Supporting information file

Chemical CO_2 fixation by cyanido bridged heterometallic Mn(II)-Zn(II) 2D coordination polymer

Parvaneh Dadmehr,[a] Rahman Bikas,[a,*] Tadeusz Lis,[b]

[a] *Department of Chemistry, Faculty of Science, Imam Khomeini International University, 34148-96818, Qazvin, Iran*
[b] *Faculty of Chemistry, University of Wroclaw, Joliot-Curie 14, Wroclaw 50-383, Poland*

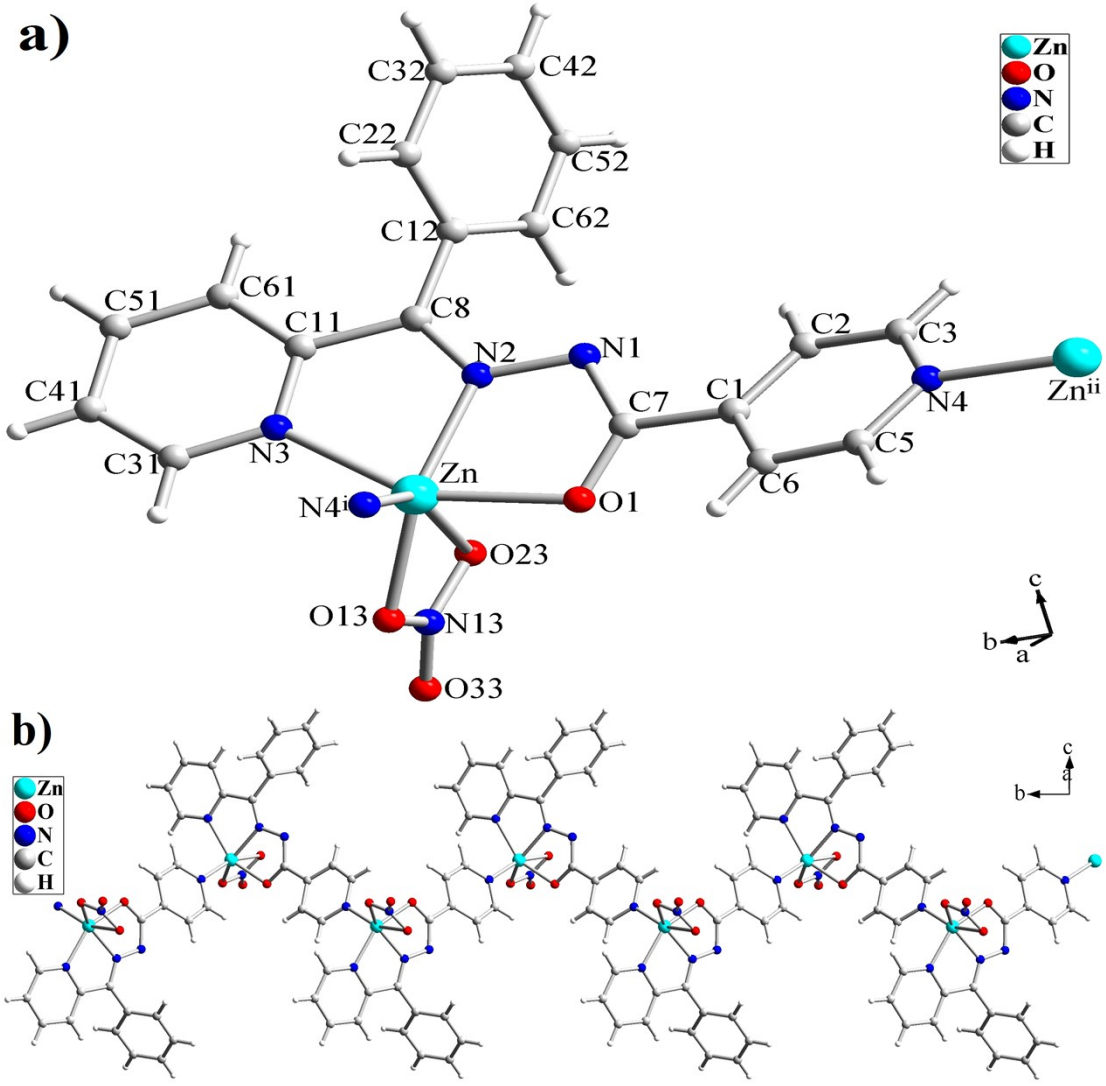


Fig. S1. a) Asymmetric unit of $[ZnL(NO_3)]_n$; b) a view of one-dimensional polymeric chain in the structure of $[ZnL(NO_3)]_n$.

* Corresponding author. *E-mail addresses*: Bikas@sci.ikiu.ac.ir ; bikas_r@yahoo.com (R. Bikas).

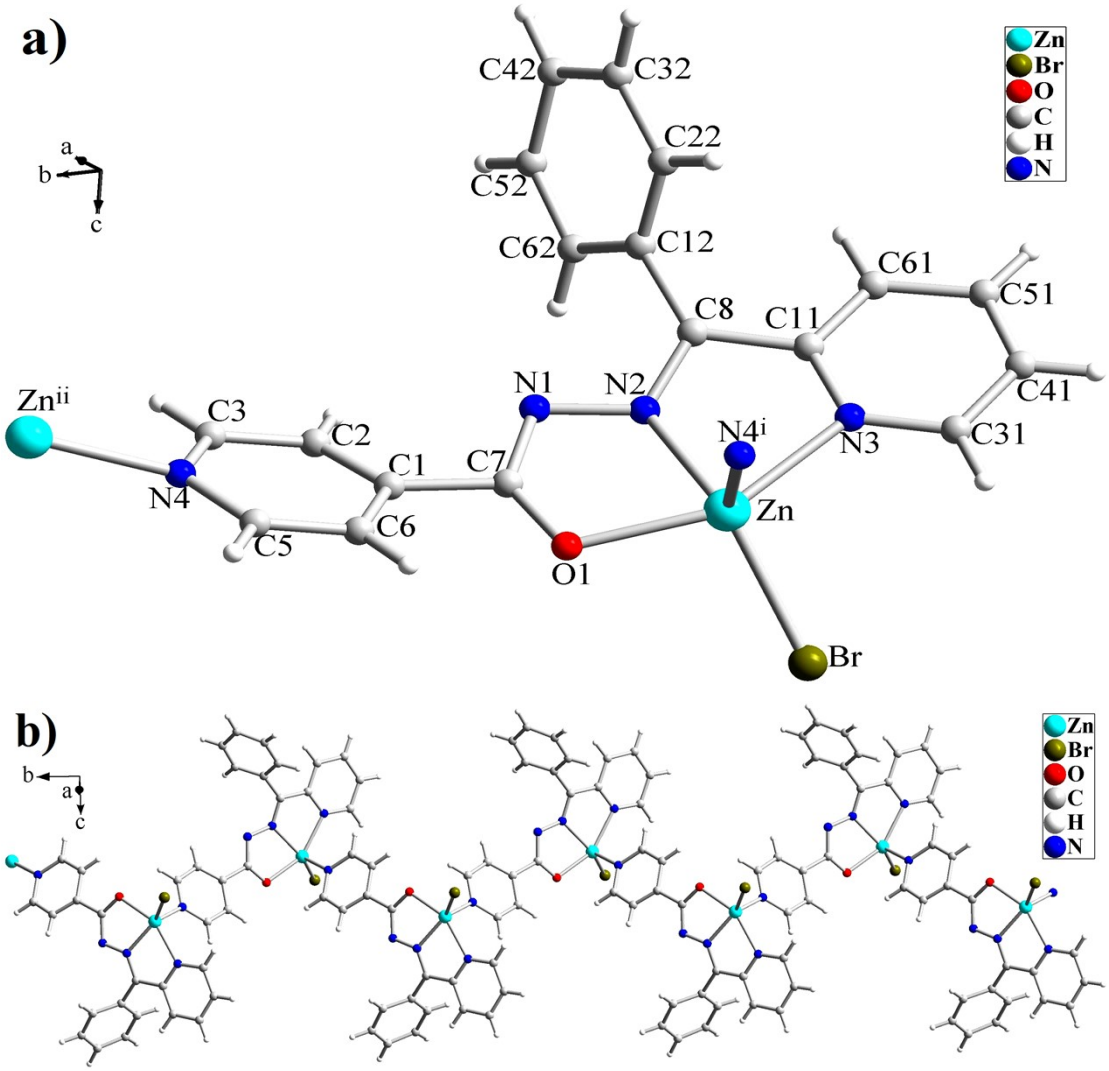


Fig. S2. a) Asymmetric unit of $[ZnLBr]_n$; b) a view of one-dimensional polymeric chain in the structure of $[ZnLBr]_n$.

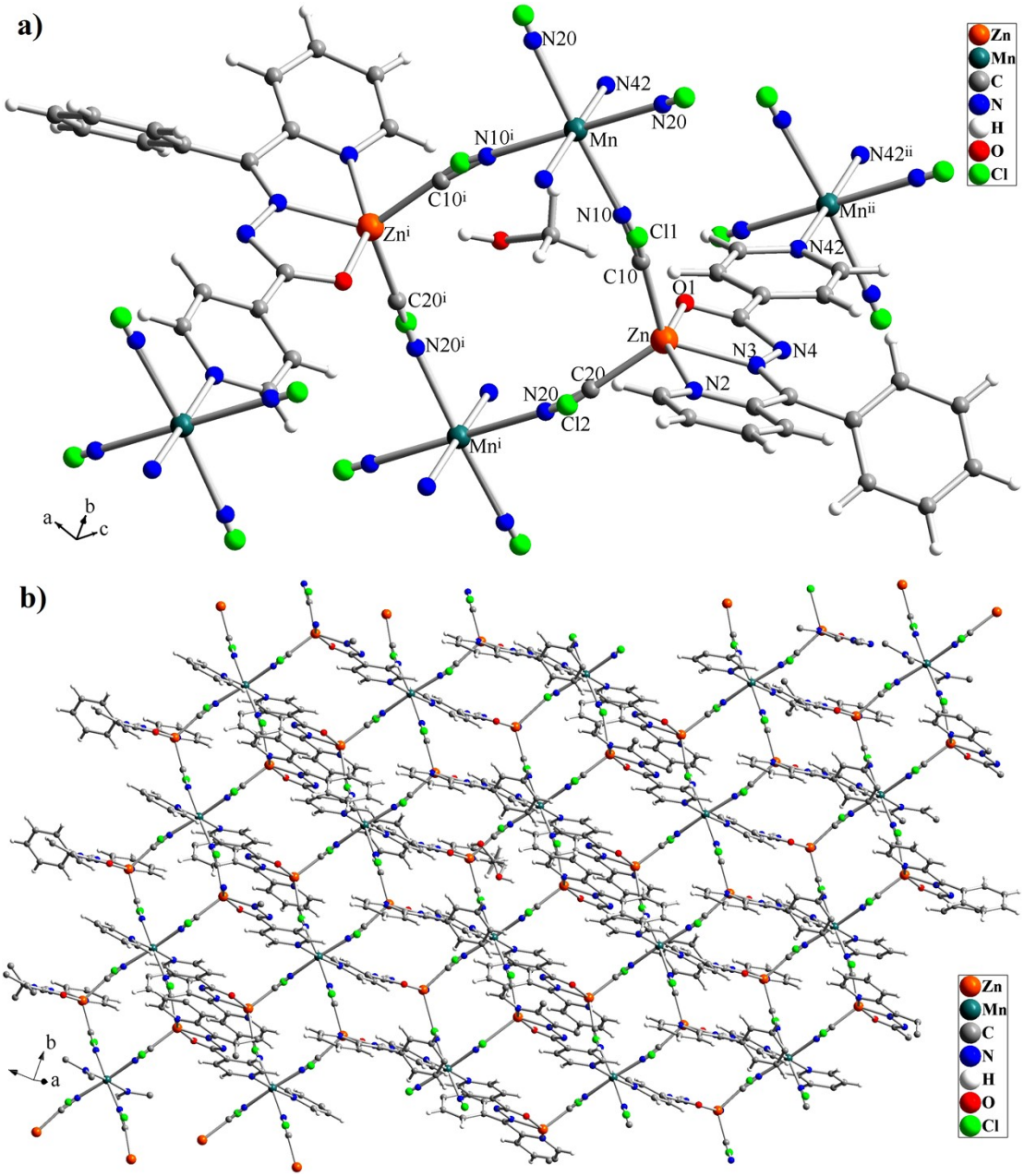


Fig. S3. a) Molecular structure of $\{[Zn(\mu\text{-}L)(\mu\text{-}NC)_{1.75}(\mu\text{-}Cl)_{0.25}Mn_{0.5}]\cdot(CH_3OH)\}_n$ (**1′**); and b) a view of two-dimensional polymeric network in its crystal.

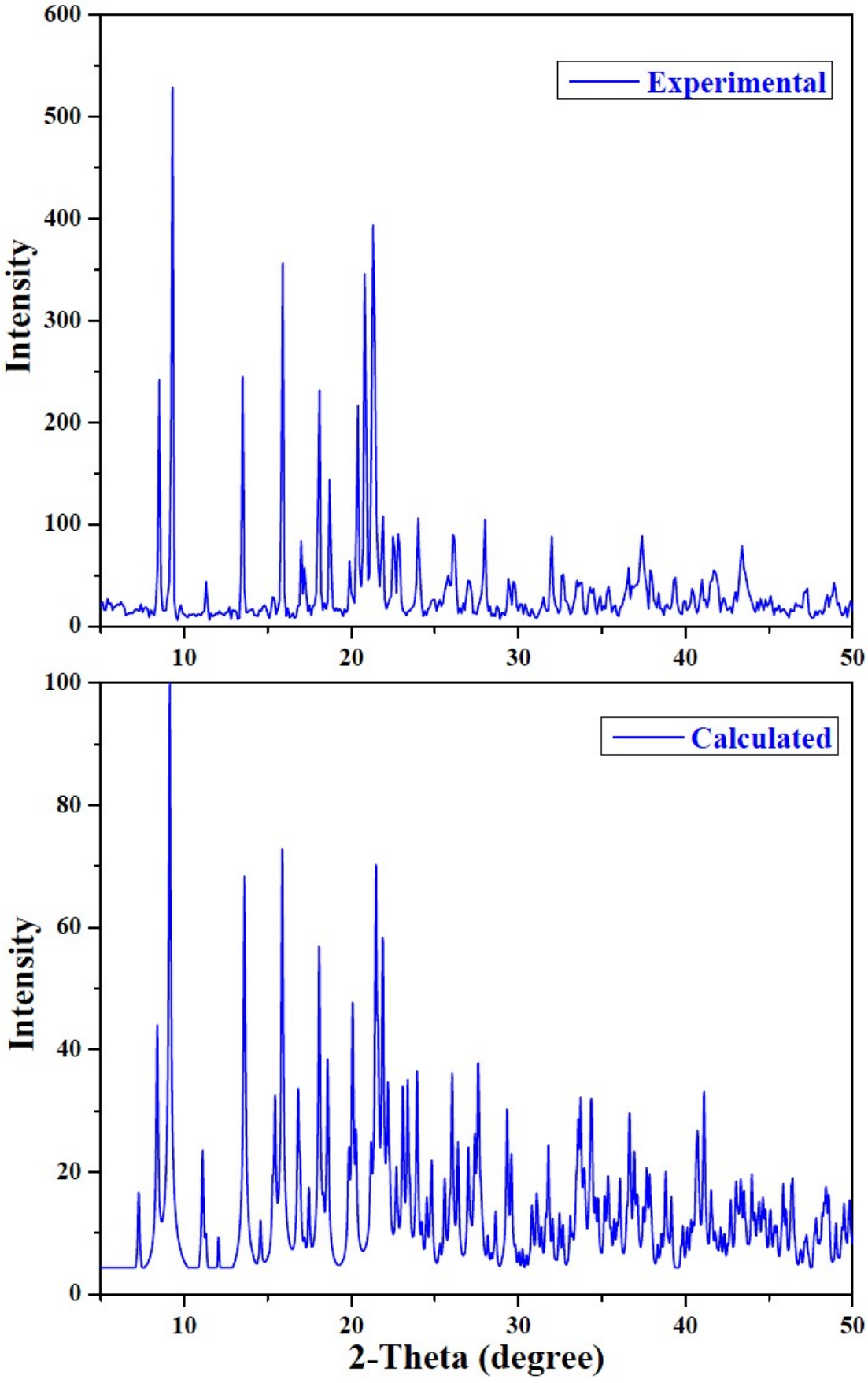


Fig. S4. Comparing experimental and simulated XRD patterns of the compound **1**

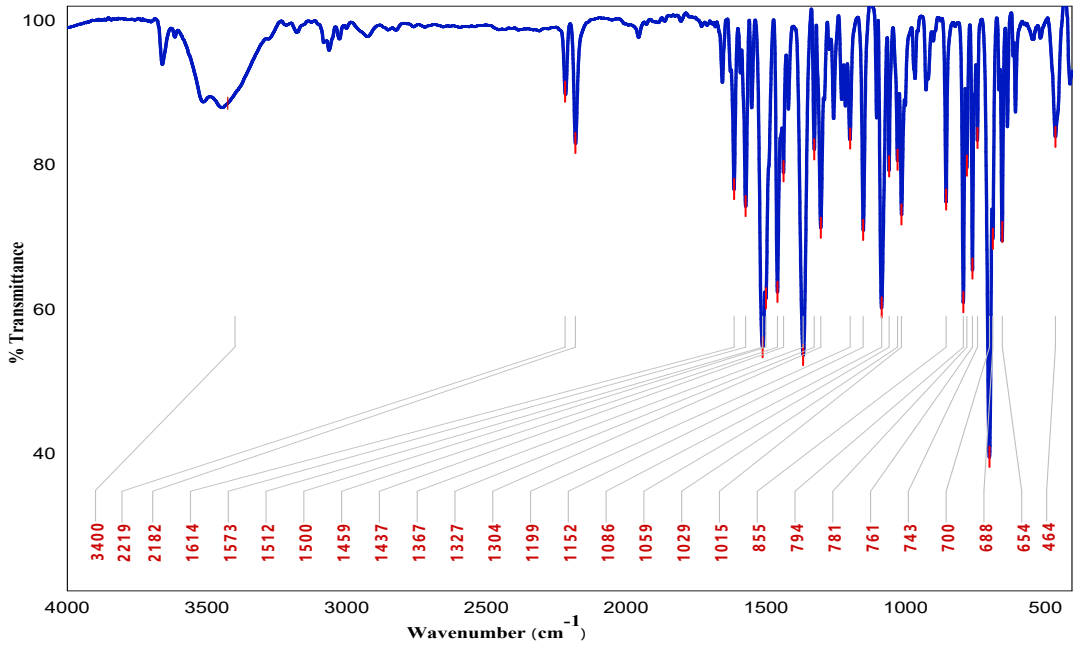


Fig. S5. The FT-IR spectra of compound **1** as KBr disk

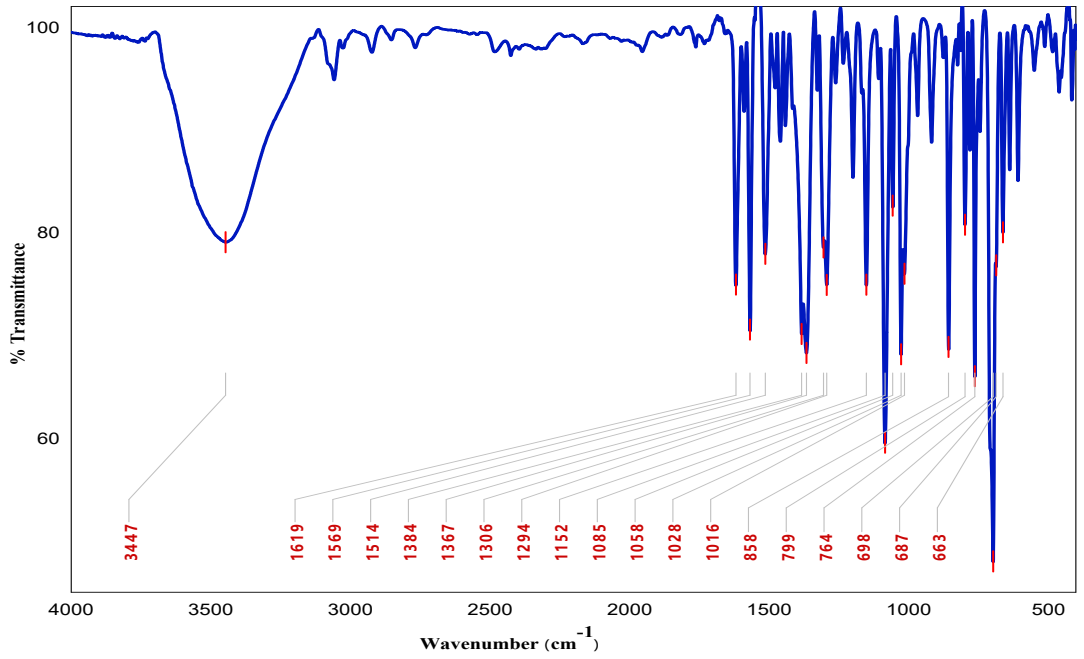


Fig. S6. The FT-IR spectra of compound $[ZnL(NO_3)]_n$ as KBr disk

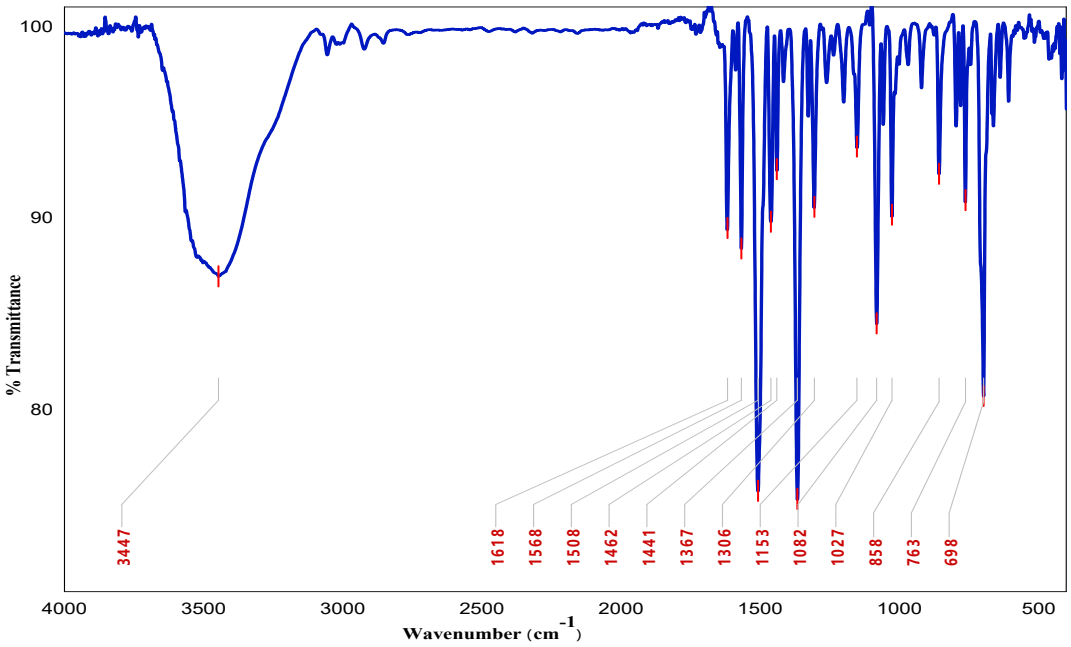


Fig. S7. The FT-IR spectra of compound $[ZnLBr]_n$ as KBr disk

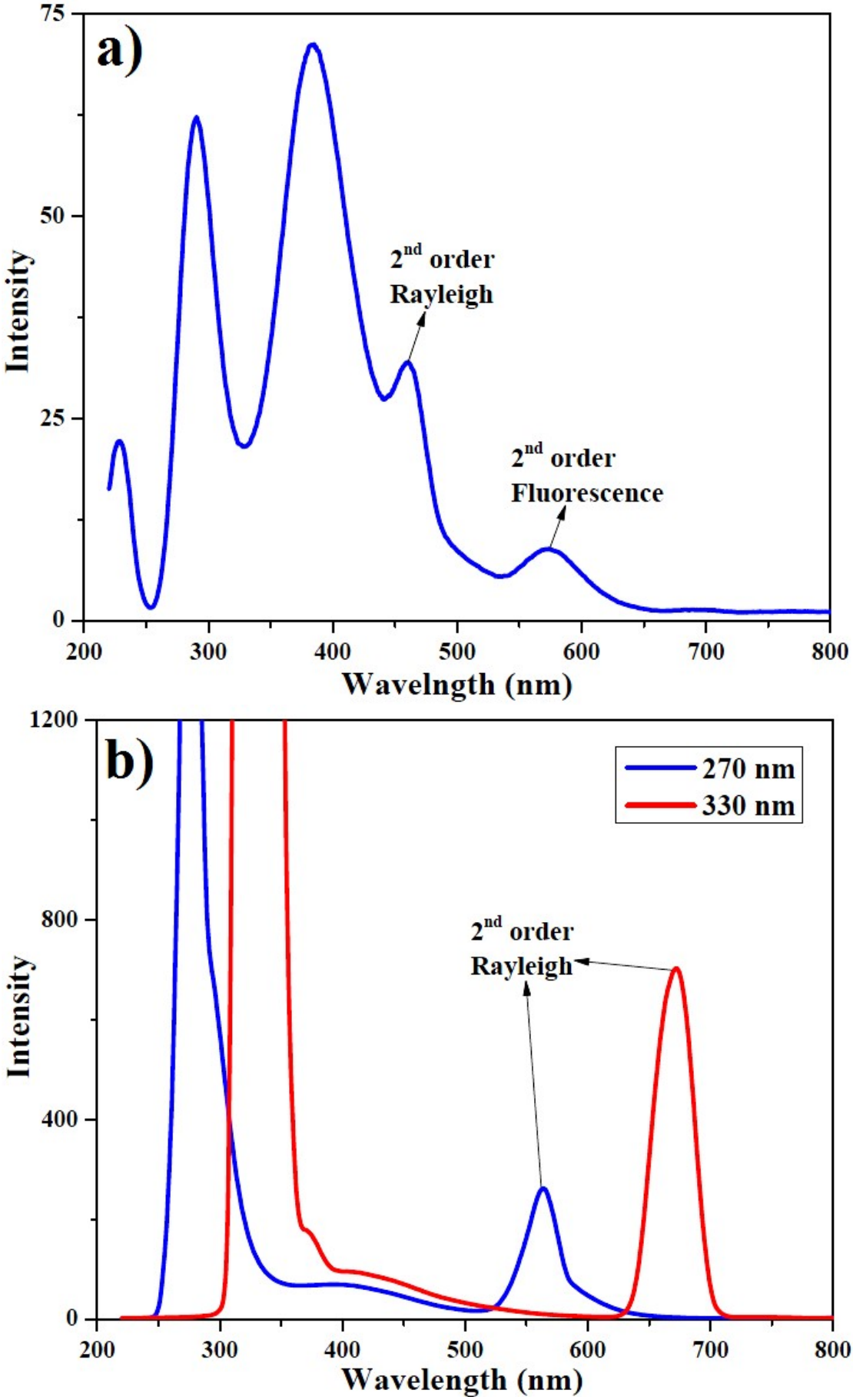


Fig. S8. Emission spectra of HL in methanol by excitation at a) 220; b) 270 and 330 nm

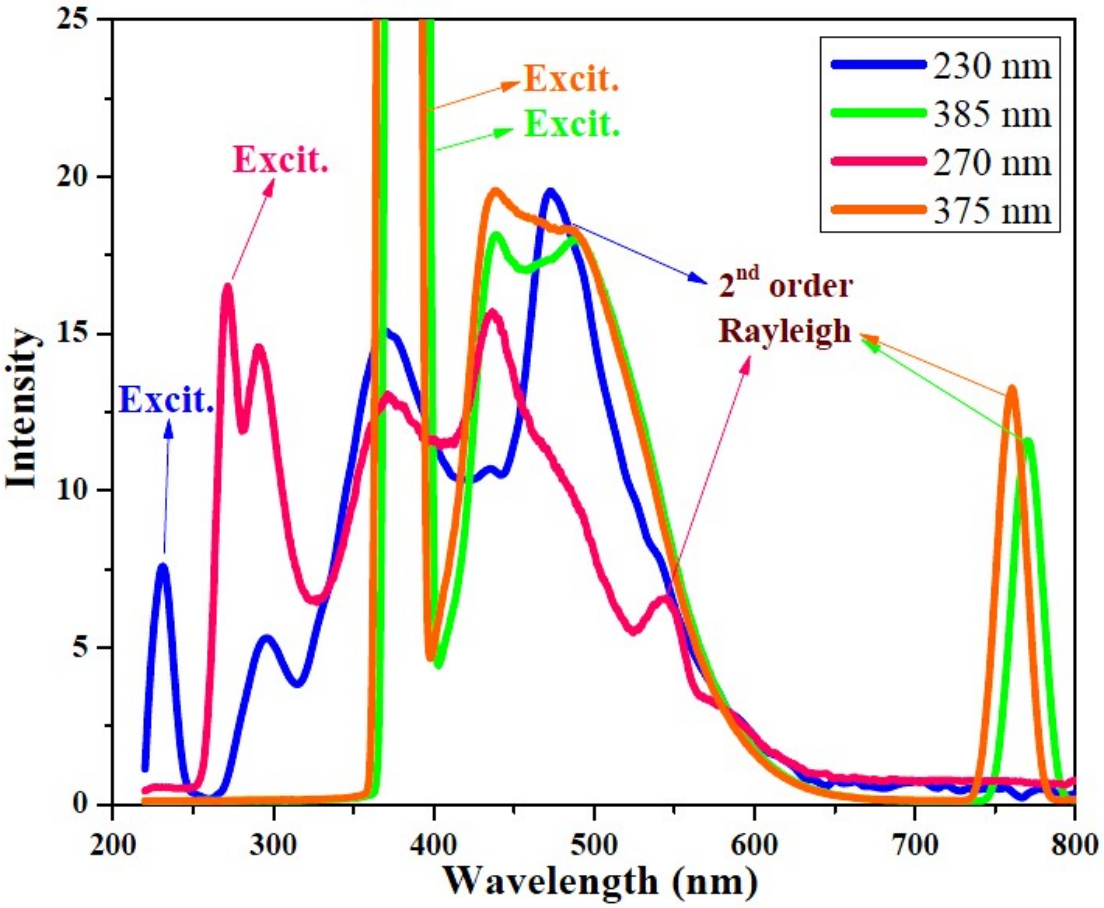


Fig. S9. Full emission spectra of compound **1** containing excitation bands, emission bands and 2nd Rayleigh scattering in the range of 200-800 nm. Excitation wavelengths: 230 nm (blue line), 270 nm (red line), 375 (orange line), and 385 nm (green line).

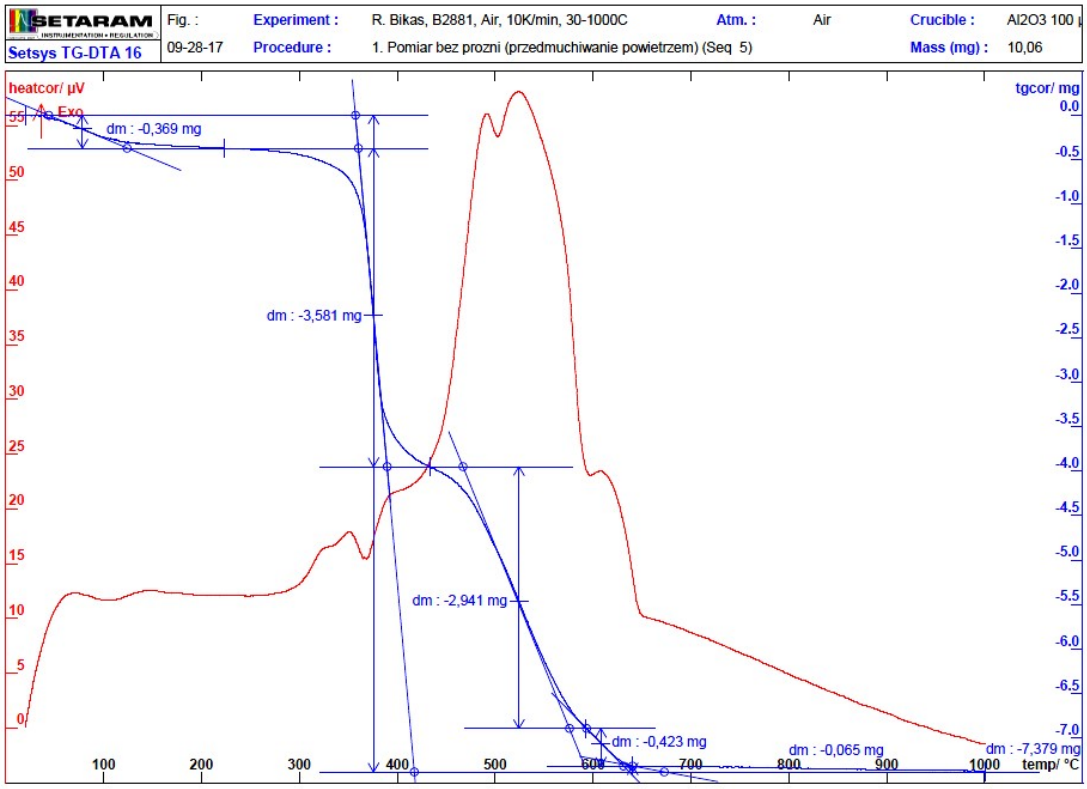


Fig. S10. TGA diagram of compound **1**

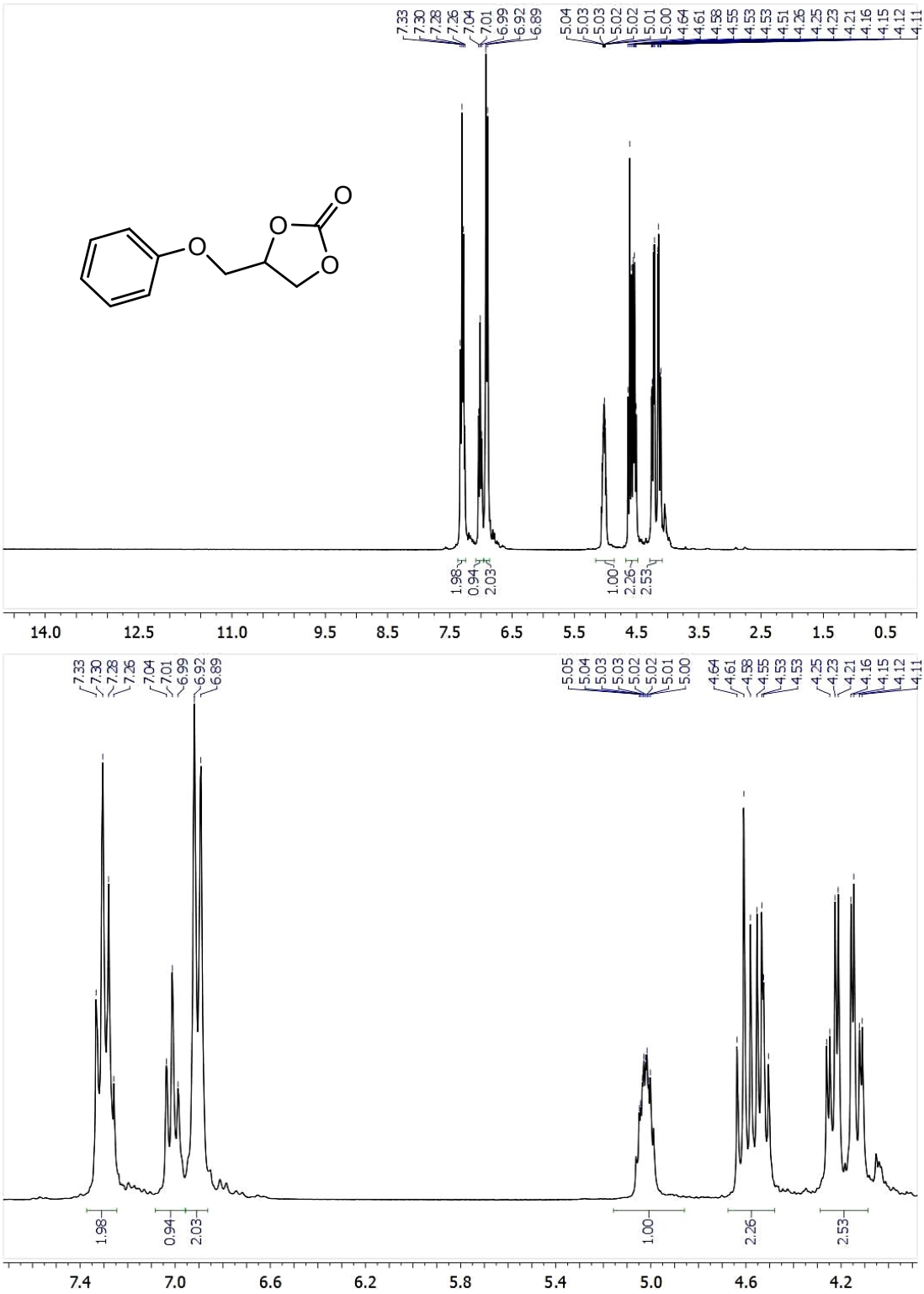


Fig. S11. ^{1}H NMR spectrum of 4-(phenoxymethyl)-1,3-dioxolan-2-one in $CDCl_3$

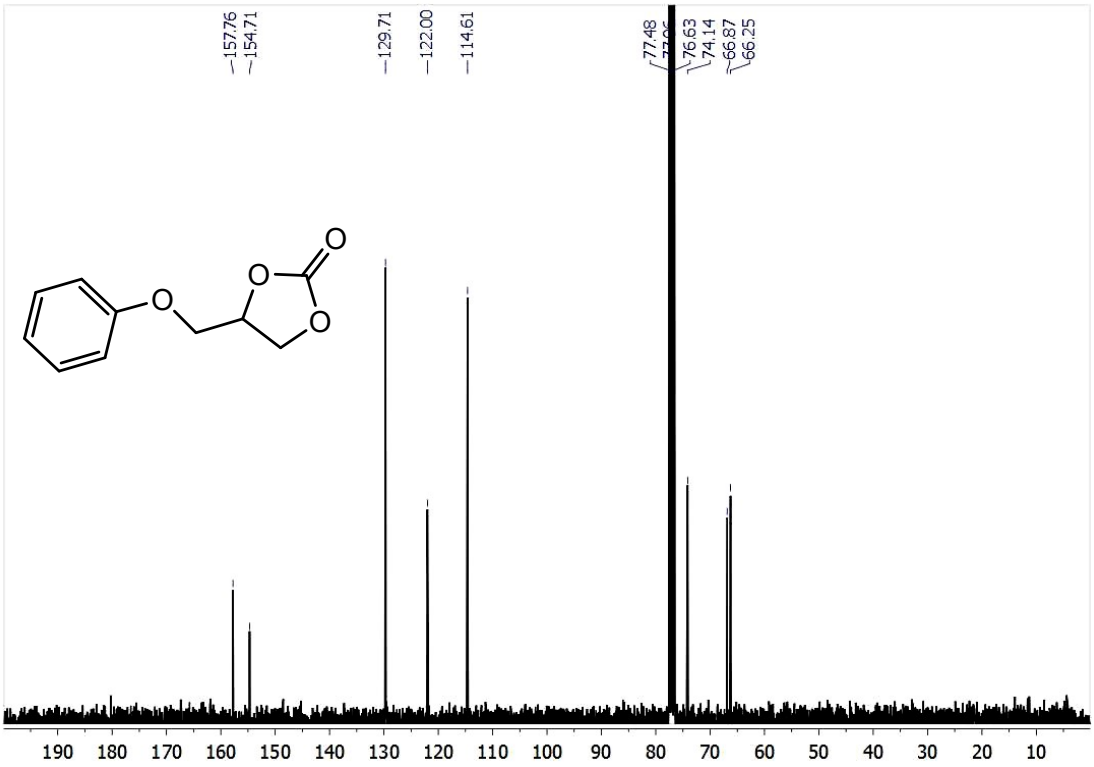


Fig. S12. ^{13}C NMR spectrum of 4-(phenoxymethyl)-1,3-dioxolan-2-one in $CDCl_3$

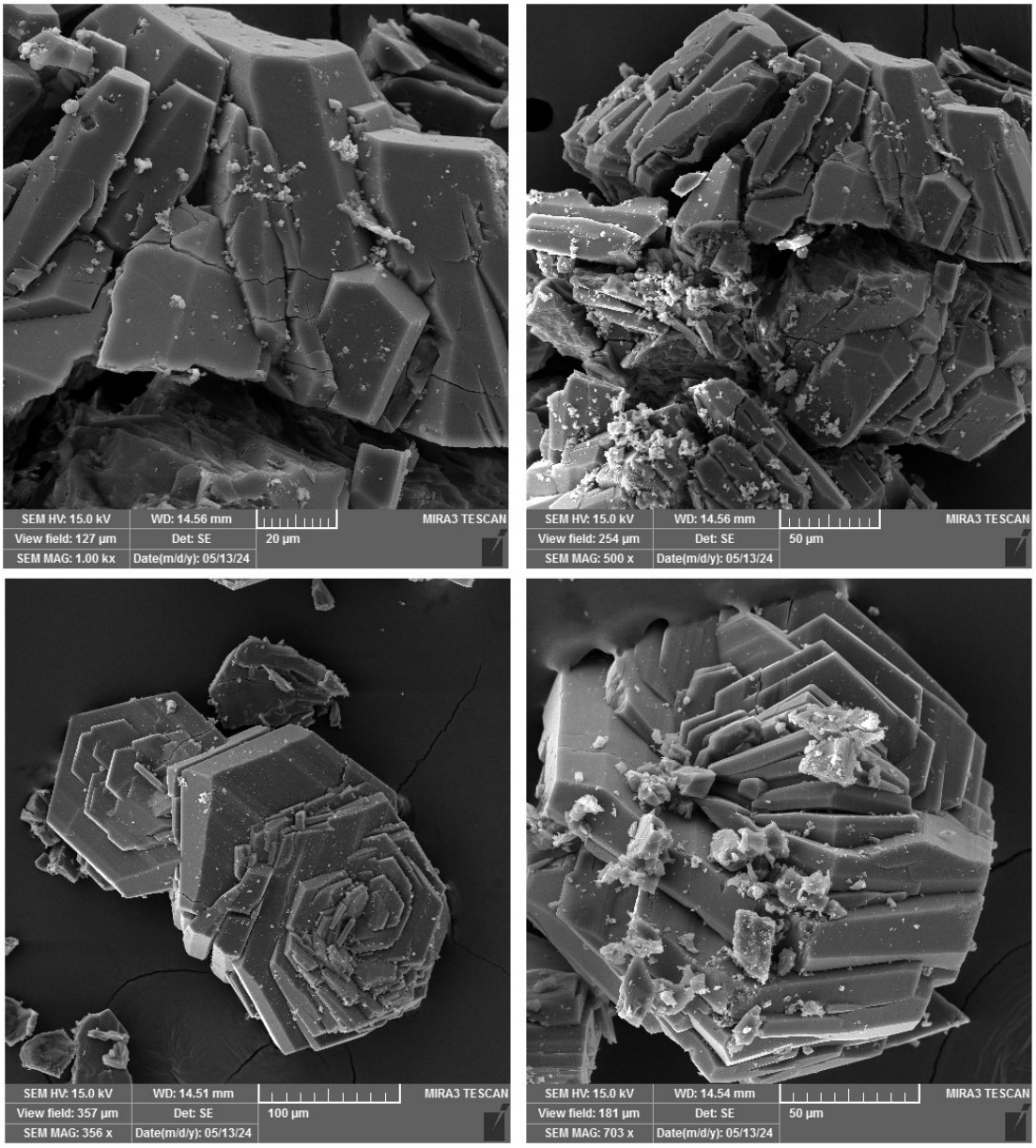


Fig. S13. SEM images of the powdered shape of compound **1** with different magnifications

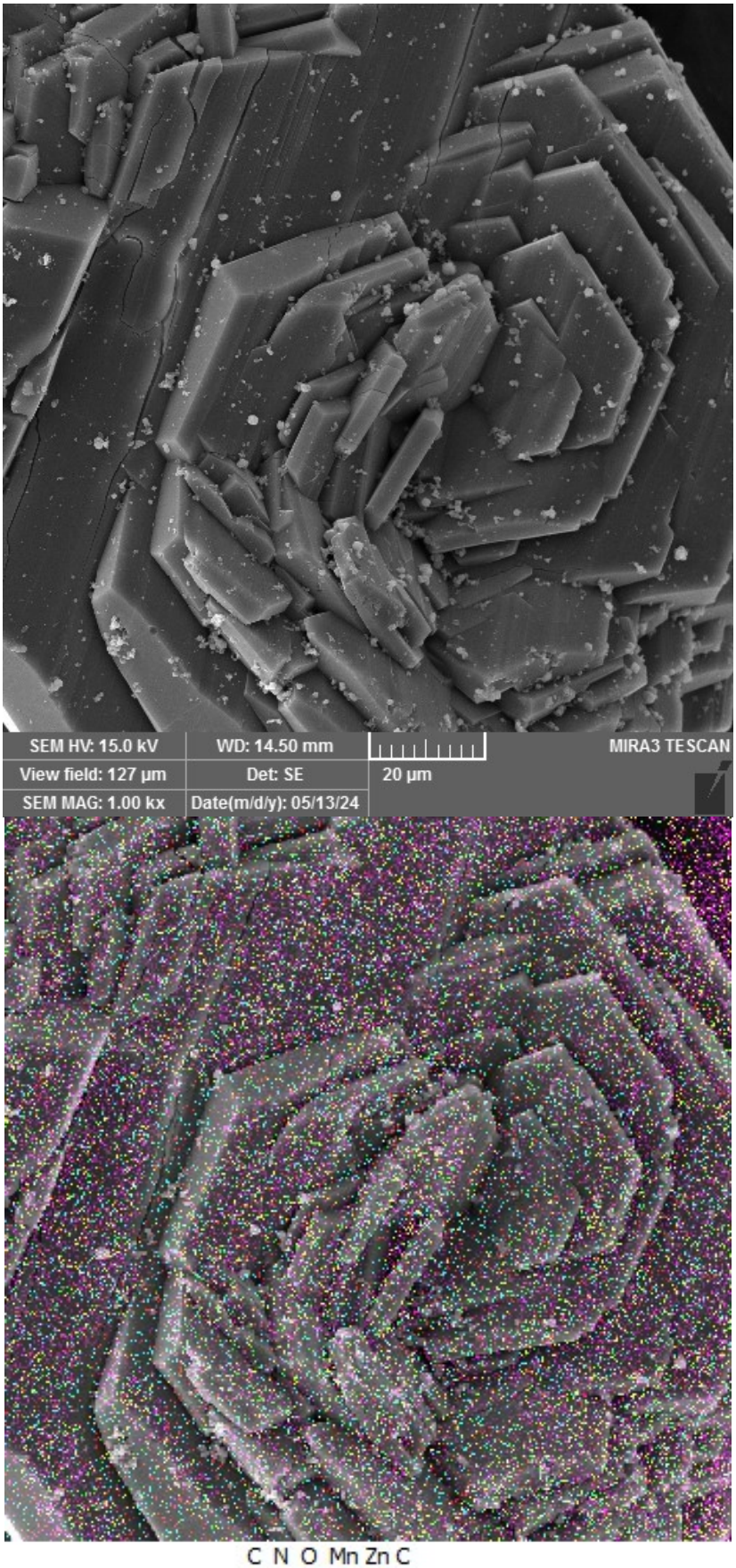


Fig. S14. Expanded SEM image of the region used for EDX analysis which is shown as inset in Fig. 7a

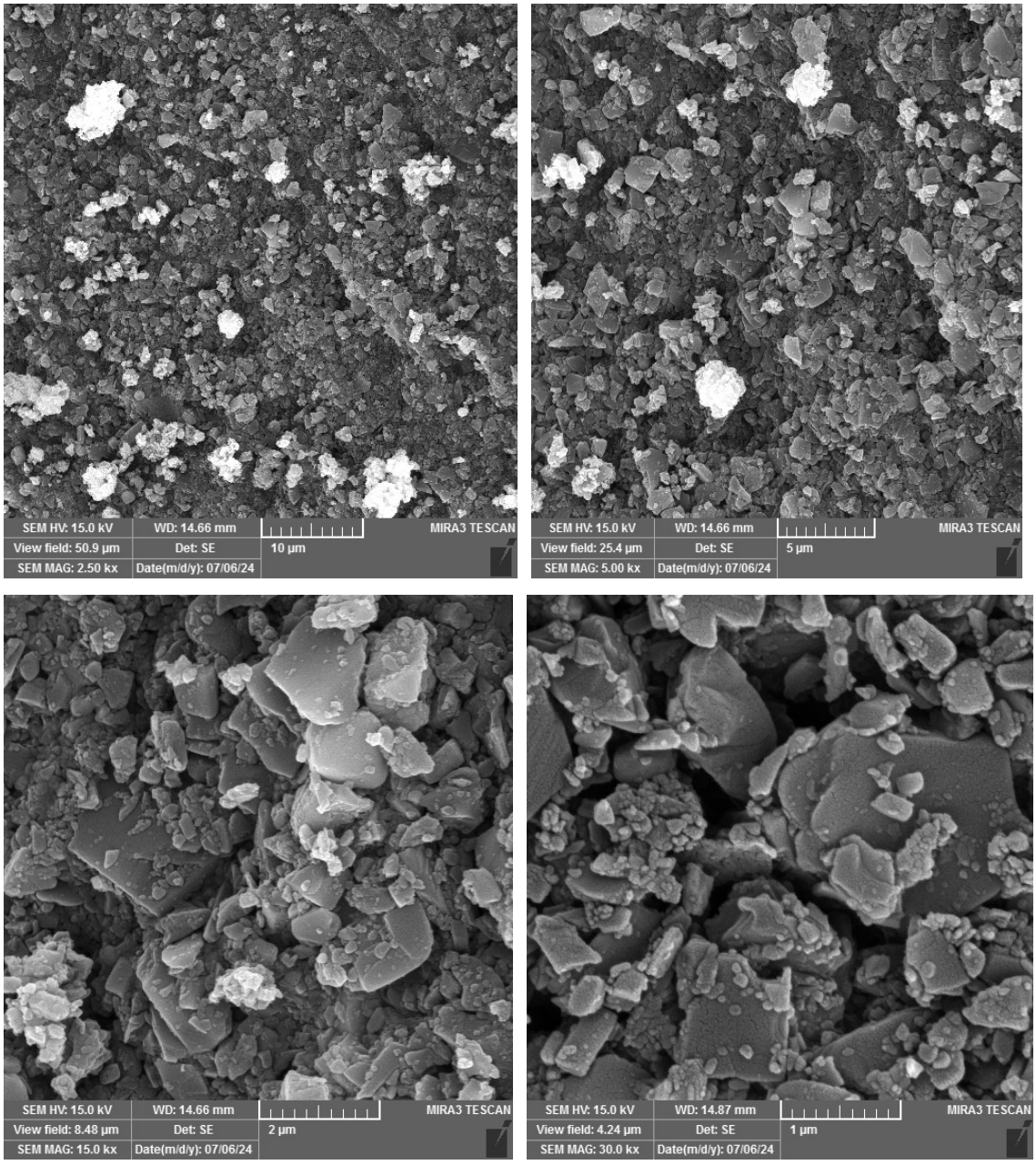


Fig. S15. SEM images with different magnifications of the recovered compound **1** after catalytic reactions

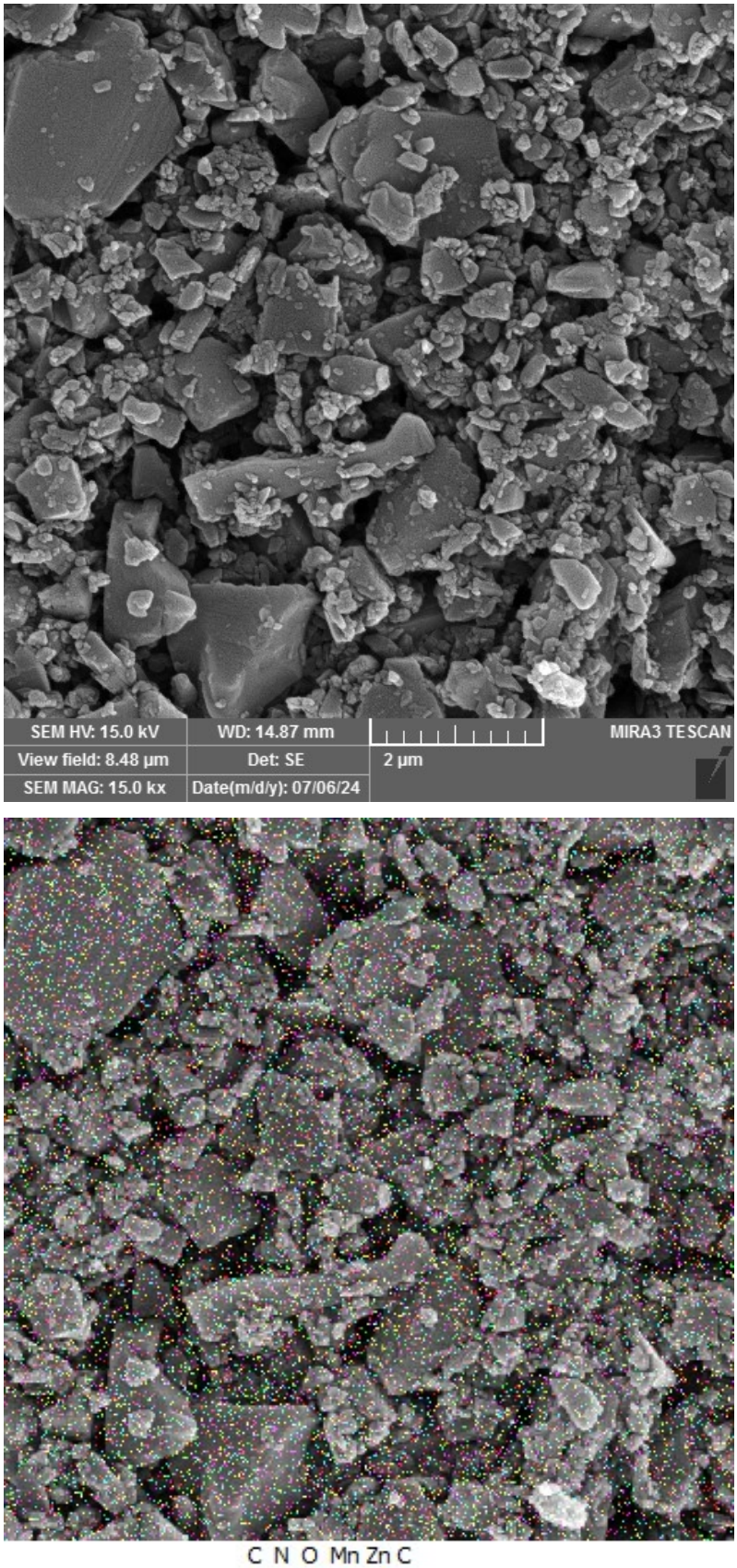


Fig. S16. Expanded SEM image of the region used for EDX analysis in the recovered catalyst which is shown as inset in Fig. 7b

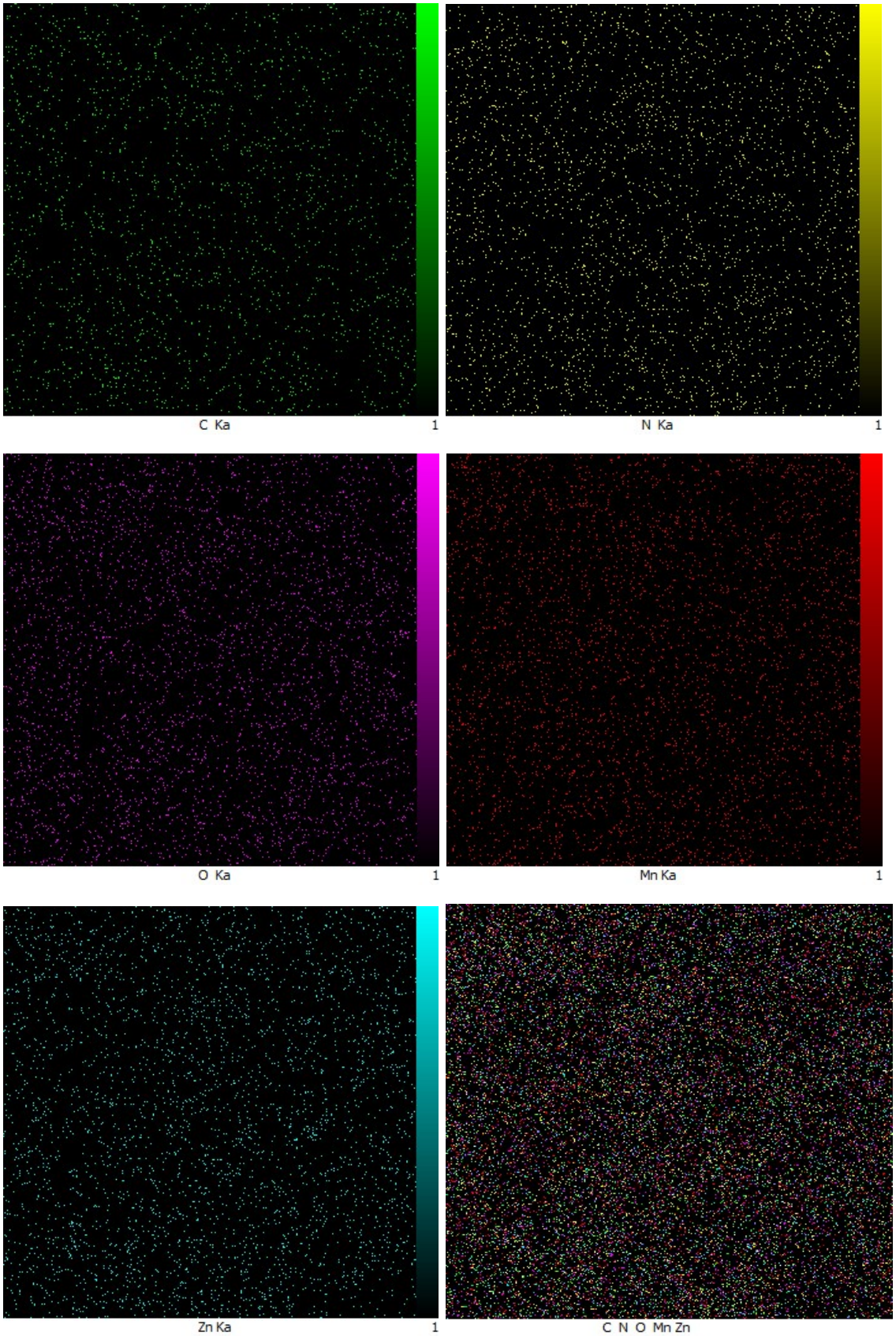


Fig. S17. Energy-dispersive X-ray spectroscopy (EDX) mapping images of the recovered catalyst after catalytic reaction

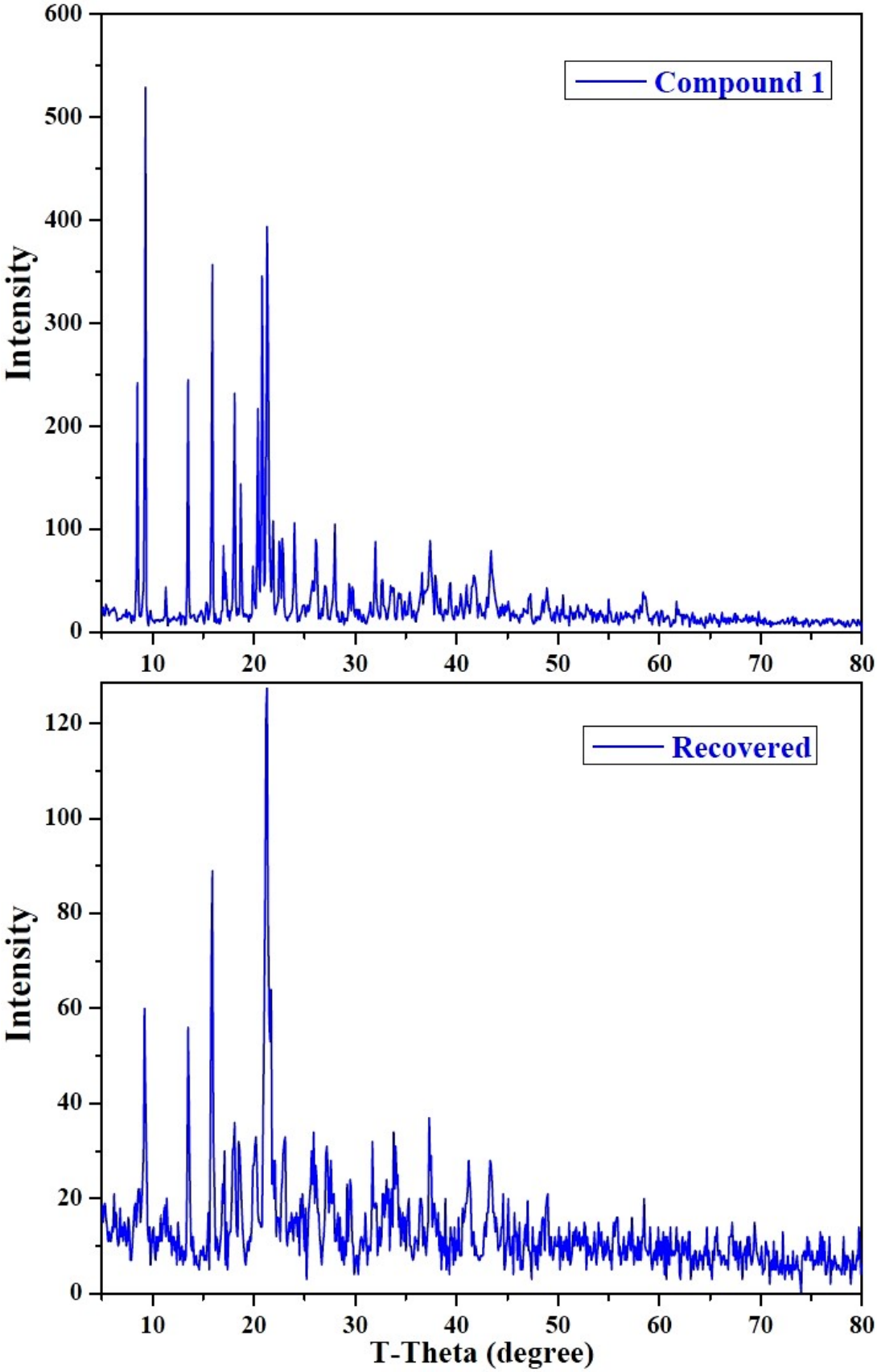
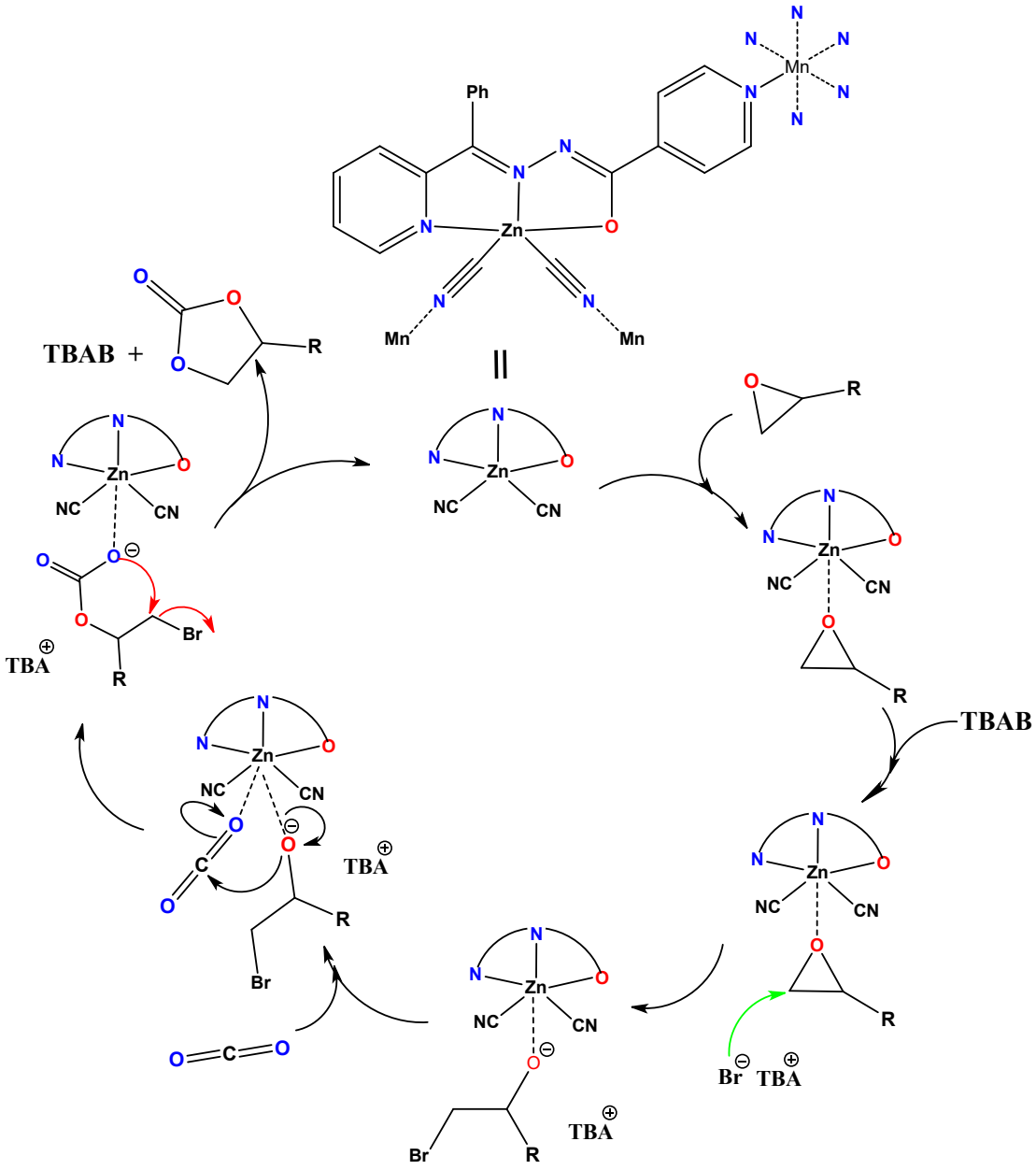


Fig. S18. Comparing XRD patterns of the fresh and recovered catalyst



Scheme S1. Proposed mechanism for chemical CO_2 fixation reaction in the presence of compound **1** (Note: Only the Zn(II) core has been considered as the active site in this mechanism but, the manganese ion can also involve in the reaction)

Table S1. Crystal data and structure refinement for **[ZnL(NO$_3$)]$_n$**, **[ZnLBr]$_n$** and **1′**

Compound	**[ZnL(NO$_3$)]$_n$**	**[ZnLBr]$_n$**	**Compound 1′**
CCDC No.	2340736	2340734	2340733
net formula	$C_{18}H_{13}N_5O_4Zn \cdot CH_4O$	$C_{18}H_{13}BrN_4OZn$	$C_{39.5}H_{26}Cl_{0.5}MnN_{11.5}O_2Zn_2 \cdot 2(CH_4O)$
M_r/g mol^{-1}	460.74	446.60	961.30
crystal size/mm	0.53×0.48×0.40	0.14×0.04×0.02	0.30 × 0.26 × 0.07
T/K	80	80	100
crystal shape, color	Block, orange	Block, orange	Plate, Yellow
crystal system	Orthorhombic	Orthorhombic	Orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$	*Pbcn*
Absorption correction	Analytical	Analytical	Analytical
a/Å	8.5902(18)	8.7892(19)	24.344(6)
b/Å	12.838(3)	13.133(3)	8.2169(18)
c/Å	17.558(4)	16.077(4)	21.057(6)
V/Å^3	1936.3(8)	1855.7(7)	4212.1(18)
Z	4	4	4
D_x/Mg m^{-3}	1.580	1.599	1.516
μ/mm^{-1}	1.31	3.49	1.51
F(000)	944	888	1956
Measured reflections	8625	4979	19539
Independent reflections	5029	3173	5985
Reflections with $I > 2\sigma(I)$	4793	1378	4706
Parameters	277	142	300
R_{int}	0.017	0.116	0.032
Θ range/°	2.0-30.2	2.0-25.5	2.7-25.0
T_{min}, T_{max}	0.601, 0.665	0.745, 0.923	0.712, 0.911
H,k,l	$-11 \le h \le 5$ $-18 \le k \le 14$ $-24 \le l \le 13$	$-6 \le h \le 10$ $-15 \le k \le 15$ $-19 \le l \le 19$	$-32 \le h \le 23$ $-9 \le k \le 11$ $-29 \le l \le 19$
$R[F^2 > 2\sigma(F^2)]$	0.033	0.094	0.046
$R_w(F^2)$	0.082	0.183	0.100
S	1.10	0.96	1.10
Shift/error$_{max}$	0.001	0.001	0.001
Max electron density/e Å^{-3}	0.46	1.45	0.45
Min electron density/e Å^{-3}	-0.43	-0.95	-0.39

Table S2. Selected bond lengths (Å) and angles (°) in **[ZnL(NO$_3$)]$_n$**

Bond	**Length/Å**	**Bond**	**Length/Å**
Zn–O13	2.026(3)	C3–N4	1.338(4)
Zn–N2	2.057(2)	N4–C5	1.341(4)
Zn–N4^{i}	2.068(2)	N4–Zn^{ii}	2.068(2)
Zn–O1	2.084(2)	C7–O1	1.265(3)
Zn–N3	2.154(3)	C7–N1	1.333(4)
O13–N13	1.247(5)	N1–N2	1.380(3)
O23–N13	1.251(4)	N2–C8	1.282(4)
N13–O33	1.208(5)		
Angle	**Deg/°**	**Angle**	**Deg/°**
O13–Zn–N2	141.17(12)	N4^{i}–Zn–O1	91.86(9)
O13–Zn–N4^{i}	101.21(11)	O13–Zn–N3	100.69(11)
N2–Zn–N4^{i}	117.55(10)	N2–Zn–N3	76.08(10)
O13–Zn–O1	102.05(10)	N4^{i}–Zn–N3	99.78(10)
N2–Zn–O1	75.82(9)	O1–Zn–N3	151.86(9)

Symmetry codes: (i) −*x*, *y*+1/2, −*z*+3/2;(ii) −*x*, *y*−1/2, −*z*+3/2.

Table S3. Selected bond lengths (Å) and angles (°) in **[ZnLBr]$_n$**

Bond	**Length/Å**	**Bond**	**Length/Å**
Zn–N2	2.066(17)	C3–N4	1.32(2)
Zn–N4^{i}	2.099(15)	N4–C5	1.38(2)
Zn–O1	2.108(12)	N4–Zn^{ii}	2.099(15)
Zn–N3	2.198(17)	C7–N1	1.33(3)
Zn–Br	2.375(4)	N1–N2	1.39(2)
O1–C7	1.27(2)	N2–C8	1.32(3)
N3–C31	1.35(2)		
Angle	**Deg/°**	**Angle**	**Deg/°**
N2–Zn–N4^{i}	107.5(7)	O1–Zn–N3	151.3(6)
N2–Zn–O1	76.1(6)	N2–Zn–Br	139.0(5)
N4^{i}–Zn–O1	90.9(6)	N4^{i}–Zn–Br	113.6(5)
N2–Zn–N3	75.3(7)	O1–Zn–Br	102.4(4)
N4^{i}–Zn–N3	96.2(6)	N3–Zn–Br	100.1(5)

Symmetry codes: (i) −*x*+2, *y*−1/2, −*z*+1/2;(ii) −*x*+2, *y*+1/2, −*z*+1/2.

Table S4. Hydrogen-bond geometry (Å, °) in the compound **1**

D*–H···*A	***D*–H**	**H···*A***	***D*···*A***	***D*–H···*A***
O1*M*–H1*M*···O1	0.84	2.00	2.805(5)	161