1	Cl2	89.14(18)		C13A	C14A	C15A	111.2(8)
N2	Mn1	Cl2	89.14(18)		C16A	C15A	C14A	123.2(15)
N2^{1}	Mn1	N2	178.3(4)		N2A	C16A	C15A	123.6(13)
N2A^{1}	Mn1	Cl1	88.6(4)		C18	C17	C14	121.3(4)
N2A	Mn1	Cl1	88.6(4)		C22	C17	C14	120.8(4)
N2A^{1}	Mn1	Cl2	91.4(4)		C22	C17	C18	117.84(16)

N2A	Mn1	Cl2	91.4(4)		C19	C18	C17	120.8(2)
N2A[1]	Mn1	N2A	177.2(8)		C18	C19	C20	120.8(2)
C1	N1	Mn1	120.6(4)		C19	C20	C21	118.57(16)
C5	N1	Mn1	122.9(4)		C19	C20	C23[2]	122.37(15)
C5	N1	C1	116.4(3)		C21	C20	C23[2]	119.03(15)
C2	C1	N1	122.9(5)		C20	C21	C22	120.5(2)
C1	C2	C3	121.7(5)		C17	C22	C21	121.4(2)
C2	C3	C4	116.0(3)		C9	C23	C20[2]	114.59(11)
C2	C3	C6	124.0(7)		C23[3]	C23	C9	122.99(14)
C4	C3	C6	119.9(7)		C23[3]	C23	C20[2]	122.42(15)
C5	C4	C3	119.3(4)		C23[3]	C23	C20A[2]	122.42(15)
N1	C5	C4	123.6(4)		C1D	C1B	C1I	127.2(12)
C1A	N1A	Mn1	126.4(10)		C1D	C1B	C1J	123.5(14)
C1A	N1A	C5A	114.5(6)		C1I	C1B	C1J	109.3(10)
C5A	N1A	Mn1	119.0(9)		C1E	C1C	C1G	126.3(12)
N1A	C1A	C2A	124.6(10)		C1E	C1C	C1L	124.7(15)
C3A	C2A	C1A	119.9(10)		C1G	C1C	C1L	109.0(11)
C4A	C3A	C2A	113.4(7)		C1B	C1D	C1M	112.4(12)
C3A	C4A	C5A	123.9(11)		C1B	C1D	C1H	155.2(14)
N1A	C5A	C4A	123.7(9)		C1H	C1D	C1M	92.1(11)
C7	C6	C3	120.6(4)		C1C	C1E	C1F	154.3(13)
C7	C6	C11	117.65(17)		C1C	C1E	C1K	117.0(11)
C11	C6	C3	121.7(4)		C1F	C1E	C1K	88.1(10)
C8	C7	C6	121.2(2)					

Table S19 Torsion Angles for [(MnCl2)●4DMB.

A	B	C	D	Angle/°		A	B	C	D	Angle/°
Mn1	N1	C1	C2	172.9(5)		C10	C9	C23	C23[2]	57.57(19)
Mn1	N1	C5	C4	-173.7(4)		C11	C6	C7	C8	-2.9(4)
Mn1	N1A	C1A	C2A	174.9(7)		N2	C12	C13	C14	3.7(9)
Mn1	N1A	C5A	C4A	-175.3(6)		C12	N2	C16	C15	0.4(10)
Mn1	N2	C12	C13	-173.9(4)		C12	C13	C14	C15	-4.3(11)
Mn1	N2	C16	C15	172.9(6)		C12	C13	C14	C17	174.2(5)
Mn1	N2A	C12A	C13A	-179.1(6)		C13	C14	C15	C16	3.2(12)
Mn1	N2A	C16A	C15A	179.0(7)		C13	C14	C17	C18	32.8(9)
N1	C1	C2	C3	1.1(11)		C13	C14	C17	C22	-149.4(5)
C1	N1	C5	C4	2.9(9)		C14	C15	C16	N2	-1.3(11)
C1	C2	C3	C4	2.4(10)		C14	C17	C18	C19	179.8(6)
C1	C2	C3	C6	-175.6(6)		C14	C17	C22	C21	179.7(6)
C2	C3	C4	C5	-3.1(9)		C15	C14	C17	C18	-148.9(5)
C2	C3	C6	C7	27.4(8)		C15	C14	C17	C22	29.0(10)
C2	C3	C6	C11	-149.6(5)		C16	N2	C12	C13	-1.6(9)
C3	C4	C5	N1	0.5(9)		N2A	C12A	C13A	C14A	0.00(4)
C3	C6	C7	C8	179.9(5)		C12A	N2A	C16A	C15A	0.00(8)
C3	C6	C11	C10	179.8(5)		C12A	C13A	C14A	C15A	0.00(7)
C4	C3	C6	C7	-150.5(5)		C13A	C14A	C15A	C16A	0.00(9)
C4	C3	C6	C11	32.4(7)		C14A	C15A	C16A	N2A	-0.01(11)
C5	N1	C1	C2	-3.7(10)		C16A	N2A	C12A	C13A	0.00(3)
N1A	C1A	C2A	C3A	0.00(3)		C17	C14	C15	C16	-175.2(6)
C1A	N1A	C5A	C4A	0.00(8)		C17	C18	C19	C20	-1.3(4)

C1A	C2A	C3A	C4A	0.00(7)		C18	C17	C22	C21	-2.4(4)
C2A	C3A	C4A	C5A	0.01(11)		C18	C19	C20	C21	1.1(4)
C3A	C4A	C5A	N1A	-0.01(12)		C18	C19	C20	C23[1]	179.0(2)
C5A	N1A	C1A	C2A	0.00(3)		C19	C20	C21	C22	-1.5(4)
C6	C3	C4	C5	175.0(4)		C20	C21	C22	C17	2.2(4)
C6	C7	C8	C9	2.3(4)		C22	C17	C18	C19	1.9(4)
C7	C6	C11	C10	2.7(4)		C23	C9	C10	C11	179.2(2)
C7	C8	C9	C10	-1.3(3)		C23[1]	C20	C21	C22	-179.5(2)
C7	C8	C9	C23	-179.5(2)		C1G	C1C	C1E	C1F	-167.8(15)
C8	C9	C10	C11	1.1(3)		C1G	C1C	C1E	C1K	-1.4(11)
C8	C9	C23	C20[1]	55.6(2)		C1I	C1B	C1D	C1M	0.8(11)
C8	C9	C23	C20A[1]	55.6(2)		C1I	C1B	C1D	C1H	-169.8(14)
C8	C9	C23	C23[2]	-124.26(16)		C1J	C1B	C1D	C1M	-178.3(9)
C9	C10	C11	C6	-1.8(4)		C1J	C1B	C1D	C1H	11.0(18)
C10	C9	C23	C20[1]	-122.60(18)		C1L	C1C	C1E	C1F	10.6(19)
C10	C9	C23	C20A[1]	-122.60(18)		C1L	C1C	C1E	C1K	177.0(11)

Table S20 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for [(MnCl2)●4DMB.

Atom	*x*	*y*	*z*	U(eq)
H1	6294	9093	6411	68
H2	5352	9133	5379	70
H4	5218	5866	5440	65
H5	6211	5903	6475	61
H1A	5871	8891	6695	56
H2A	4897	8915	5649	64
H4A	5854	6063	5062	58
H5A	6777	6105	6092	61
H7	5100	8889	4083	46
H8	4233	8852	2975	42
H10	3001	6110	3695	38
H11	3877	6140	4801	42
H7A	4188	9036	4626	101
H8A	3369	9038	3518	108
H10A	3905	5961	3190	106
H11A	4659	5895	4336	107
H12	8743	9097	6434	64
H13	9770	9132	5433	73
H15	9685	5873	5385	76
H16	8701	5923	6411	76
H12A	8149	8868	6058	53
H13A	9109	8925	5042	47
H15A	10100	6109	5697	63
H16A	9132	6103	6690	52
H18	11118	8873	4797	41
H19	11998	8891	3694	37

H21	10764	6145	2974	43
H22	9897	6115	4085	46
H18A	10226	9054	4276	86
H19A	11124	9054	3195	86
H21A	11650	5972	3532	106
H22A	10763	5959	4588	98
H1GA	9525	9268	3077	446
H1GB	8694	9072	2519	446
H1GC	8711	8512	3331	446
H1IA	5502	5867	3255	398
H1IB	6103	5779	2509	398
H1IC	6432	6509	3198	398
H1JA	6032	3436	3390	566
H1JB	6706	3614	2698	566
H1JC	5713	4107	2668	566
H1LA	8523	11105	2471	685
H1LB	9436	11018	2944	685
H1LC	8602	11676	3277	685
H1MA	8007	6511	4041	362
H1MB	7399	6294	4769	362
H1MC	6955	6779	4020	362
H1HA	8373	4352	4029	286
H1HB	7629	3921	4606	286
H1HC	8053	5090	4717	286
H1FA	6579	10559	4007	307
H1FB	7313	11176	4505	307
H1FC	6991	9998	4742	307
H1KA	6886	8536	3994	411
H1KB	7441	8726	4756	411
H1KC	7917	8176	4046	411

FTIR

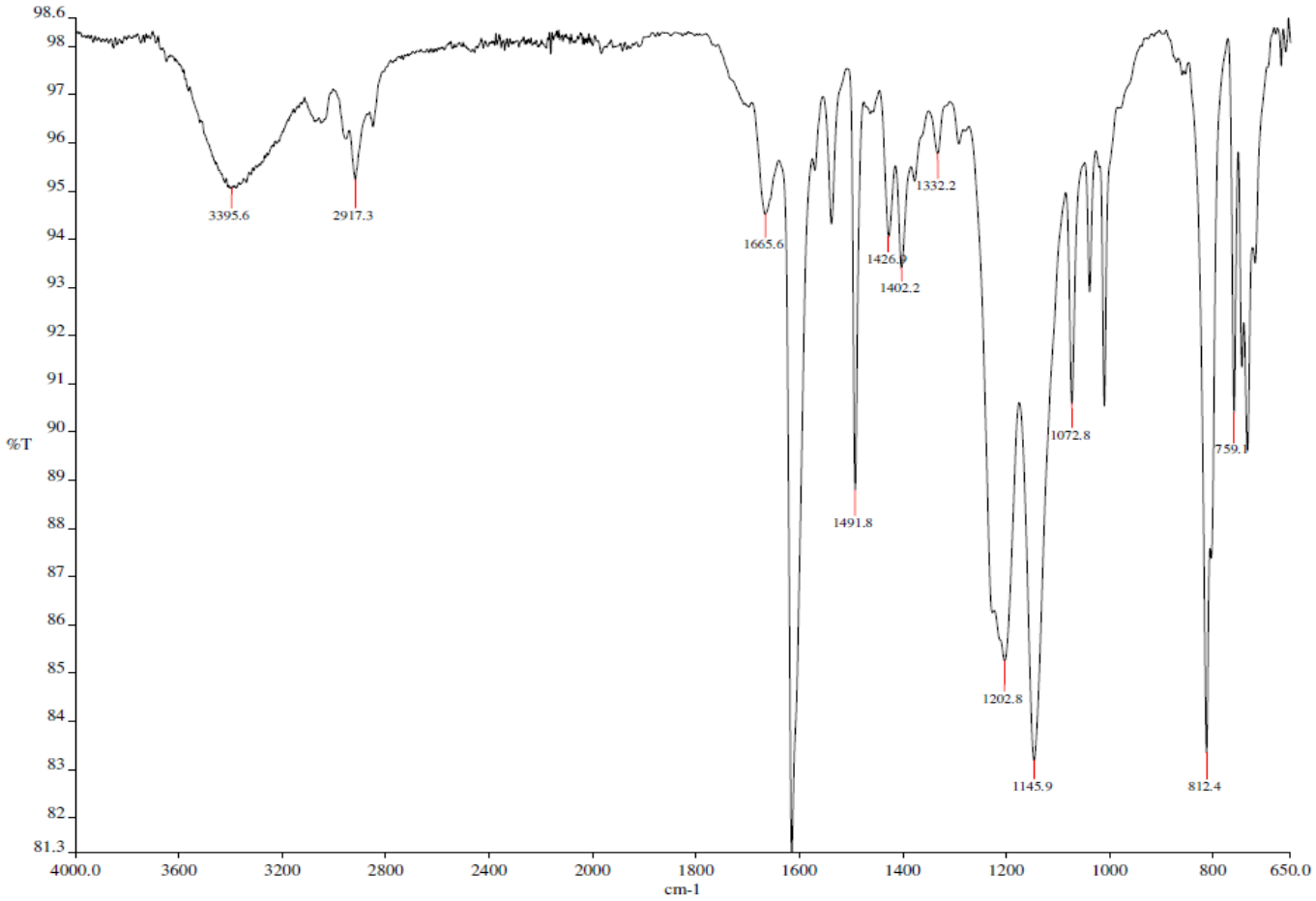

Figure S11. FTIR of tppe Cu post collapse.

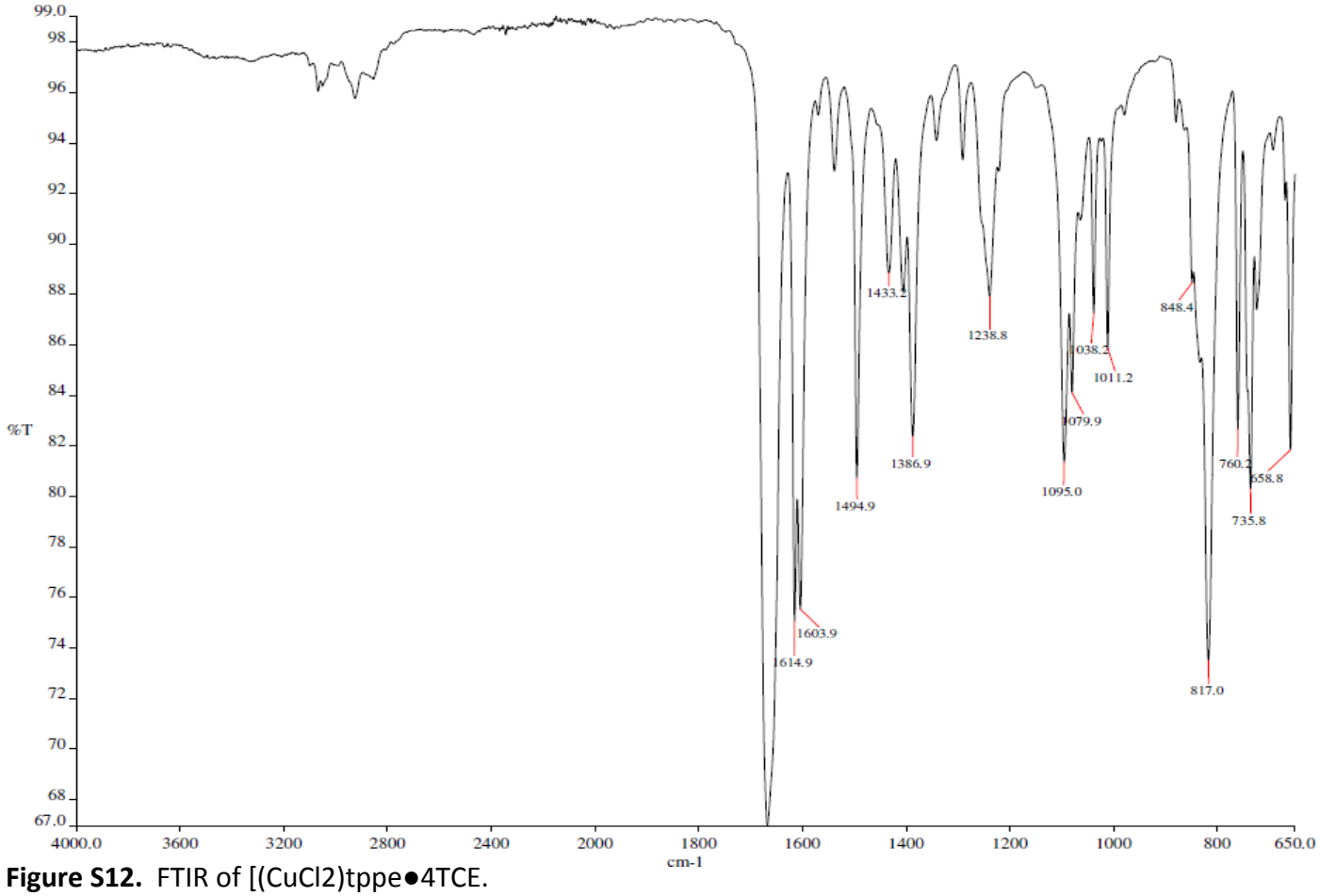

Figure S12. FTIR of [(CuCl2)tppe●4TCE.

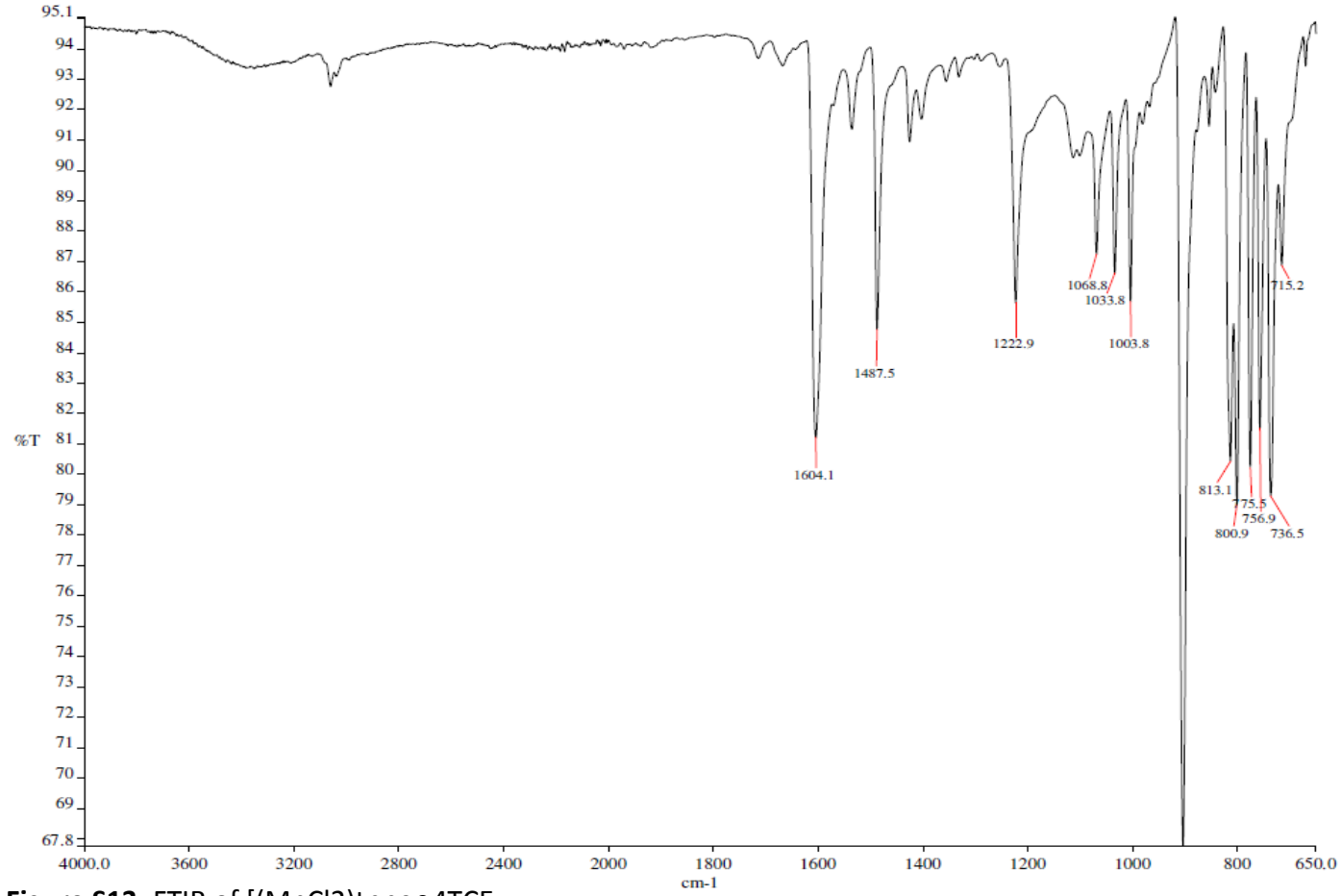

Figure S13. FTIR of [(MnCl2)tppe●4TCE.

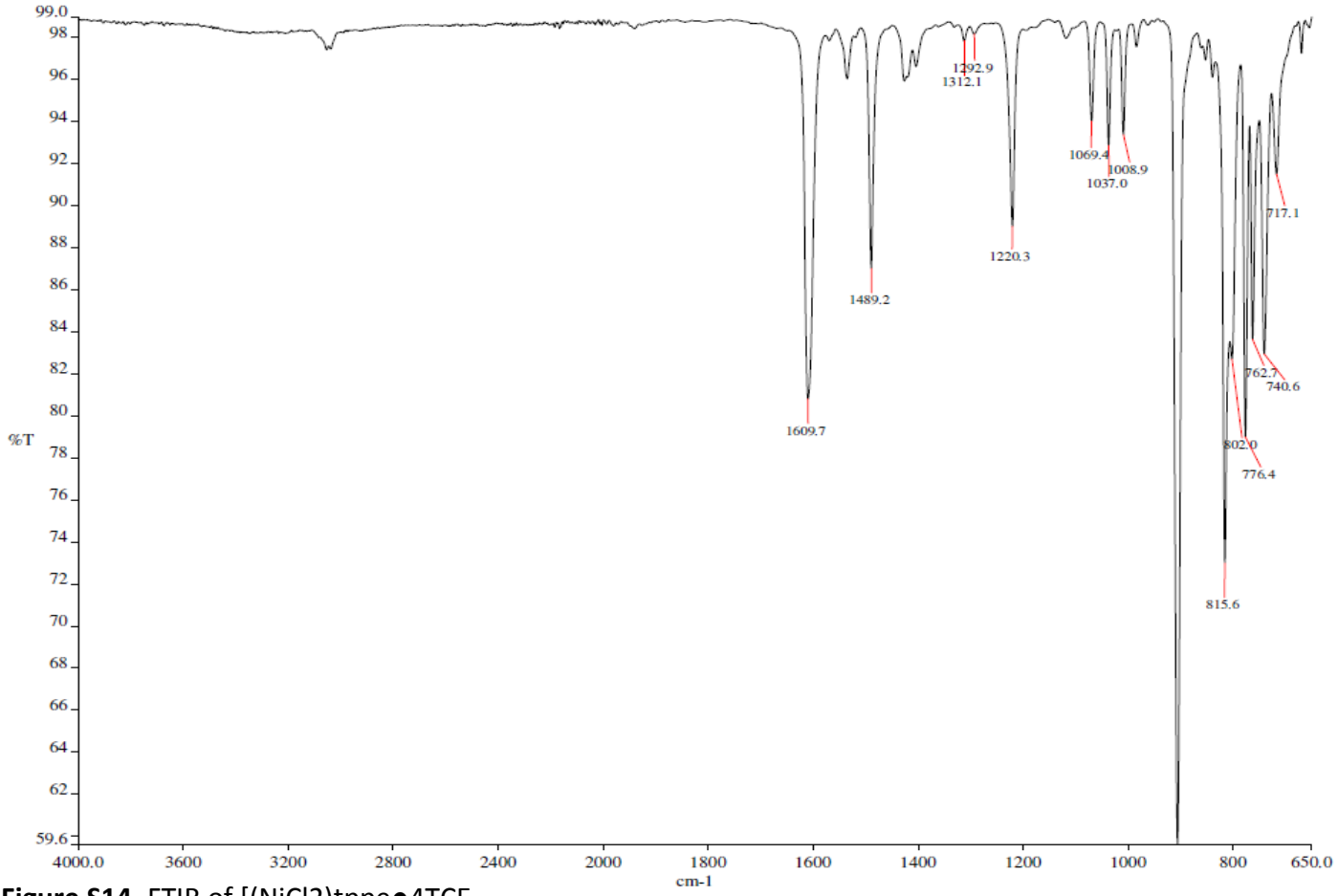

Figure S14. FTIR of [(NiCl2)tppe●4TCE.

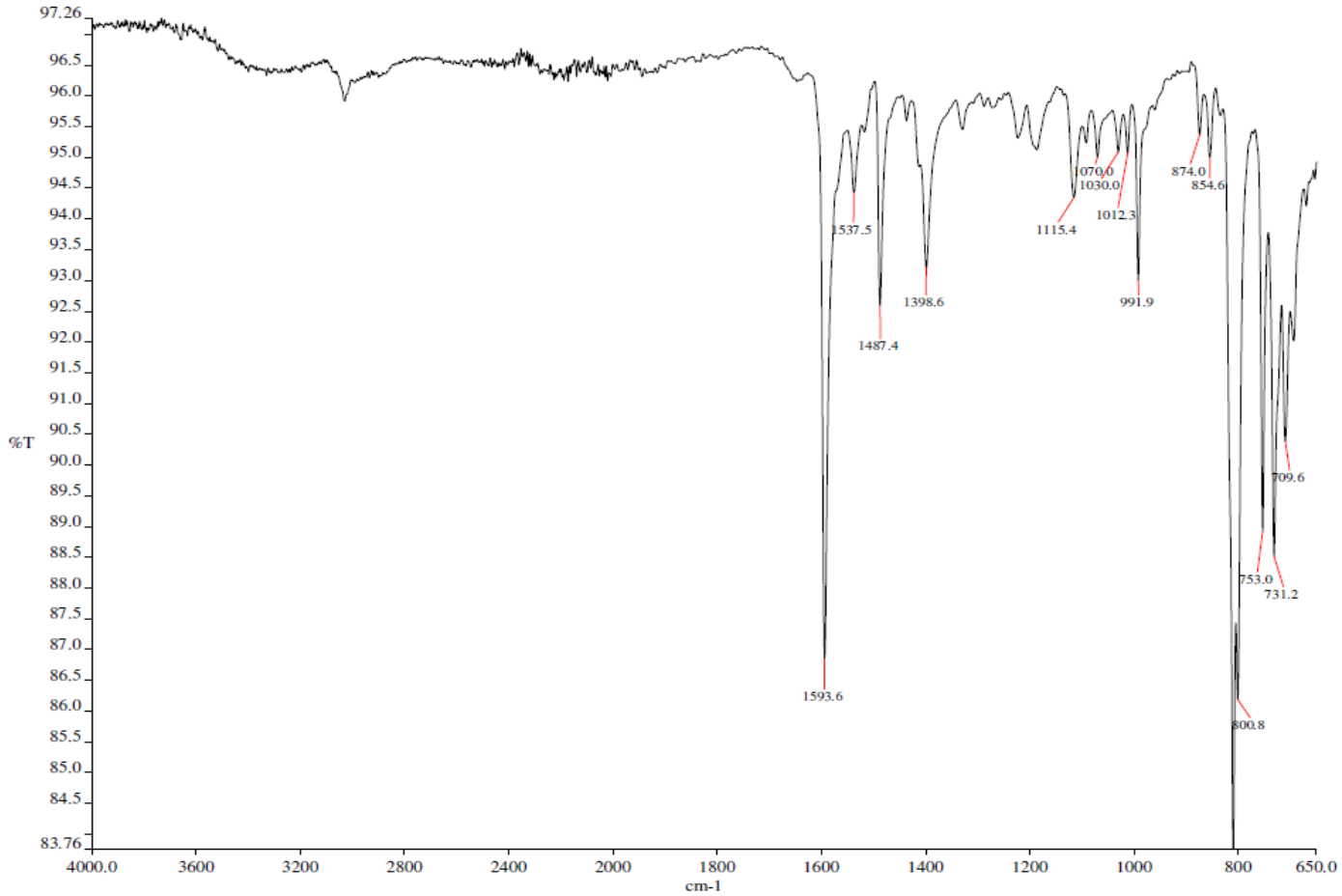

Figure S15. FTIR of tppe.

Fluorescence

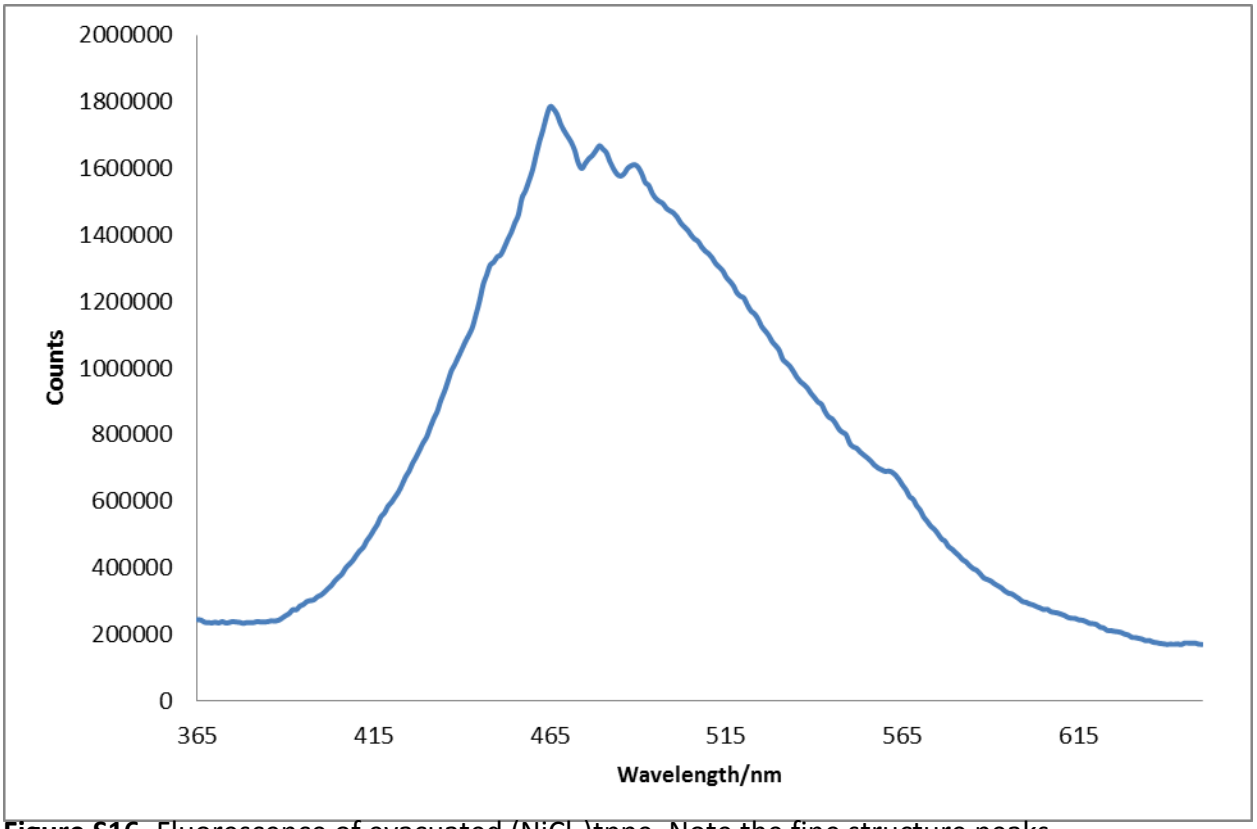

Figure S16. Fluorescence of evacuated ($NiCl_2$)tppe. Note the fine structure peaks.

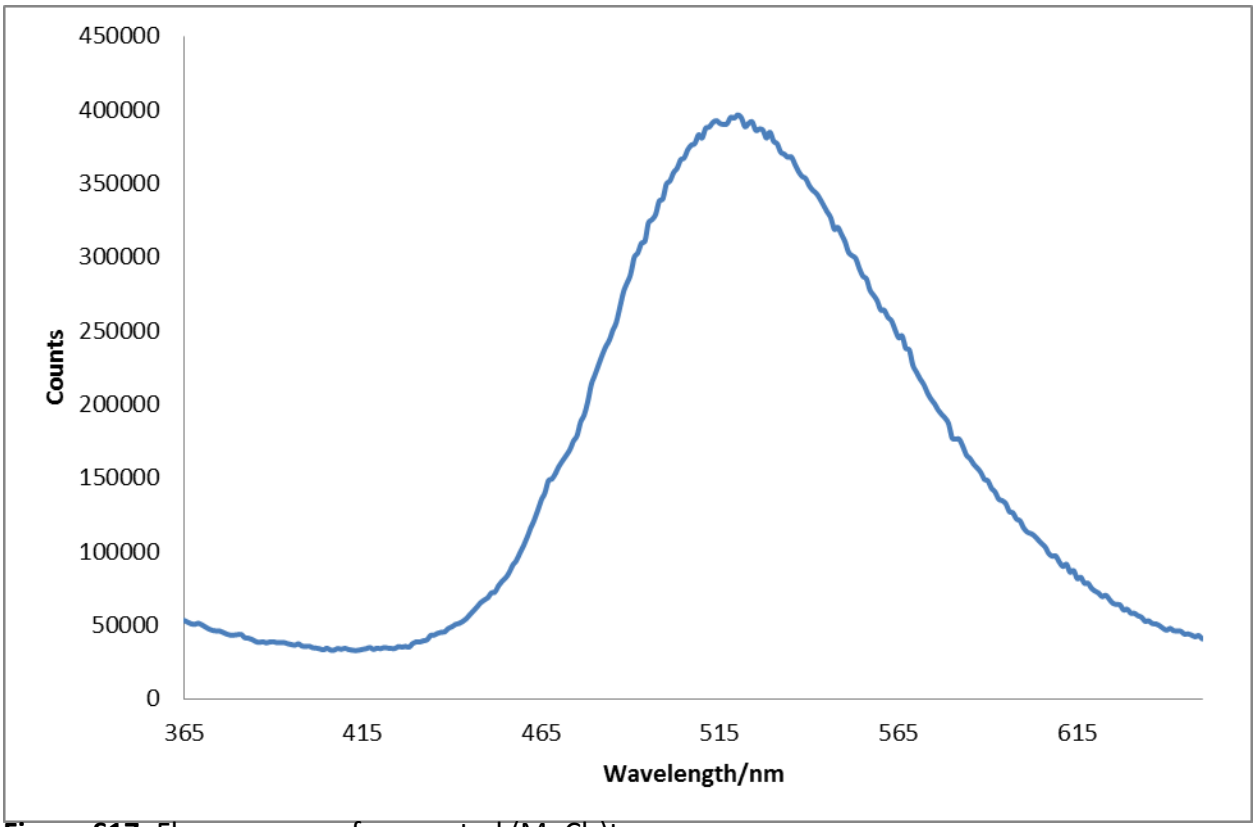

Figure S17. Fluorescence of evacuated ($MnCl_2$)tppe.

GC-MS/TGA

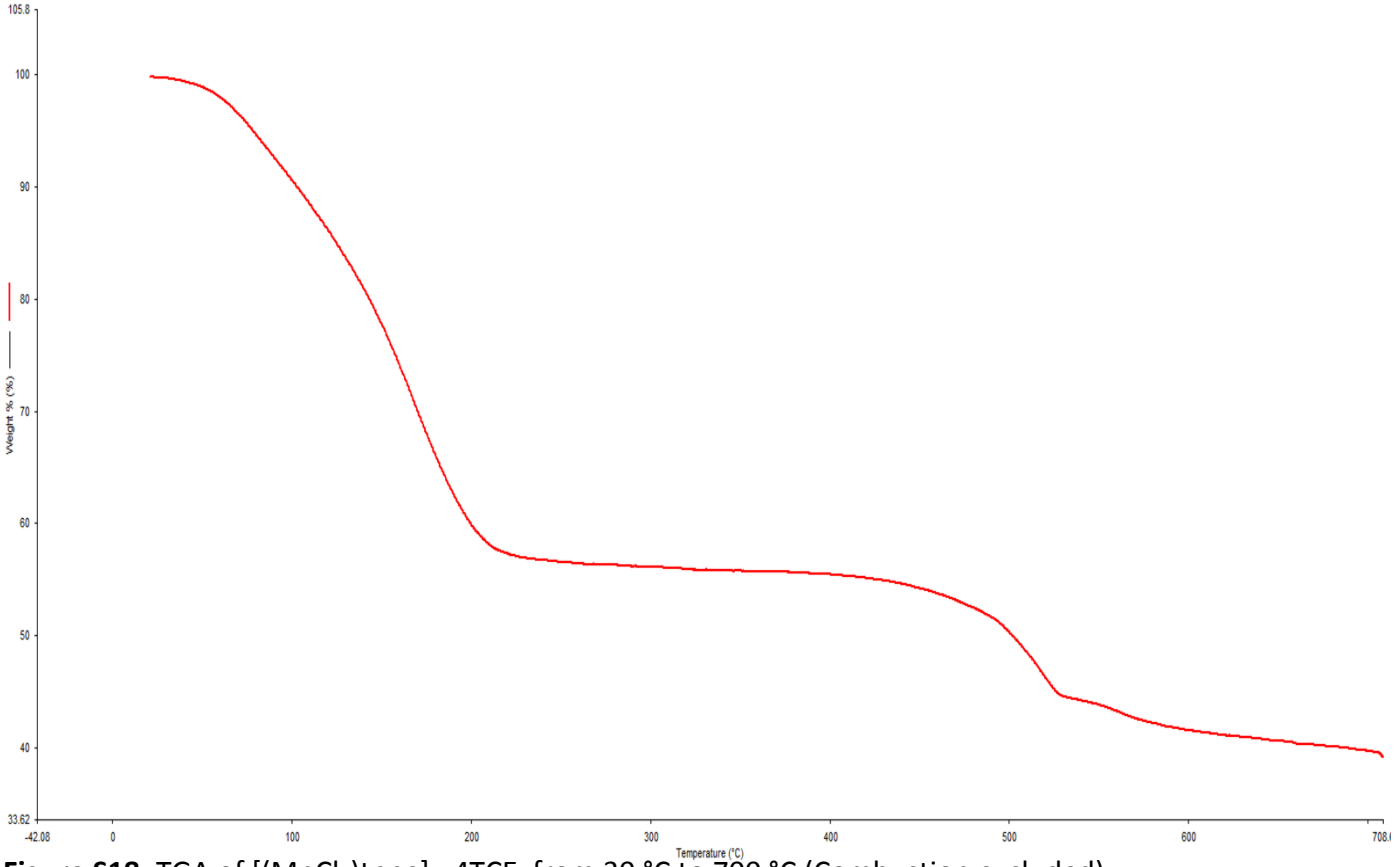

Figure S18. TGA of [($MnCl_2$)tppe] •4TCE from 30 °C to 700 °C (Combustion excluded).

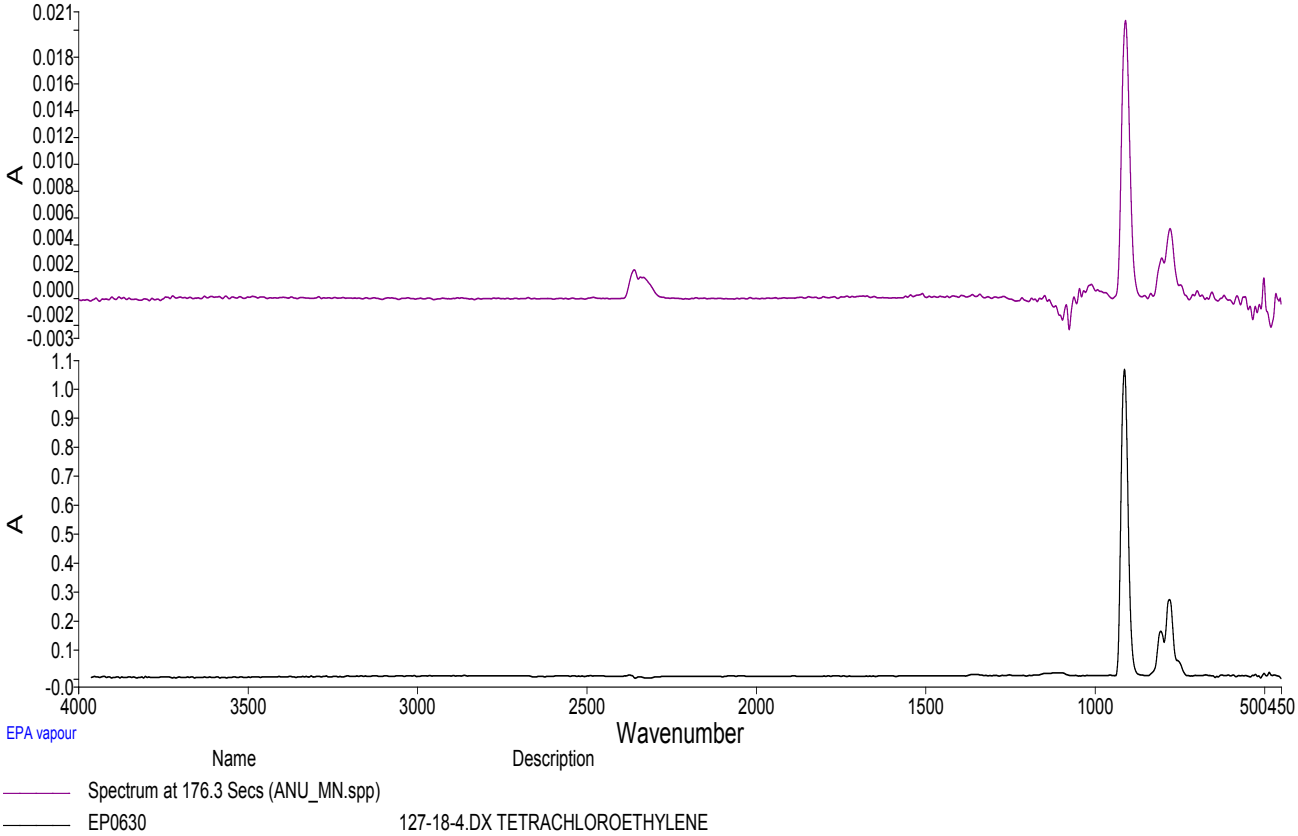

Figure S19. Comparison of infrared spectra at 80% intial weight of [($MnCl_2$)tppe] •4TCE and library spectra of TCE. Note the peak at 2250 is due to CO_2 impurties in the gas feed.

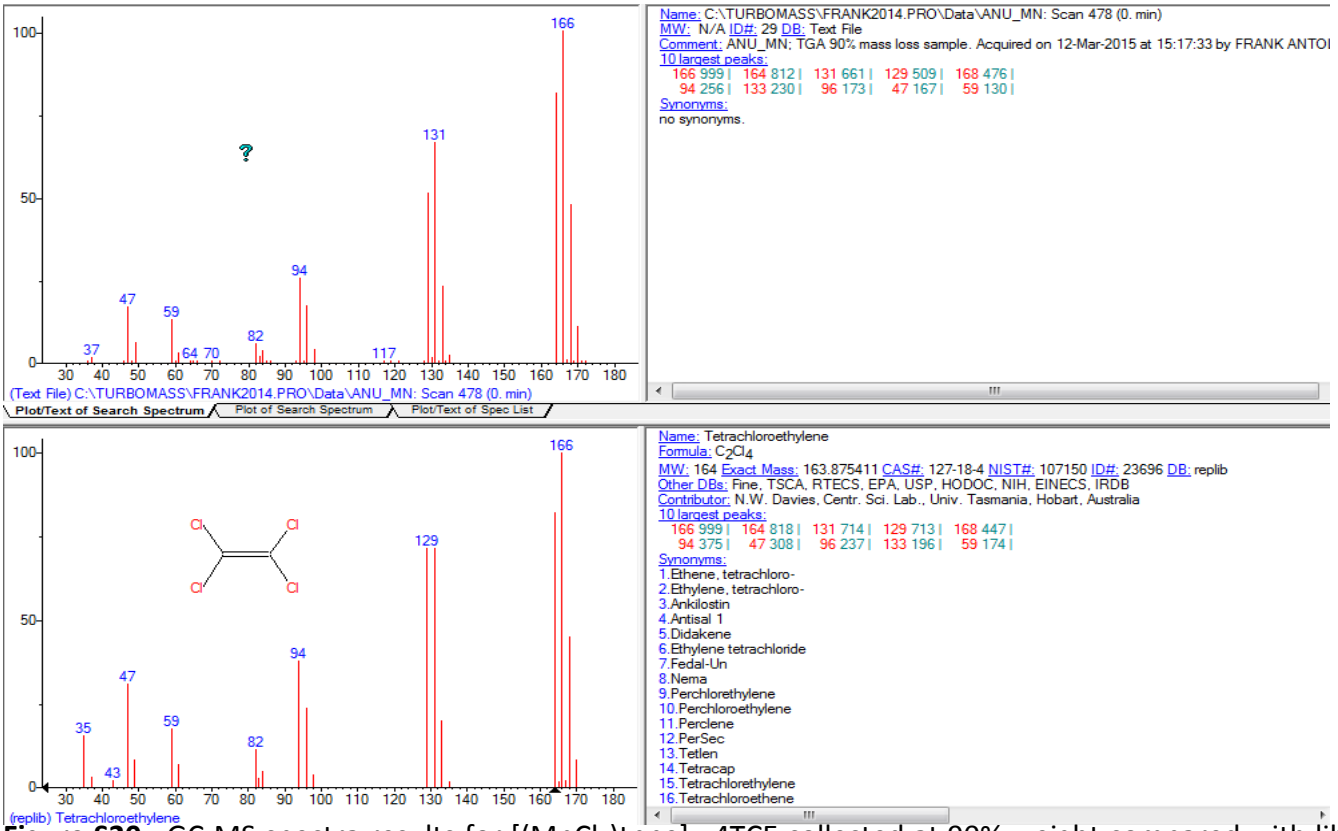

Figure S20. GC-MS spectra results for [($MnCl_2$)tppe] •4TCE collected at 90% weight compared with library spectrum of TCE.

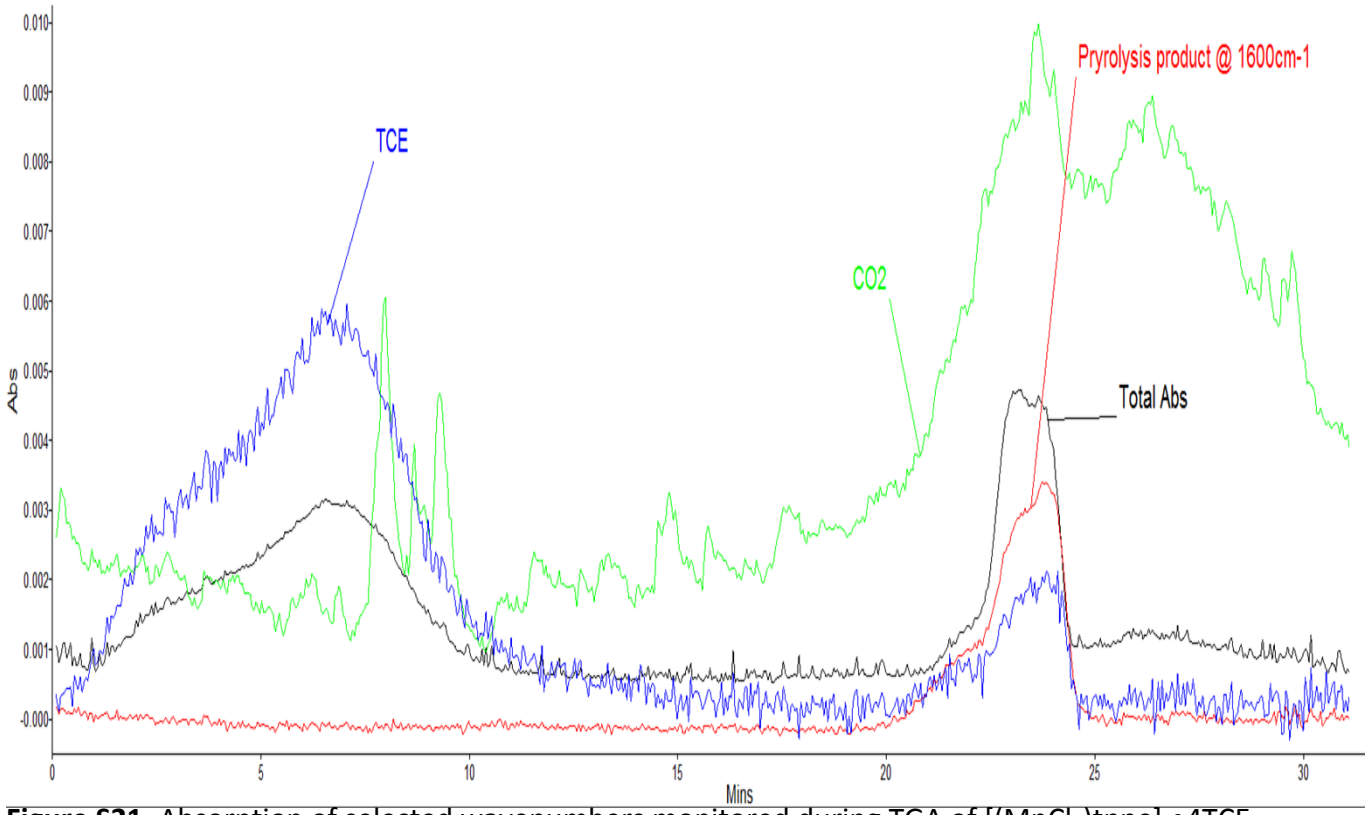

Figure S21. Absorption of selected wavenumbers monitored during TGA of [($MnCl_2$)tppe] •4TCE.

Black: total absorption, Blue: TCE(910cm-1), Green: CO_2(2350cm-1), Red: Pyrolysis product(1600cm-1)

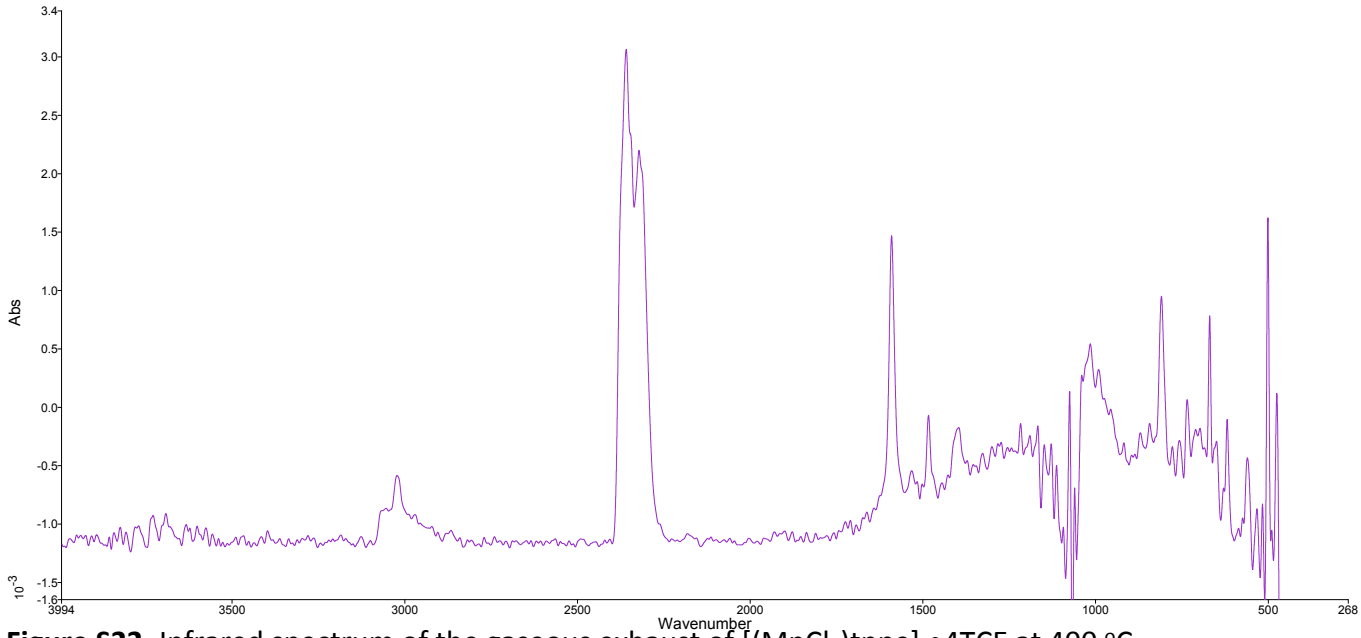

Figure S22. Infrared spectrum of the gaseous exhaust of [($MnCl_2$)tppe] •4TCE at 400 °C.

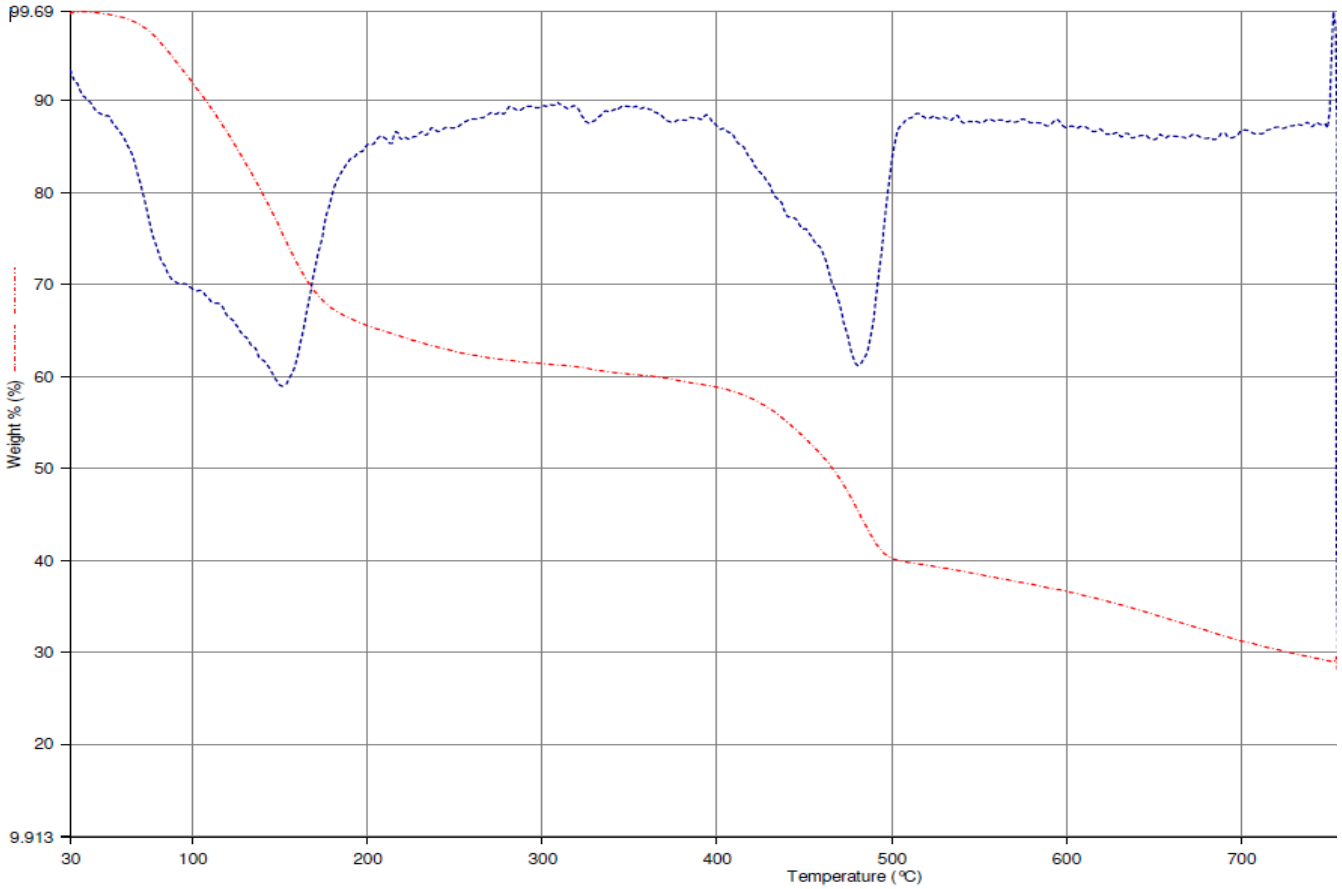

Figure S23. TGA of [($NiCl_2$)tppe] •4TCE from 30 °C to 700 °C (Combustion excluded).

PXRD

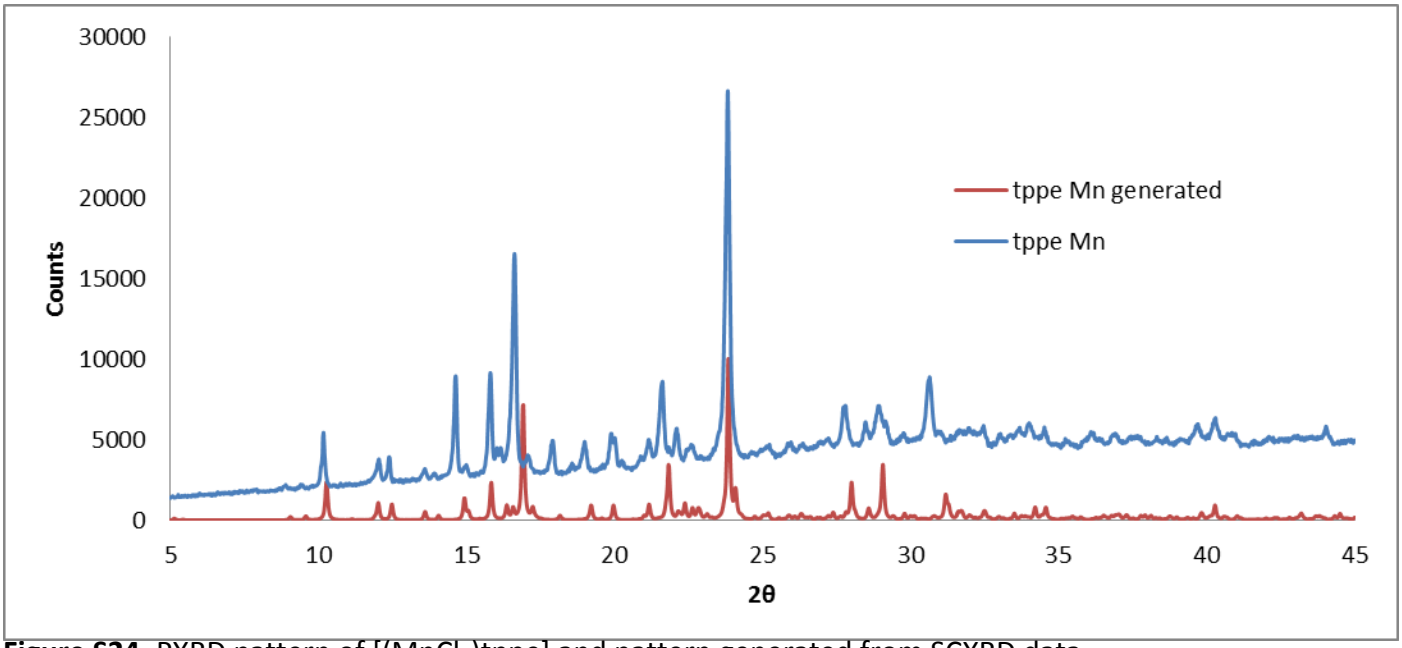

Figure S24. PXRD pattern of [($MnCl_2$)tppe] and pattern generated from SCXRD data.

Gas isotherms

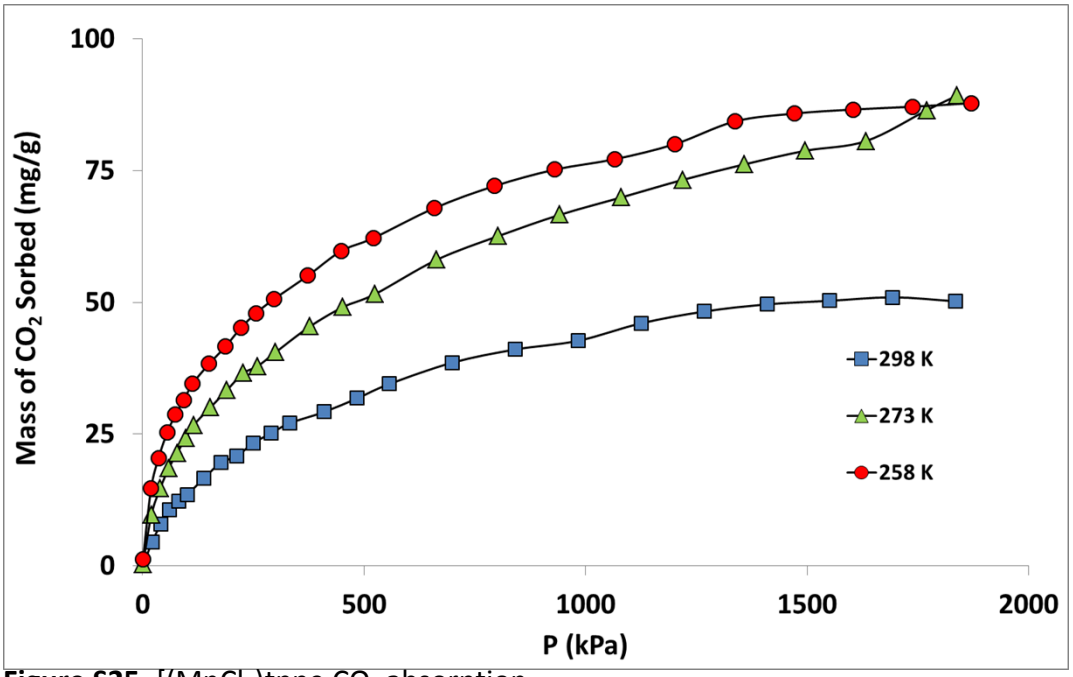

Figure S25. [($MnCl_2$)tppe CO_2 absorption.

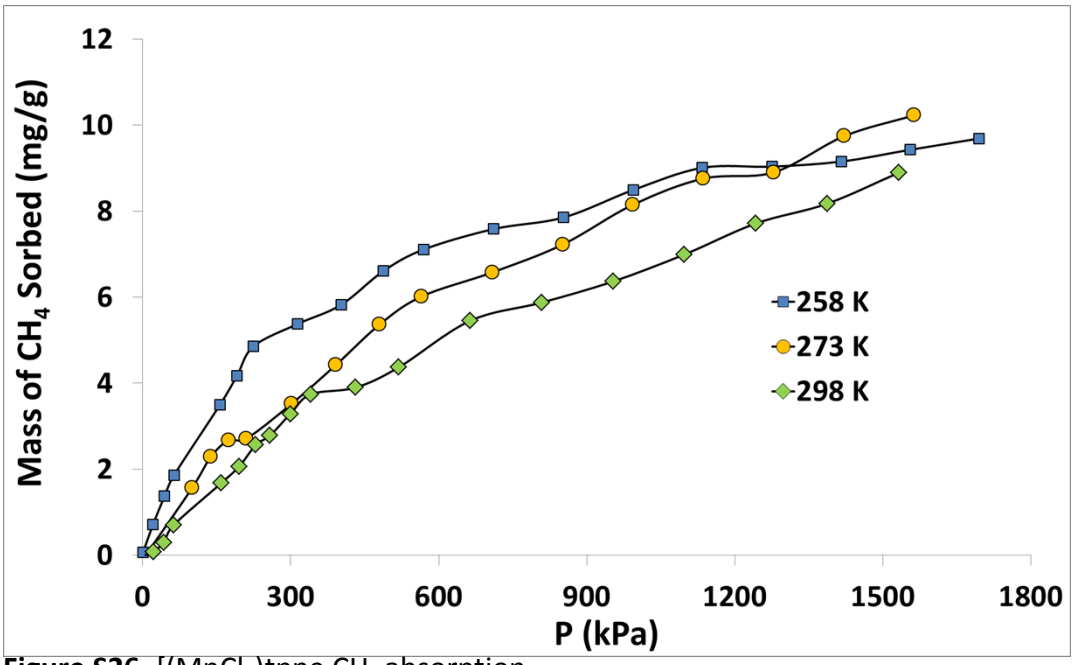

Figure S26. [($MnCl_2$)tppe CH_4 absorption.

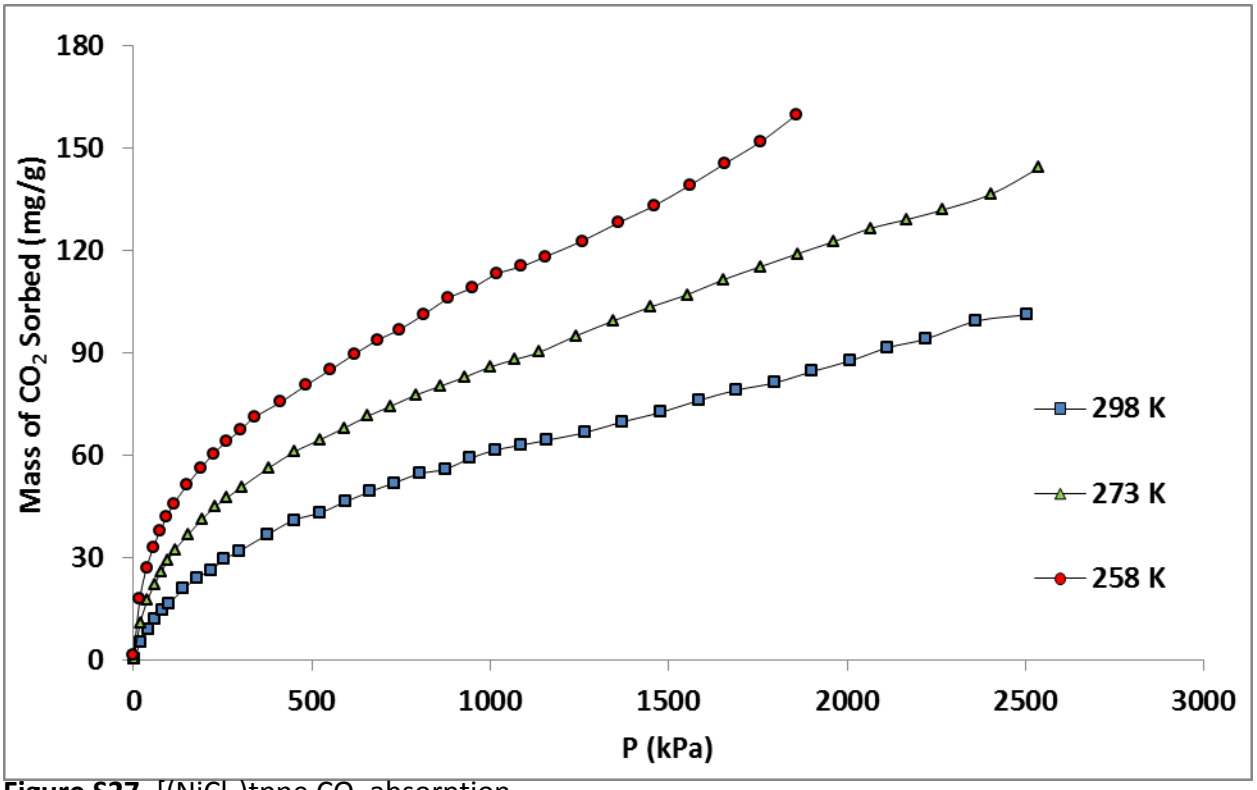

Figure S27. [($NiCl_2$)tppe CO_2 absorption.

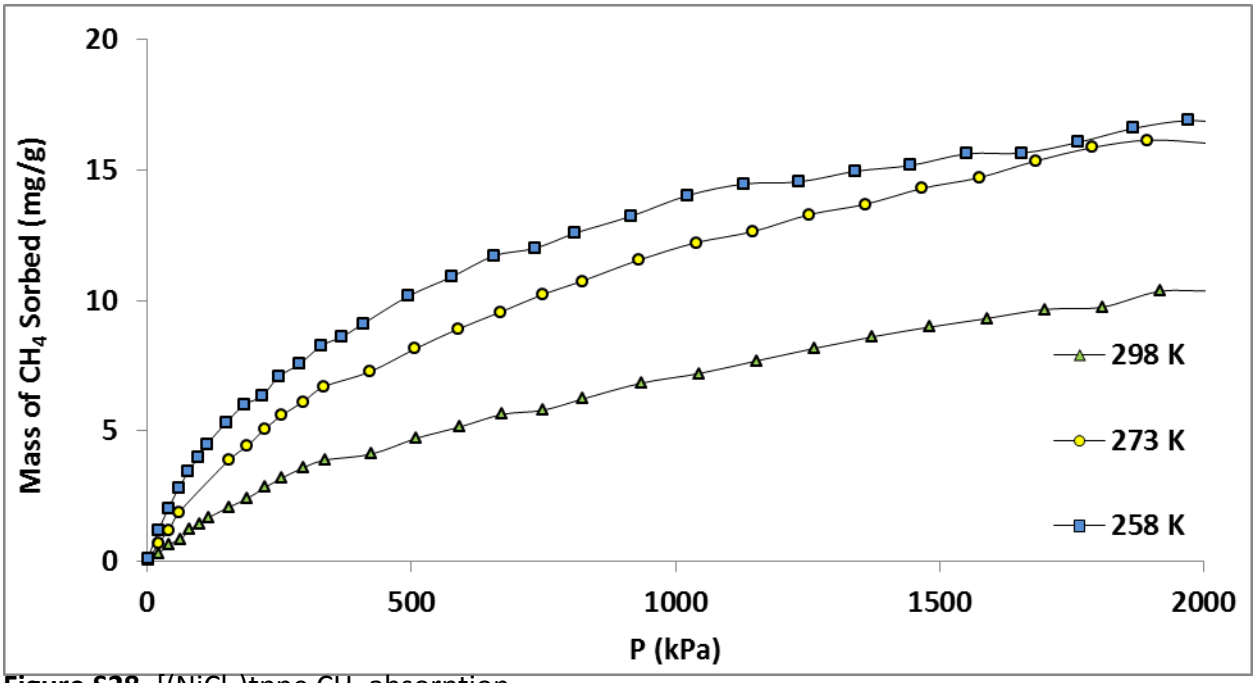

Figure S28. [($NiCl_2$)tppe CH_4 absorption.

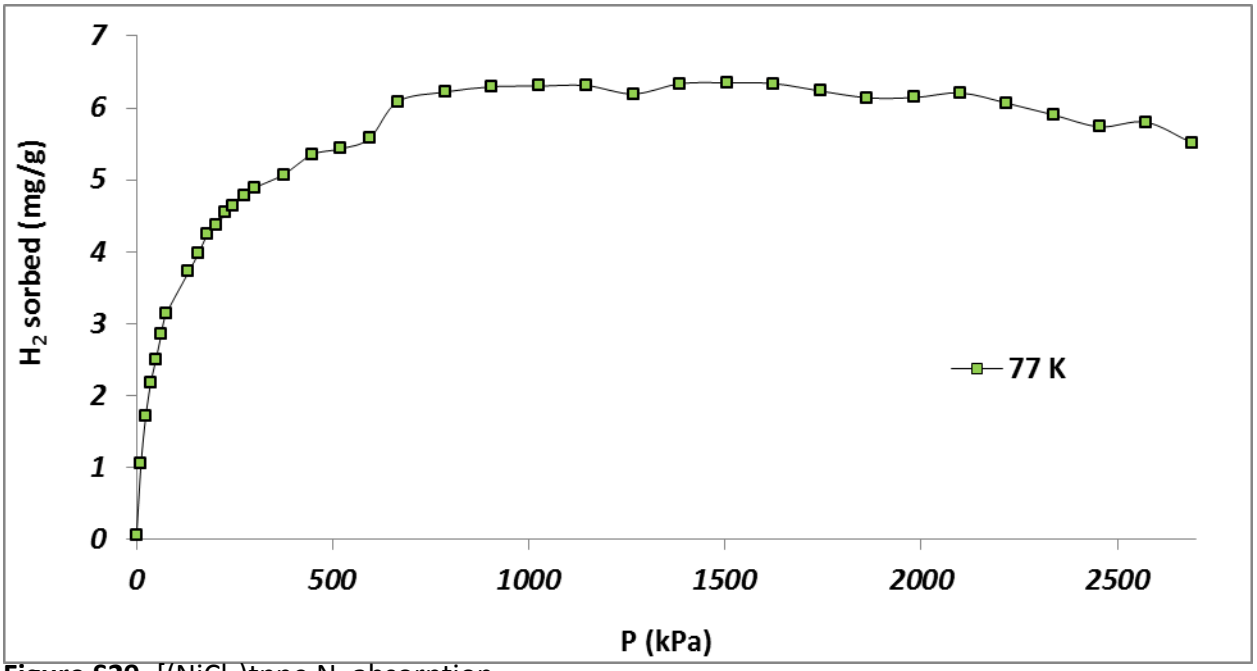

Figure S29. [($NiCl_2$)tppe N_2 absorption.

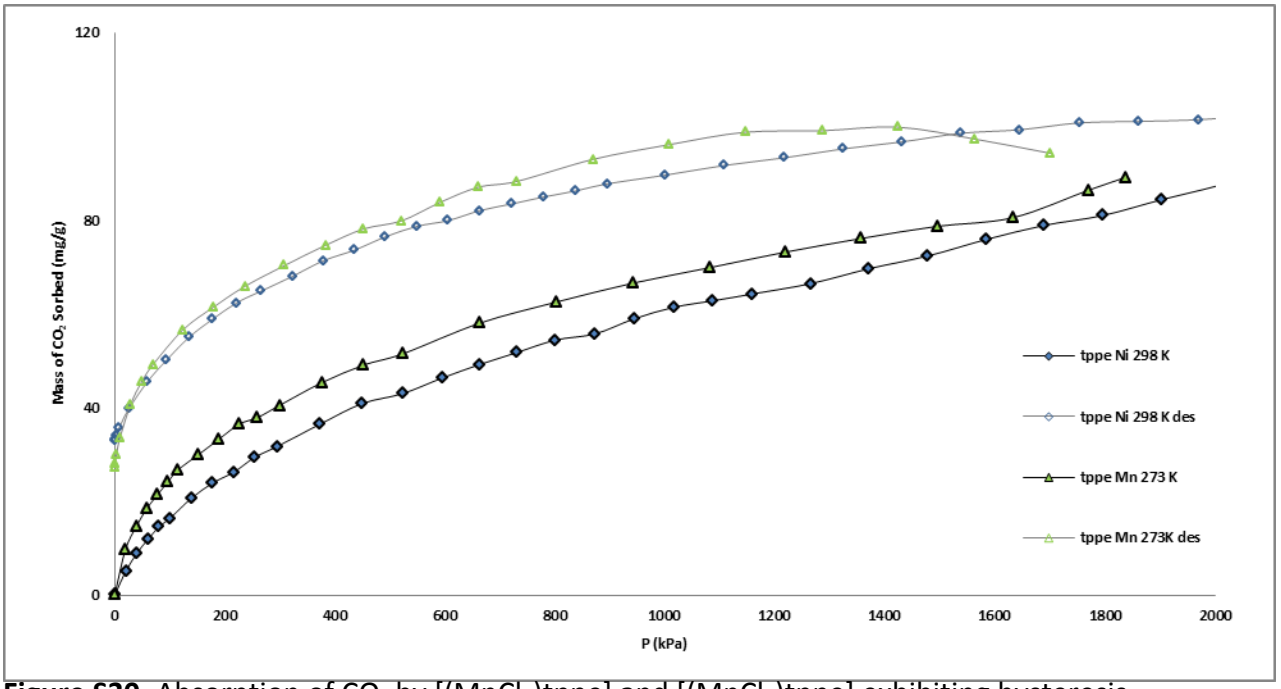

Figure S30. Absorption of CO_2 by [($MnCl_2$)tppe] and [($MnCl_2$)tppe] exhibiting hysteresis.