Supporting Information

A Novel Mn_4-Co_2 nanocluster@photosensitizers/ SalenCo(III) catalyze the copolymerization of carbon dioxide and propylene oxide

ZhiWei Yang, LongChao Du[a]

[a]Address correspondence to Longchao Du, School of Chemistry and Chemical Engineering, the Key Laboratory of Environment-friendly Polymer Materials of Anhui Province & Key Laboratory of Structure and Functional Regulation of Hybrid Materials (Anhui University), Ministry of Education, Hefei, 230601, PRC.
E-mail address: dulongchao@sina.com

1.1 Measurement

The ^{1}H-NMR was recorded on a nuclear magnetic resonance (NMR) spectrometer (avanceii, 400MHz). Samples were dissolved in $CDCl_3$ or CD_3SOCD_3 with tetramethylsilane as an internal standard. The Mn, Co content of the catalysts was quantified by inductively coupled plasma optical emission spectroscopy (ICP-AES; ICPS-8100, Shimadzu and ICP-MS; iCAPQ, Thermo Scientific). The ultraviolet visible absorption spectrum was recorded on Shimadzu UV-3600 spectrophotometer. The matrix assisted laser desorption/ionization time-of-flight was measured using a Bruker Autoflex (MALDI-TOF) mass spectrometer III.

1.2 Electrochemical measurements

The three-electrode system connected to the electrochemical workstation of chinstruments (CHI600E) is used for electrochemical measurement. Use glass carbon disk as working electrode (diameter 3mm, just polished). Use a platinum plate as the counter electrode (diameter 3mm, just polished). The reference electrode is $Ag/AgCl_2$

electrode (0.01M $AgNO_3$, 0.1 M $Bu^n_4NPF_6$ in acetonitrile). The electrolyte solution is 0.1M Bu^n_4NPF in 1,2-dichloroethane. Before the measurement, the solvent shall be purged with saturated argon for more than 30 minutes to remove oxygen to avoid affecting the test results. During the measurement, argon is continuously injected. Before dissolving the cluster **I**, record the background voltammogram of the electrolyte. The reported potential is internally referenced to NHE and calibrated by the possibility of ferrocene/ferrocene measured under the same conditions. Scanning rate: 100mV/s. The arrow shows the scanning direction. Using the Nernst equation {E_{NHE} (V) = $E_{Ag/AgCl}$ (V)+ 0.197 V)}, all potentials are calculated according to the normal hydrogen electrode (NHE) scale.

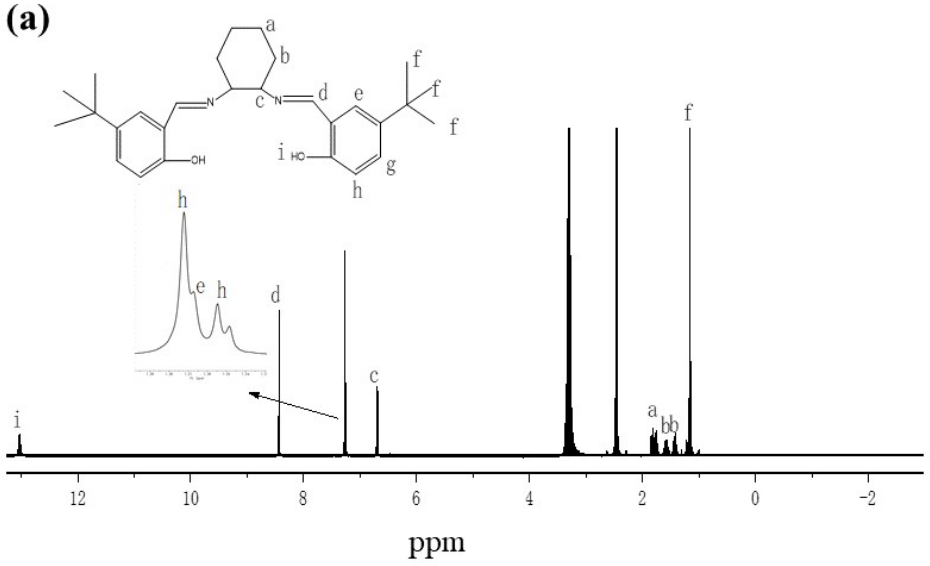
1.3. Structure determination.

The data collection for single crystal X-ray diffraction was carried out on a Bruker Smart APEX II CCD diffractometer at 293 K, the usage of a Cu-Ka radiation (λ =1.54186 Å). Data rate reductions and absorption corrections had been carried out the usage of the SAINT and SADABS programs, respectively. The structure used to be solved through direct methods and sophisticated with full-matrix least squares on F2 the usage of the SHELXTL software program package. All non-hydrogen atoms have been sophisticated anisotropically, and all the hydrogen atoms have been set in geometrically calculated positions and subtle isotropically the usage of a driving model. X-ray photoelectron spectroscopy (XPS) using the Thermo EscaLab Xi+X-ray photoelectron spectrometer.

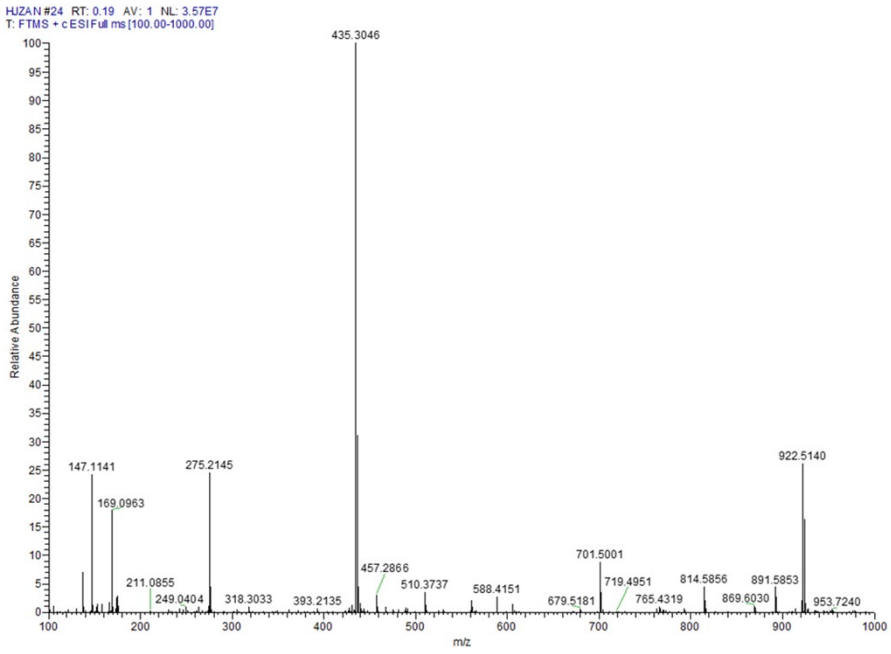
1.4. Characterization of compound 1, compound 2, S1, S2, cluster **I**

Compound 1：

(a)


a
b
c
d
e
f
f
f
g
h
i
OH
HO
h
e
h
d
c
i
a
b
b
f
12
10
8
6
4
2
0
−2
ppm

(b)


HUZAN #24 RT: 0.19 AV: 1 NL: 3.57E7
T: FTMS + c ESI Full ms [100.00-1000.00]
Relative Abundance
m/z
435.3046
922.5140
147.1141
275.2145
169.0963
211.0855
249.0404
318.3033
393.2135
457.2866
510.3737
588.4151
679.5181
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719.4951
765.4319
814.5856
869.6030
891.5853
953.7240

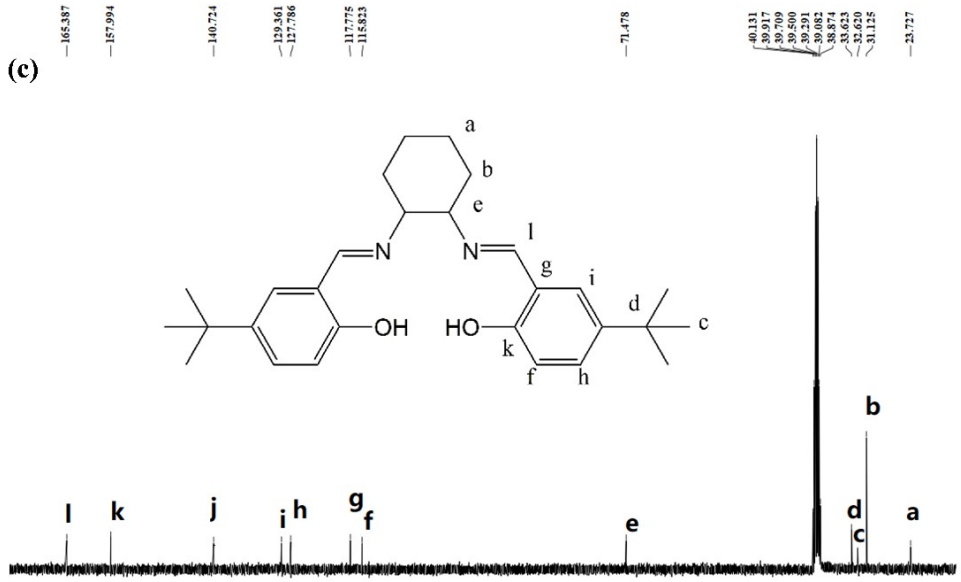
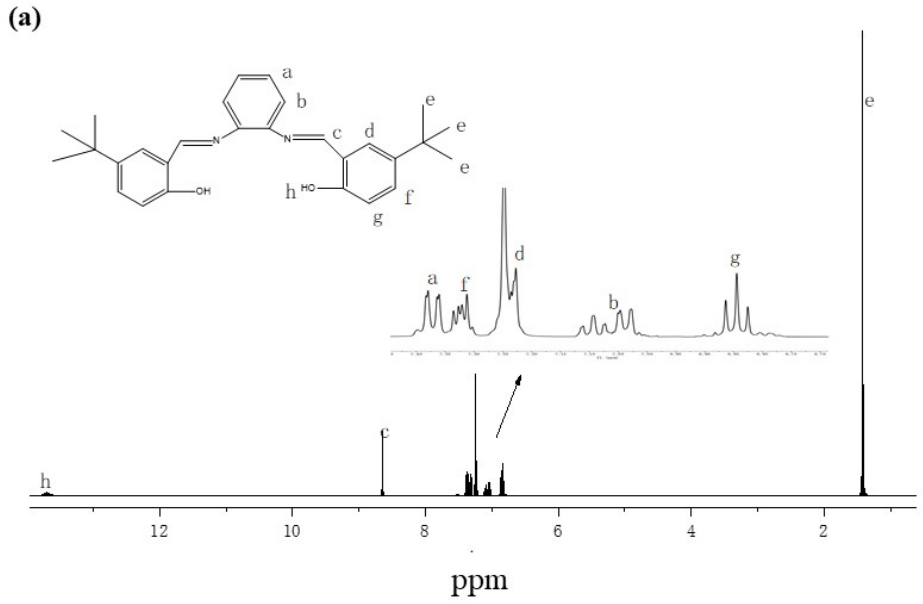


Fig. S1 (a) Compound 1 ^{1}H NMR (400 MHz, DMSO-d6); (b) Compound 1 mass spectrum; (c) Compound 1 ^{13}C NMR (400 MHz, DMSO-d6)

Compound 2：



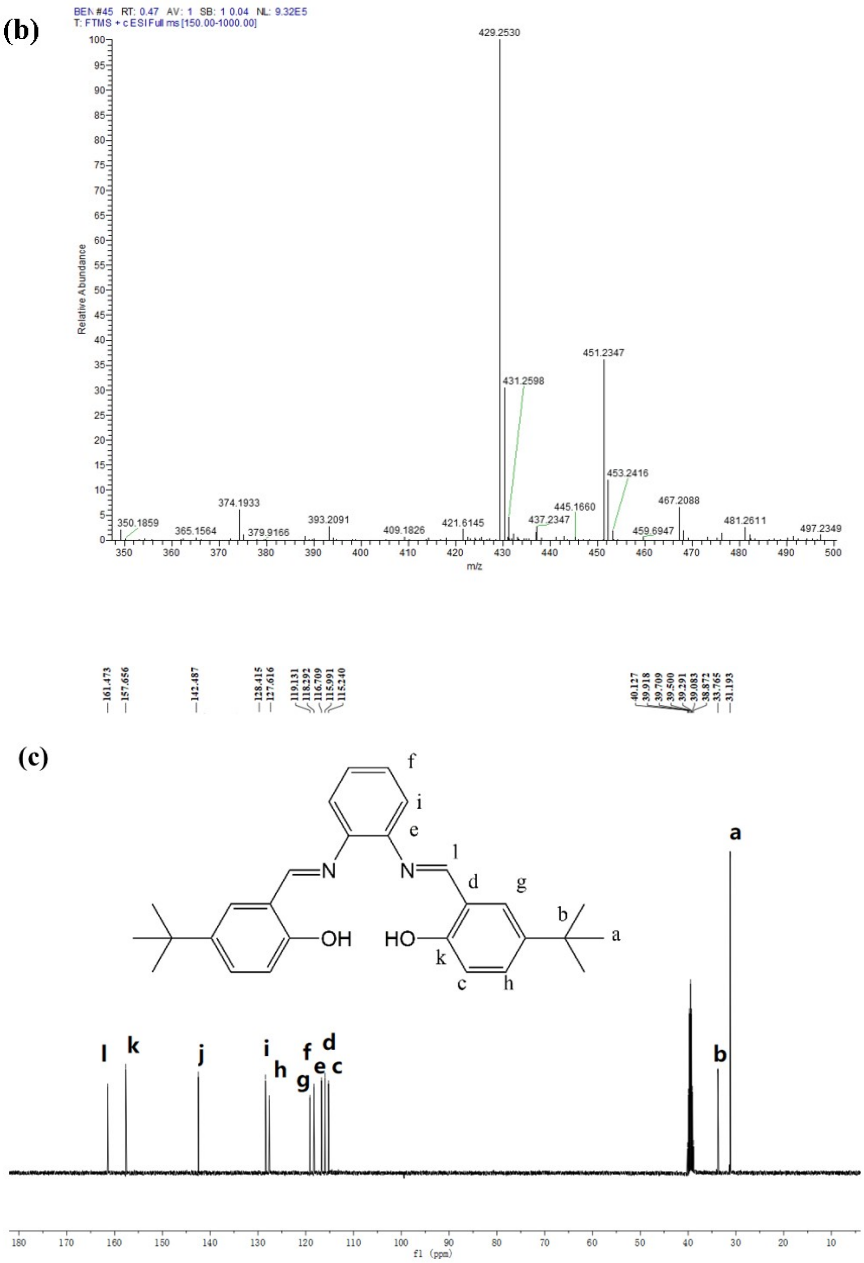
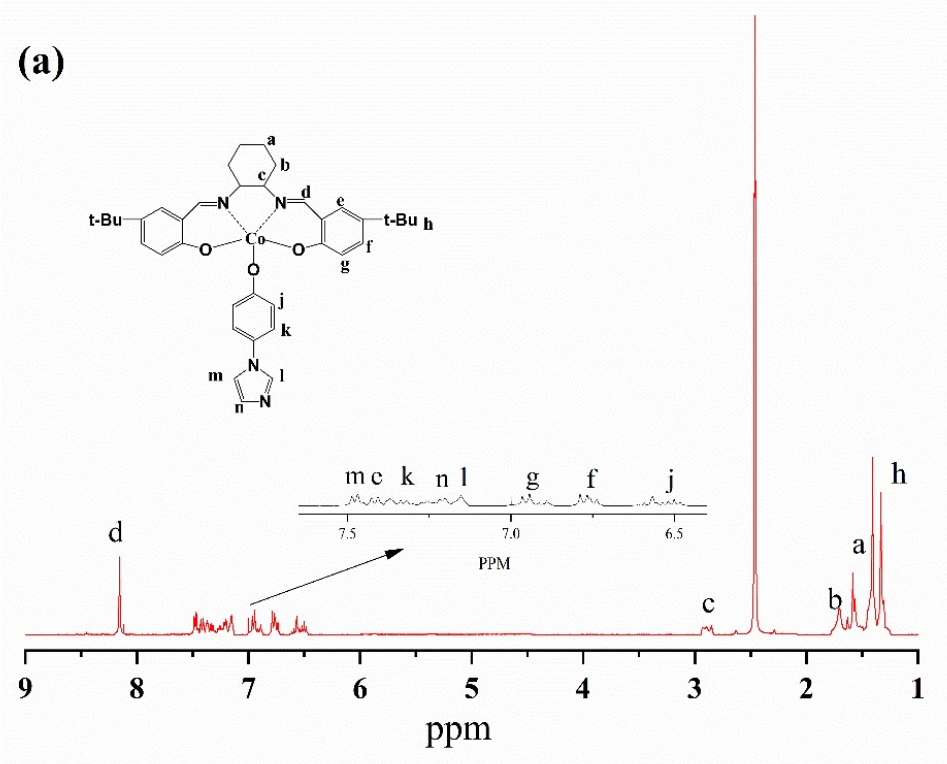


Fig. S2 (a) Compound 2 ^{1}H NMR (400 MHz, Chloroform-d); (b) Compound 2 mass spectrum; (c) Compound 2 ^{13}C NMR (400 MHz, DMSO-d6)

S1：



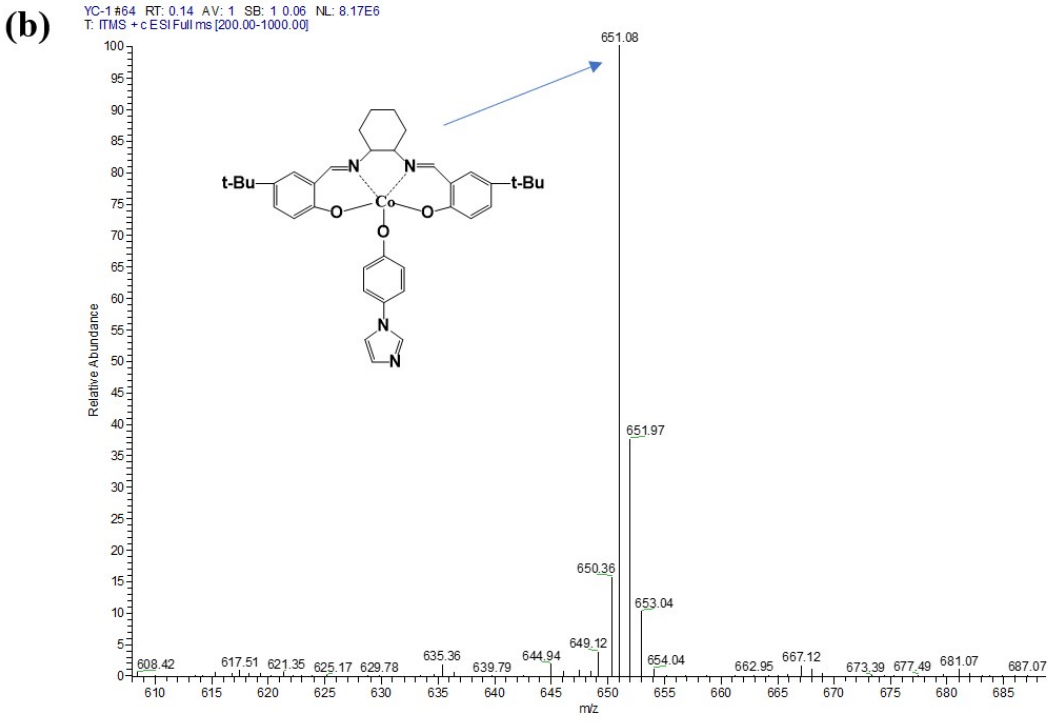
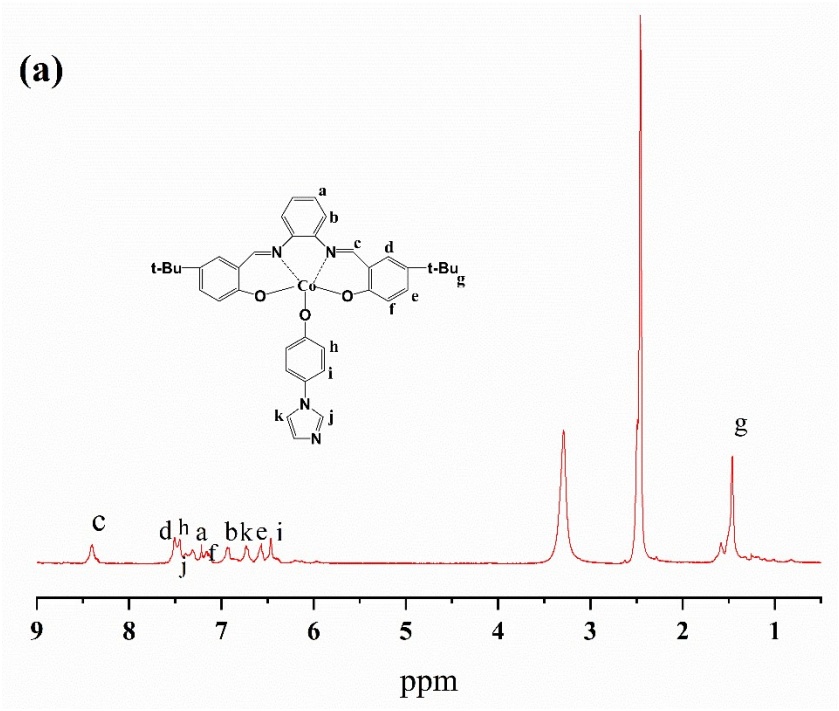


Fig. S3 (a) S1 ^{1}H NMR (400 MHz, DMSO-d6); (b) S1 mass spectrum

S2:



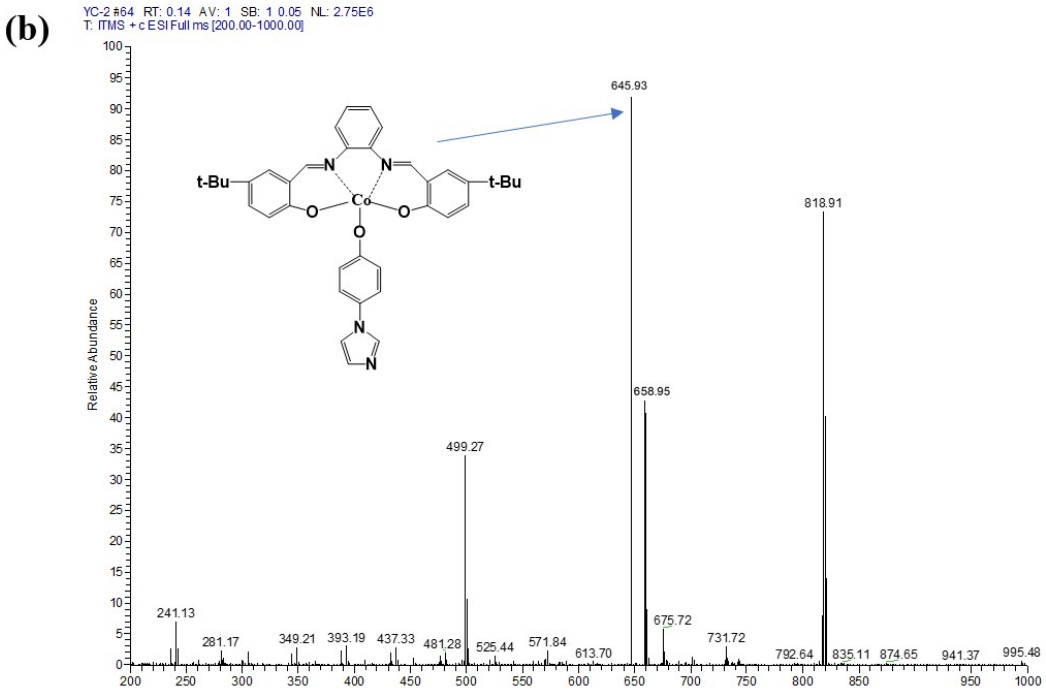


Fig. S4 (a) S2 ^{1}H NMR (400 MHz, DMSO-d6); (b) S2 mass spectrum

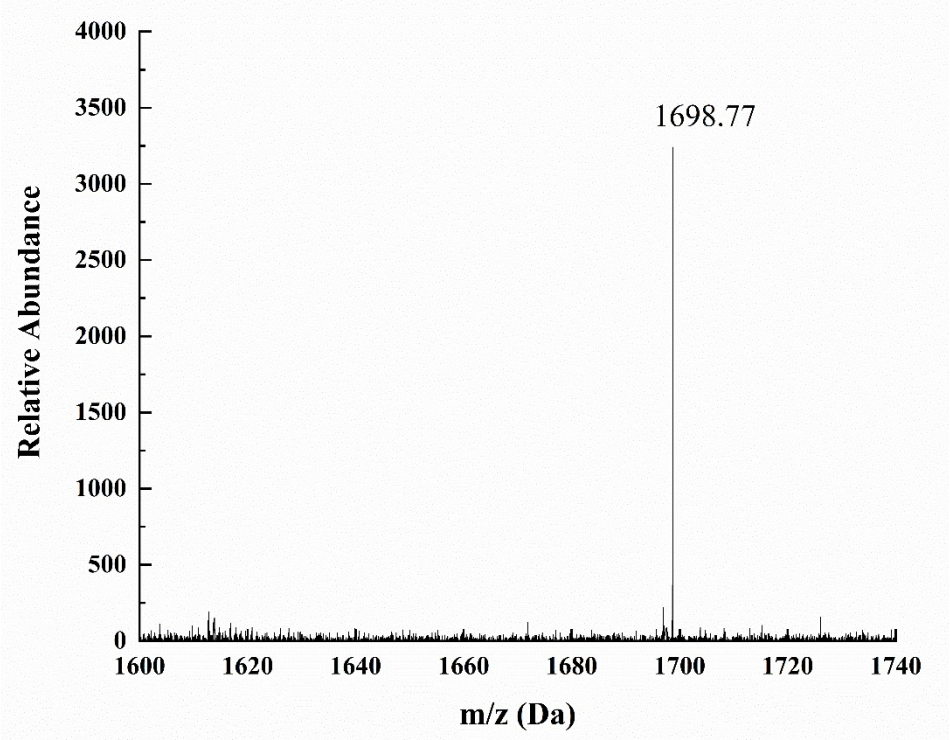


Fig. S5. The MALDI mass spectra analysis of the cluster **I**.

crystals.

1.5 Polymer ^{1}H-NMR and composite catalyst characterisation

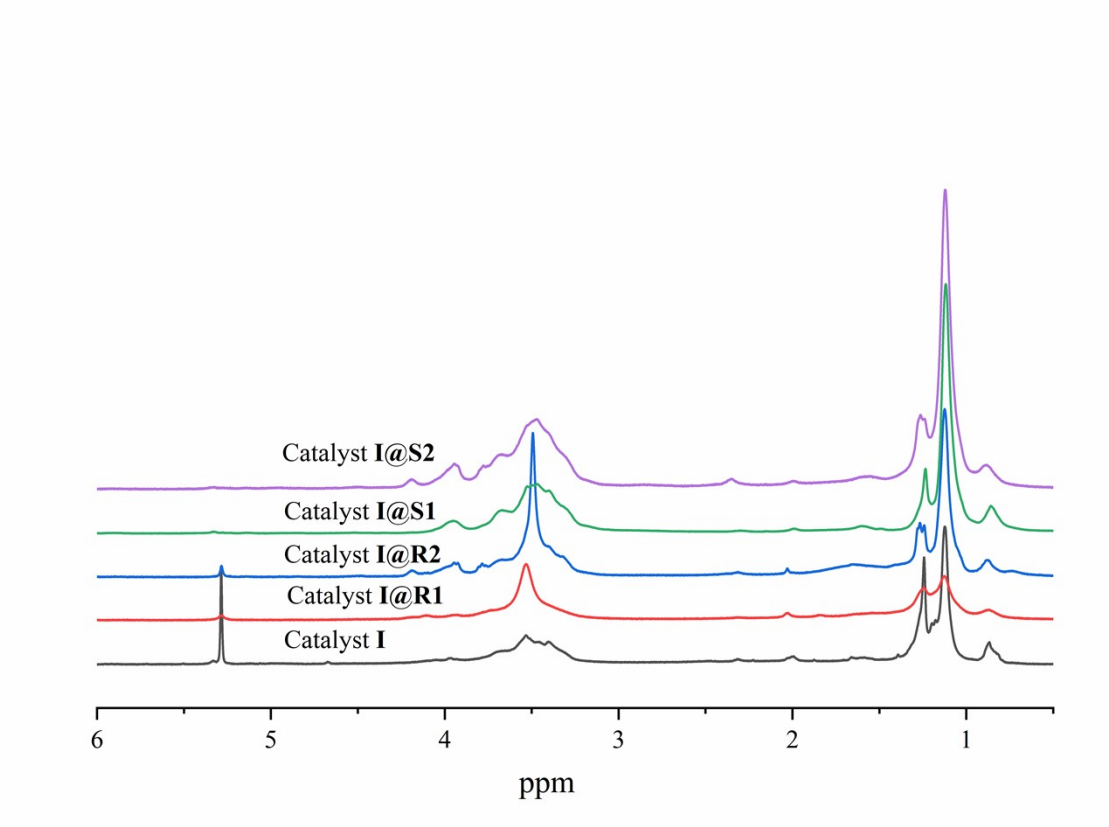


Fig. S6. The ^{1}H NMR of the copolymerization products for **I**, **I@R1**, **I@R2**, **I@S1** and **I@S2** without light sources, 60 ℃, 6h and 2 MPa CO_2.

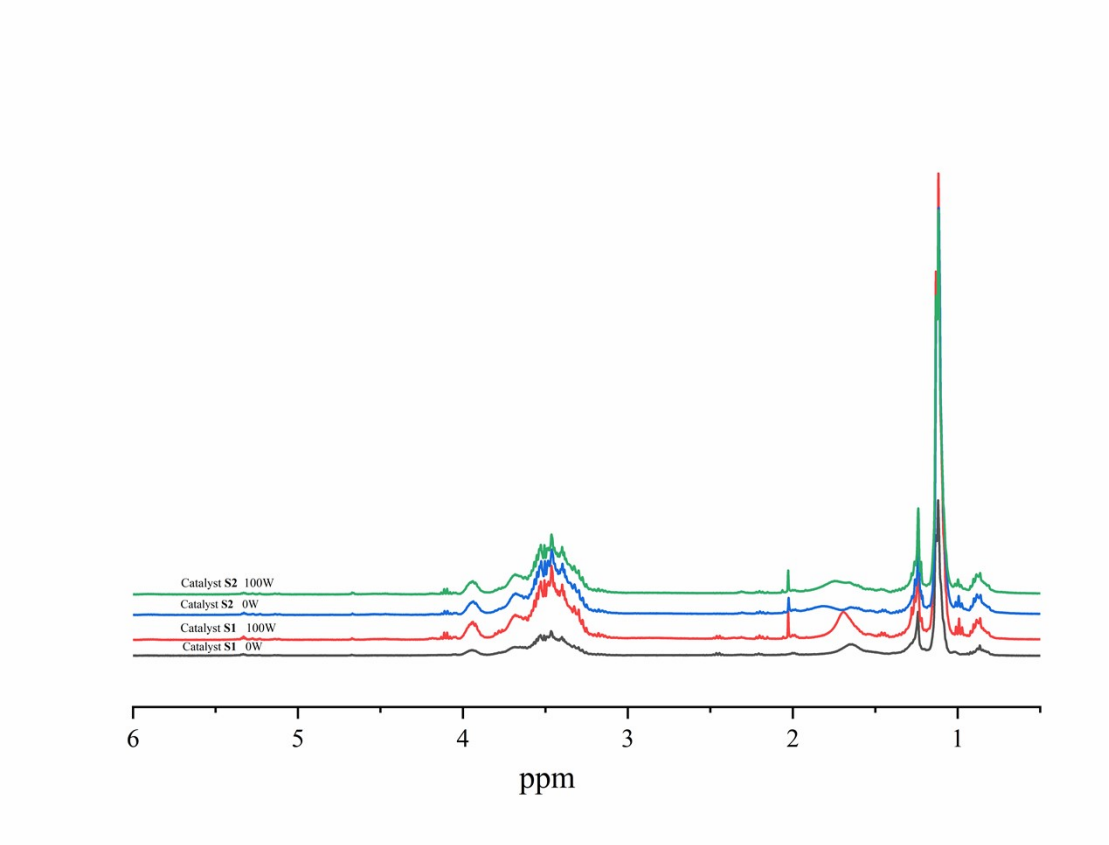


Fig. S7 The ^{1}H NMR of the copolymerization products for **S1** and **S2** with 0W or 100W light sources at 60 ℃, 6h and 2 MPa CO_2.

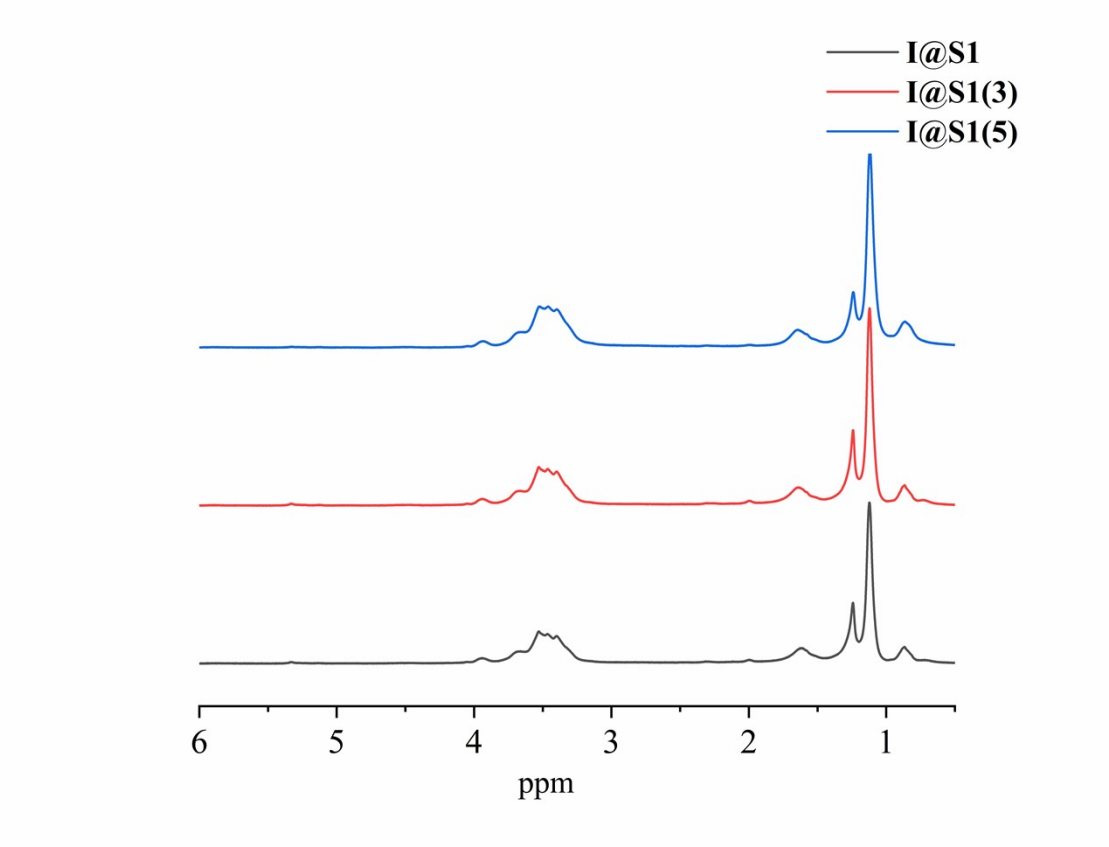


Fig. S8 The ^{1}H NMR of the copolymerization products for **I@S1**, **I@S1(3)** and **I@S1(5)** with 100W light sources, 60 ℃, 6h and 2 MPa CO_2.

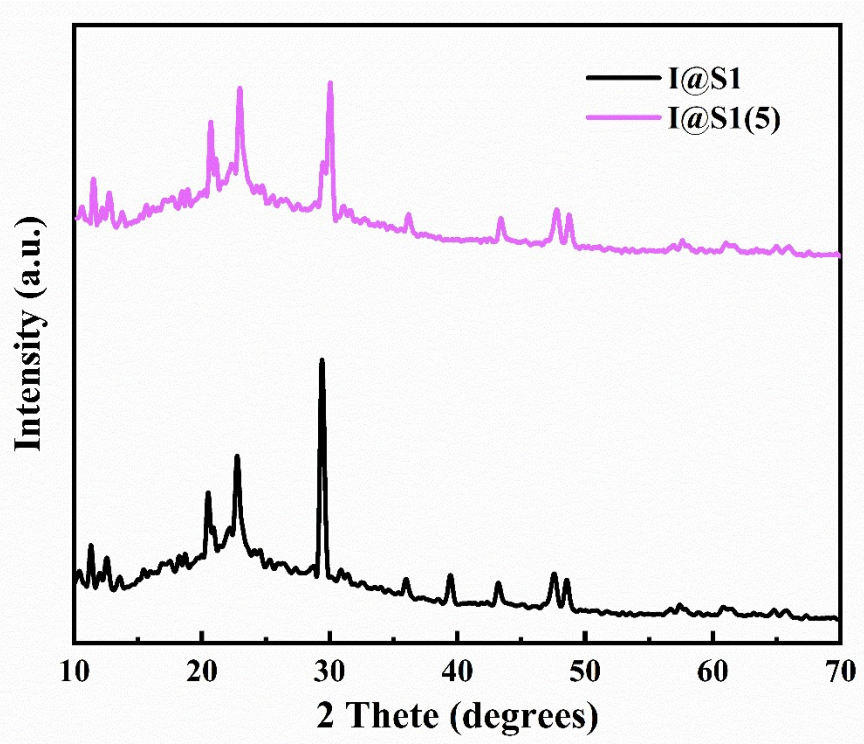


Fig. S9 XRD patterns of **I@S1** and **I@S1(5)**

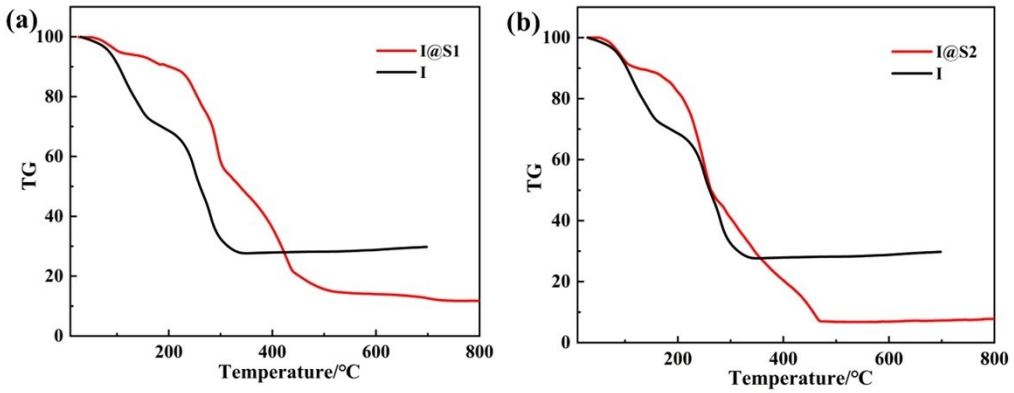


Fig. S10 TG analysis of composite catalysts: (a) **I, I@S1** and (b) **I, I@S2.**

1.6 Filter Information

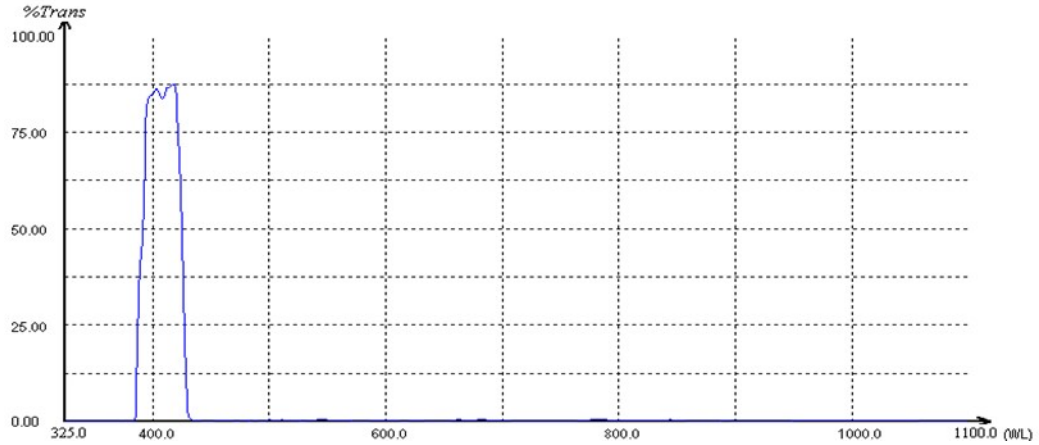


Fig. S11 The light transmittance of the filter can reach about 90% in the range of 395nm~421nm.

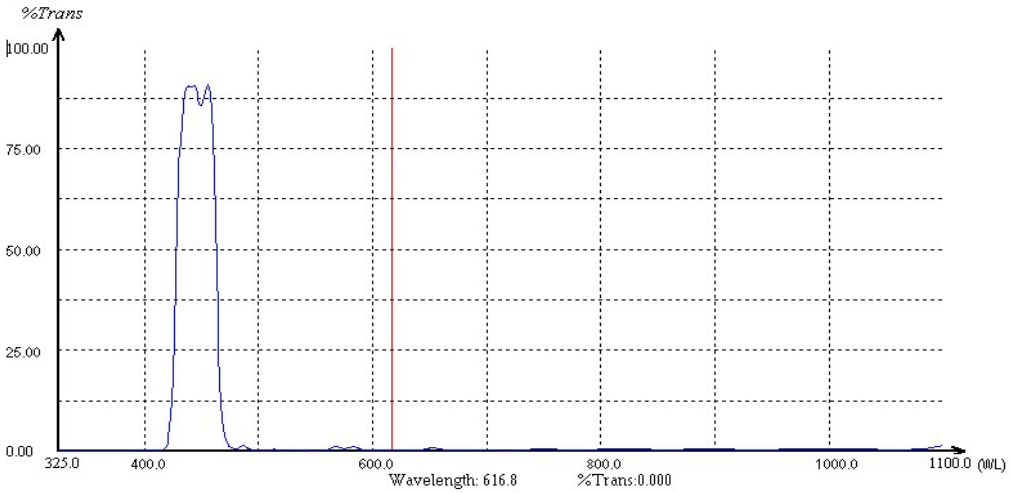


Fig. S12 The light transmittance of the filter can reach about 90% in the range of 433nm~459nm.

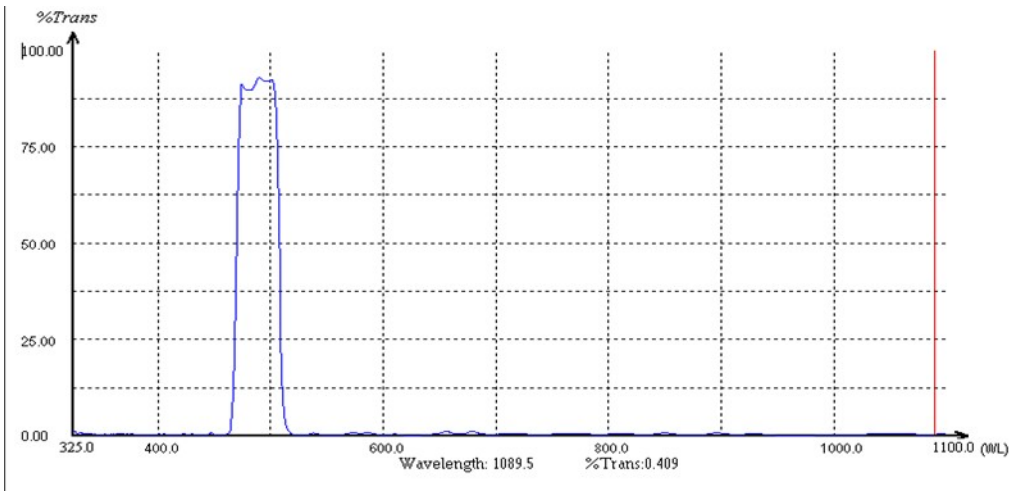


Fig. S13 The light transmittance of the filter can reach about 90% in the range of 472nm~505nm.

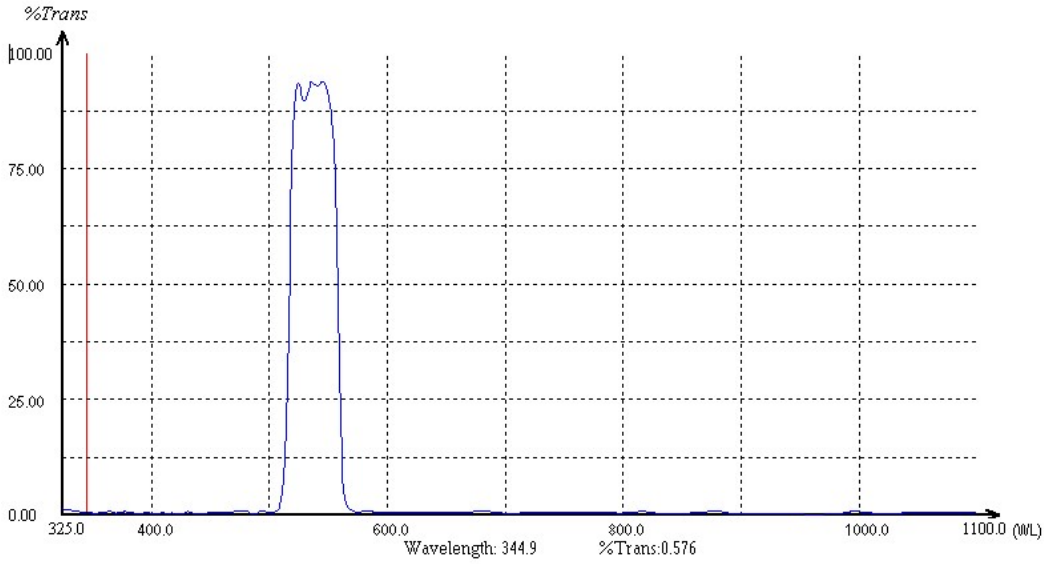


Fig. S14 The light transmittance of the filter can reach about 90% in the range of 520nm~554nm.

1.7 Crystal structure information

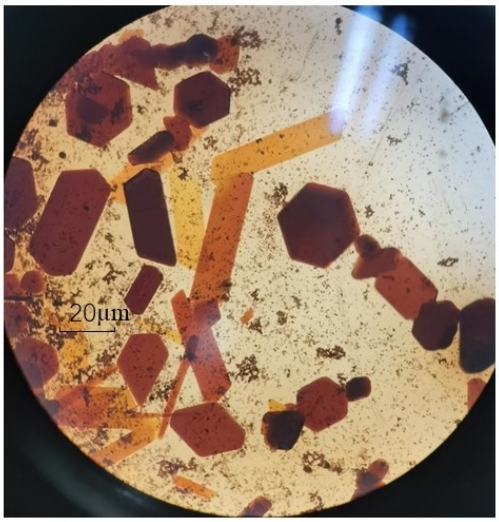


Fig. S15. The digital photo of the clusters **I** [$Mn_4Co_2O_2(Bu^tCO_2)_{10}(C_5H_5N)_4$]

Table S1 Crystal and refinement data for clusters **I**

Empirical formula	$C_{70}H_{110}Co_2Mn_4N_4O_{22}$
Formula weight	1697.23
Temperature/K	293
Crystal system	orthorhombic
Space group	Pbcn
a/Å	14.1256(5)
b/Å	23.1528(7)
c/Å	28.0634(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	9178.1(5)
Z	4

ρ_{calc} g/cm^3	1.228
μ/mm^{-1}	7.624
F(000)	3552.0
Crystal size/mm^3	0.23 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54186)
2Θ range for data collection/°	7.636 to 139.25
Index ranges	-12 ≤ h ≤ 17, -21 ≤ k ≤ 28, -14 ≤ l ≤ 34
Reflections collected	22065
Independent reflections	8249 [R_{int} = 0.0363, R_{sigma} = 0.0383]
Data/restraints/parameters	8249/555/506
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0599, wR_2 = 0.1449
R indexes [all data]	R_1 = 0.0841, wR_2 = 0.1618

Table S2 Atomic coordinates (×10^4) and equivalent isotropic displacement arameters (A^2×10^3) for clusters I. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	X	Y	Z	U(eq)
Co1	5000	5906.7(3)	7500	29.0(2)
Co2	5000	7118.4(3)	7500	29.1(2)
Mn1	5818.3(5)	6351.4(3)	6508.9(2)	39.22(18)
Mn2	3311.9(5)	6686.0(3)	6838.9(2)	38.94(18)
O1	5224.4(18)	6513.4(10)	7935.9(9)	28.8(5)
O2	6783(2)	7037.2(13)	6654.8(11)	48.9(8)
O3	5267(2)	5496.0(12)	6378.0(11)	49.1(8)
O4	4586(2)	5293.6(11)	7070.2(10)	42.1(7)
O5	3524(2)	6349.1(14)	6144.8(11)	54.6(8)
O6	3543(2)	5866.0(12)	7831.2(10)	39.5(6)
O7	2622(2)	5992.3(13)	7197.6(12)	51.2(8)

O8	5028(2)	7728.9(11)	7979.1(10)	41.6(7)
O9	4947(3)	6689.0(14)	5961.3(11)	53.4(8)
O10	6596(2)	7166.6(12)	7432.5(10)	41.1(7)
O11	6310(2)	7536.2(12)	8414.7(11)	48.1(8)
N1	6814(3)	6150.8(18)	5868.4(15)	59.7(11)
N2	1807(3)	6912(2)	6536.9(16)	59.6(11)
C1	2802(3)	5765.2(17)	7593.4(16)	40.4(9)
C2	4730(13)	8789(7)	8361(7)	87(4)
C3	4942(8)	4428(3)	6015(3)	140(4)
C4	5610(3)	7836.8(16)	8308.8(15)	40.7(9)
C5	1462(6)	5076(4)	7416(3)	118(3)
C6	7005(3)	7262.7(18)	7042.5(16)	40.9(9)
C7	7697(8)	6016(4)	5004(3)	153(5)
C8	4785(3)	5185.9(17)	6642.7(16)	42.9(10)
C9	5233(17)	8868(6)	8244(6)	95(5)
C10	4127(4)	6523.7(19)	5852.2(17)	51.8(11)
C11	835(6)	7513(4)	6052(3)	112(3)
C12	5425(4)	8390(2)	8593.4(18)	63.6(14)
C13	7786(8)	6504(4)	5247(3)	143(4)
C14	2073(4)	5342(2)	7799(2)	59.5(13)
C15	3747(9)	5926(4)	5160(3)	148(4)
C16	7855(4)	7682(2)	7046.9(19)	57.2(12)
C17	5101.4	8213(7)	9078(4)	107(4)
C18	4391(5)	4619(2)	6446(2)	70.8(16)
C19	397(5)	6554(4)	6189(3)	109(3)
C20	3843(6)	6526(3)	5328(2)	79.9(17)
C21	2602(6)	4859(3)	8057(4)	125(3)
C22	1614(5)	7414(3)	6334(3)	86(2)
C23	4386(8)	4163(3)	6822(3)	136(4)

C24	7331(6)	6557(3)	5676(2)	96(3)
C25	3370(6)	4764(4)	6299(3)	132(3)
C26	1190(5)	6496(3)	6466(3)	89(2)
C27	7157(8)	5588(4)	5189(3)	150(5)
C28	8701(4)	7343(3)	7203(3)	102(2)
C29	4544(8)	6834(5)	5024(3)	142(3)
C30	8031(5)	7935(3)	6551(2)	97(2)
C31	2897(8)	6842(5)	5273(3)	152(4)
C32	6757(6)	5669(3)	5620(3)	104(3)
C33	6386(9)	8698(6)	8658(7)	91(4)
C34	222(5)	7073(4)	5978(3)	106(3)
C35	6178(13)	8513(8)	8952(7)	105(4)
C36	7652(6)	8164(3)	7398(3)	100(2)
C37	4536(11)	8251(7)	8889(5)	97(4)
C38	1481(6)	5660(3)	8145(3)	119(3)
H2A	4939.06	8877.59	8044.36	131
H2B	4684.17	9138.73	8543.53	131
H2C	4120.52	8605.9	8347.77	131
H3A	4901.18	4718.42	5771.92	210
H3B	4684.09	4071.93	5896.96	210
H3C	5593.34	4370.92	6101.28	210
H5A	1160.49	5375.82	7235.36	177
H5B	989.15	4835.09	7560.32	177
H5C	1849.97	4846.29	7207.86	177
H7	7998.46	5968.82	4711.8	183
H9A	5777.54	8922.21	8044.38	143
H9B	5102.13	9218.48	8414.16	143
H9C	4697.14	8767.56	8050.7	143
H11	732.01	7873.59	5915.63	135

H13	8151.85	6805.47	5128.65	171
H15A	4341.44	5729.97	5194.99	221
H15B	3564.72	5926.05	4830.25	221
H15C	3272.28	5732	5344.79	221
H17A	4539.67	7982.27	9051.21	160
H17B	4966.43	8551.38	9264.41	160
H17C	5590.06	7992.73	9231.33	160
H19	-13.75	6244.94	6146.19	131
H21A	3038.86	4679.22	7840.69	187
H21B	2157.53	4577.2	8169.59	187
H21C	2943.73	5017.93	8322.02	187
H22	2030.74	7719.03	6386.09	103
H23A	5015.74	4111.63	6942.64	204
H23B	4164.71	3806.42	6687.39	204
H23C	3973.34	4277.93	7076.56	204
H24	7393.25	6903.62	5841.08	116
H25A	3037.07	4923.49	6566.23	198
H25B	3056.72	4417.97	6194.72	198
H25C	3379.02	5039.41	6043.47	198
H26	1297.64	6142	6612	107
H27	7064.31	5245.47	5022.35	180
H28A	8590.2	7188.56	7515.88	153
H28B	9246.04	7590.29	7210.54	153
H28C	8809.48	7031.75	6983.77	153
H29A	4667.14	7209.13	5155.12	213
H29B	4294.59	6874.64	4707.08	213
H29C	5121.89	6616.22	5012.36	213
H30A	8194.4	7629.61	6334.5	145
H30B	8541.38	8208.12	6566.34	145

H30C	7468.39	8125.15	6441.13	145
H31A	2429.94	6660.79	5472.24	228
H31B	2695.54	6824.82	4947	228
H31C	2971.14	7238.06	5367.22	228
H32	6416.9	5363.6	5750.47	125
H33A	6849.71	8424.77	8766.96	137
H33B	6320.79	9001.25	8889.33	137
H33C	6584.77	8858.97	8359.59	137
H34	-309.09	7123.71	5786.28	128
H35A	6217.95	8197.9	9173.17	158
H35B	6026.89	8861.76	9119.91	158
H35C	6775.01	8557.97	8792.13	158
H36A	7113.95	8381.8	7291.88	149
H36B	8193.14	8414.24	7419.42	149
H36C	7521.99	8002.02	7706.25	149
H37A	4001.57	8210.35	8680.2	146
H37B	4419.57	8559.03	9110.36	146
H37C	4631.9	7897.19	9060.52	146
H38A	1877.78	5823.32	8387.7	179
H38B	1035.44	5399.36	8287.98	179
H38C	1146.59	5963.04	7983.58	179

Table S3 Selected bond lengths (Å) for clusters **I**.

Co1-Co2	2.8053(11)
Co1-O1	1.889(2)
Co1-O1[1]	1.889(2)
Co1-O4	1.953(3)
Co1-O4[1]	1.953(3)
Co1-O6	2.260(3)
Co1-O6[1]	2.260(3)
Co2-O1[1]	1.886(2)
Co2-O1	1.886(2)
Co2-O8[1]	1.951(3)
Co2-O8	1.951(3)
Co2-O10	2.264(3)
Co2-O10[1]	2.265(3)
Mn1-O1[1]	2.177(3)
Mn1-O2	2.132(3)
Mn1-O3	2.160(3)
Mn1-O6[1]	2.346(3)
Mn1-O9	2.119(3)
Mn1-N1	2.330(4)
Mn2-O1[1]	2.199(3)
Mn2-O5	2.120(3)
Mn2-O7	2.131(3)
Mn2-O10[1]	2.332(3)
Mn2-O11[1]	2.160(3)
Mn2-N2	2.348(4)