Supporting Information for

An unprecedented cobalt(II)-containing Wells-Dawson-type tungstovanadate-based metal-organic framework as efficient catalyst for ring-opening polymerization of ε-caprolactone

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Preparation and characterization of Co-HZSM-5 and Co-EST-10 catalyst

Mesoporous zeolite HZSM-5 and mesoporous zeolite ETS-10 were prepared according to our reported procedure.[S1] The Co-HZSM-5 catalyst was prepared by the incipient wetness impregnation method by the use of $Co(NO_3)_2$ solution. The Co loading was 3.0 wt%. After impregnation, the sample was dried in air at ambient temperature for 24 h, and subsequently dried in an oven at 100 °C for 12 h, and finally calcined at 450 °C for 4 h. The Co-ETS-10 was prepared with the similar method.

S1 K. Yang, D. Li, L. Zhang, Q. Chen and T. Tang, RSC Adv., 2018, 8, 13671–13674.

Table S1. Selected bond lengths (Å) and angles (°) for CZU-5.

Bond lengths					
Co1–O2	2.092(8)	Co1–O2#1	2.092(8)	Co1–N1	2.138(12)
Co1–N1#1	2.138(12)	Co1–N4	2.128(11)	Co1–N4#1	2.128(11)
Co2–O1	2.127(11)	Co2–O18#2	2.059(9)	Co2–O27	2.059(9)
Co2–N7	2.101(12)	Co2–N10	2.110(14)	Co2–N15#4	2.142(12)
V1–O7	1.682(9)	V1–O14	1.733(10)	V1–O20	1.679(9)
V1–O28	1.698(9)	W1–O16	1.930(9)	W1–O17	1.901(9)
W1–O18	1.747(9)	W1–O19	1.919(9)	W1–O20	2.255(9)
W1–O21#3	1.863(10)	W2–O6	1.899(9)	W2–O19	1.906(9)
W2–O20	2.311(9)	W2–O21	1.928(10)	W2–O22	1.709(10)
W2–O23	1.908(10)	W3–O5	1.935(9)	W3–O7	2.332(9)
W3–O8	1.698(9)	W3–O9	1.914(9)	W3–O10	1.892(9)
W3–O24	1.927(9)	W4–O10	1.922(9)	W4–O24#3	1.878(9)
W4–O27	1.734(8)	W4–O28	2.222(10)	W4–O29	1.924(10)
W4–O30	1.885(9)	W5–O2	1.726(8)	W5–O3	1.931(9)
W5–O4	1.859(9)	W5–O5	1.891(9)	W5–O6	1.922(8)
W5–O7	2.263(9)	W6–O4#3	1.926(9)	W6–O17	1.898(9)
W6–O28	2.330(9)	W6–O30	1.938(8)	W6–O31	1.711(9)
W6–O32	1.891(10)	W7–O9	1.881(9)	W7–O11	1.694(10)
W7–O12	1.934(10)	W7–O13	1.900(10)	W7–O14	2.337(10)

W7–O29	1.904(9)	W8–O12	1.935(10)	W8–O14	2.315(10)
W8–O15	1.707(11)	W8–O16	1.885(9)	W8–O26	1.906(10)
W8–O32#3	1.935(10)	W9–O3	1.892(9)	W9–O13	1.914(9)
W9–O14	2.311(10)	W9–O23	1.910(9)	W9–O25	1.713(10)
W9–O26	1.914(10)				
Bond angles					
O2–Co1–O2#1	179.9(5)	O2–Co1–N1	94.0(4)	O2–Co1–N1#1	86.0(4)
O2–Co1–N4	86.3(4)	O2–Co1–N4#1	93.6(4)	O2#1–Co1–N1	86.0(4)
O2#1–Co1–N1#1	94.0(4)	O2#1–Co1–N4	93.6(4)	N1–Co1–N4	92.6(4)
O2#1–Co1–N4#1	86.3(4)	N1–Co1–N1#1	88.5(6)	N1#1–Co1–N4#1	92.6(4)
N1–Co1–N4#1	172.3(4)	N1#1–Co1–N4	172.3(4)	N4–Co1–N4#1	87.4(6)
O1–Co2–O18#2	89.0(4)	O1–Co2–O27	93.4(4)	O1–Co2–N7	85.6(4)
O18#2–Co2–N10	90.0(4)	O18#2–Co2–O27	177.6(4)	O18#2–Co2–N7	91.0(4)
O27–Co2–N7	89.1(4)	O18#2–Co2–N15#4	86.5(4)	O1–Co2–N10	175.8(5)
O27–Co2–N10	87.6(4)	O27–Co2–N15#4	93.9(4)	N7–Co2–N10	98.4(5)
O1–Co2–N15#4	82.8(4)	N7–Co2–N15#4	168.2(5)	N10–Co2–N15#4	93.0(5)
O7–V1–O14	106.2(5)	O7–V1–O20	112.8(5)	O7–V1–O28	112.4(4)
O14–V1–O20	105.5(5)	O14–V1–O28	106.3(5)	O20–V1–O28	113.0(5)
O16–W1–O17	84.9(4)	O16–W1–O18	96.3(4)	O16–W1–O19	88.6(4)
O16–W1–O20	82.3(4)	O16–W1–O21#3	164.3(4)	O17–W1–O18	102.9(4)
O17–W1–O19	157.5(4)	O17–W1–O20	85.0(4)	O17–W1–O21#3	88.8(4)
O18–W1–O19	99.2(4)	O18–W1–O20	171.8(4)	O18–W1–O21#3	99.0(4)
O19–W1–O20	72.8(3)	O19–W1–O21#3	91.8(4)	O20–W1–O21#3	82.9(4)
O6–W2–O19	155.8(4)	O6–W2–O20	84.2(4)	O6–W2–O21	89.4(4)
O6–W2–O23	86.3(4)	O19–W2–O20	71.7(3)	O19–W2–O21	88.2(4)
O19–W2–O23	89.9(4)	O20–W2–O21	80.5(4)	O20–W2–O23	85.0(4)
O21–W2–O23	165.3(4)	O5–W3–O7	71.0(3)	O5–W3–O8	102.9(4)
O5–W3–O9	88.7(4)	O5–W3–O10	154.7(4)	O5–W3–O24	88.8(4)
O7–W3–O8	173.6(4)	O7–W3–O9	83.1(4)	O7–W3–O10	83.9(3)
O7–W3–O24	81.5(4)	O8–W3–O9	98.7(4)	O8–W3–O10	102.3(4)
O8–W3–O24	96.8(4)	O9–W3–O10	85.8(4)	O9–W3–O24	164.5(4)
O10–W3–O24	90.0(4)	O10–W4–O24#3	88.4(4)	O10–W4–O27	104.9(4)
O10–W4–O28	85.4(3)	O10–W4–O29	83.3(4)	O10–W4–O30	158.2(4)
O24#3–W4–O27	99.1(4)	O24#3–W4–O28	85.3(3)	O24#3–W4–O29	166.0(4)
O24#3–W4–O30	93.2(4)	O27–W4–O28	168.9(4)	O27–W4–O29	93.9(4)

O27–W4–O30	96.3(4)	O28–W4–O29	82.9(4)	O28–W4–O30	73.2(3)
O29–W4–O30	90.4(4)	O2–W5–O3	95.6(4)	O2–W5–O4	98.2(4)
O2–W5–O5	100.8(4)	O2–W5–O6	101.6(4)	O2–W5–O7	173.7(4)
O3–W5–O4	164.9(4)	O3–W5–O5	89.2(4)	O3–W5–O6	83.9(4)
O3–W5–O7	82.2(3)	O4–W5–O5	94.0(4)	O4–W5–O6	87.5(4)
O4–W5–O7	84.6(4)	O5–W5–O6	157.1(4)	O5–W5–O7	73.3(4)
O6–W5–O7	84.1(4)	O4#3–W6–O17	89.7(4)	O4#3–W6–O28	81.2(3)
O4#3–W6–O30	88.4(4)	O4#3–W6–O31	97.9(4)	O4#3–W6–O32	163.1(4)
O17–W6–O28	84.7(4)	O17–W6–O30	154.4(4)	O17–W6–O31	103.2(4)
O17–W6–O32	86.0(4)	O28–W6–O30	69.8(3)	O28–W6–O31	172.1(4)
O28–W6–O32	82.1(4)	O30–W6–O31	102.4(4)	O30–W6–O32	88.4(4)
O31–W6–O32	99.0(5)	O9–W7–O11	103.8(5)	O9–W7–O12	157.1(4)
O9–W7–O13	88.5(4)	O9–W7–O14	84.5(4)	O9–W7–O29	86.2(4)
O11–W7–O12	99.2(5)	O11–W7–O13	102.0(5)	O11–W7–O14	170.2(4)
O11–W7–O29	103.2(5)	O12–W7–O13	87.5(4)	O12–W7–O14	72.8(4)
O12–W7–O29	87.9(4)	O13–W7–O14	72.6(4)	O13–W7–O29	154.8(4)
O14–W7–O29	82.4(4)	O12–W8–O14	73.3(4)	O12–W8–O15	100.4(5)
O12–W8–O16	155.8(4)	O12–W8–O26	87.9(4)	O12–W8–O32	87.9(4)
O14–W8–O15	171.2(4)	O14–W8–O16	82.7(4)	O14–W8–O26	72.9(4)
O14–W8–O32	83.6(4)	O15–W8–O16	103.9(5)	O15–W8–O26	101.2(5)
O15–W8–O32	102.5(5)	O16–W8–O26	87.8(4)	O16–W8–O32	86.6(4)
O26–W8–O32	156.3(4)	O3–W9–O13	87.8(4)	O3–W9–O14	82.3(4)
O3–W9–O23	86.2(4)	O3–W9–O25	102.1(4)	O3–W9–O26	154.8(4)
O13–W9–O14	73.0(4)	O13–W9–O23	157.8(4)	O13–W9–O25	99.9(5)
O13–W9–O26	88.5(4)	O14–W9–O23	85.1(4)	O14–W9–O25	171.6(4)
O14–W9–O26	72.8(4)	O23–W9–O25	102.3(4)	O23–W9–O26	88.0(5)
O25–W9–O26	103.1(5)				

Symmetry codes: #1: $-x + 1/2, -y + 1, z$; #2: $x + 1/2, y, -z + 1$; #3: $x, -y + 1/2, -z + 3/2$; #4: $-x + 1, -y, -z + 1$.

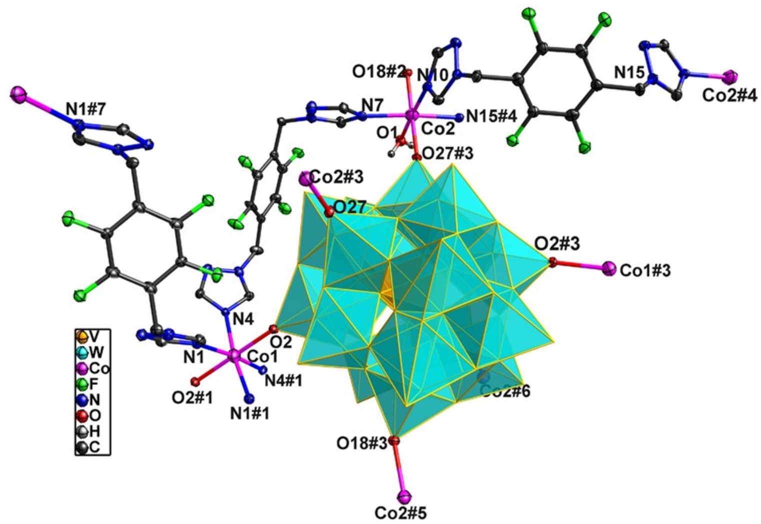

Fig. S1 The coordination environment of Co(II) ion with polyhedral representation of $[V_2W_{18}O_{62}]^{6-}$ anion in CZU-5. Symmetric codes: #1: $-x + 1/2, -y + 1, z$; #2: $x + 1/2, y, -z + 1$; #3: $x, -y + 1/2, -z + 3/2$; #4: $-x + 1, -y, -z + 1$; #5: $x - 1/2, -y + 1/2, z + 1/2$; #6: $x - 1/2, y, -z + 1$; #7: $-x + 1, -y + 1, -z + 2$.

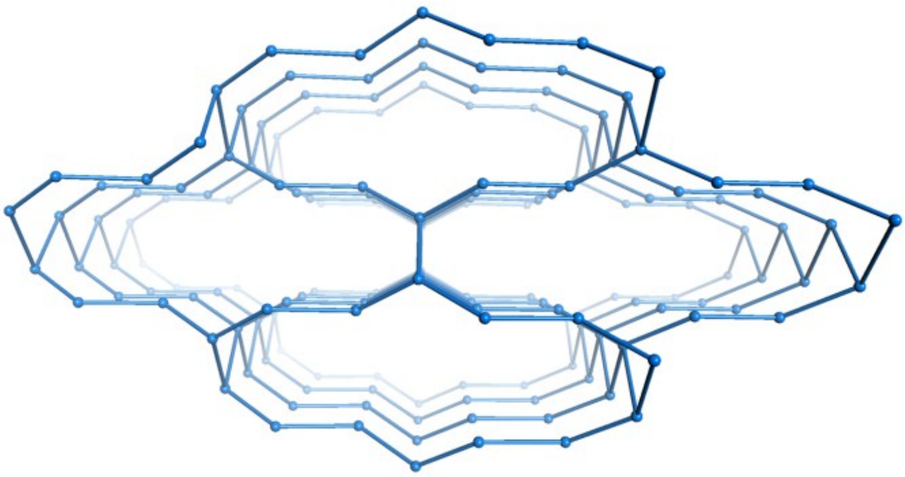

Fig. S2 Topological reprentation of the 4-connected **dia** net of $[Co(Fbtx)]_n$ in CZU-5.

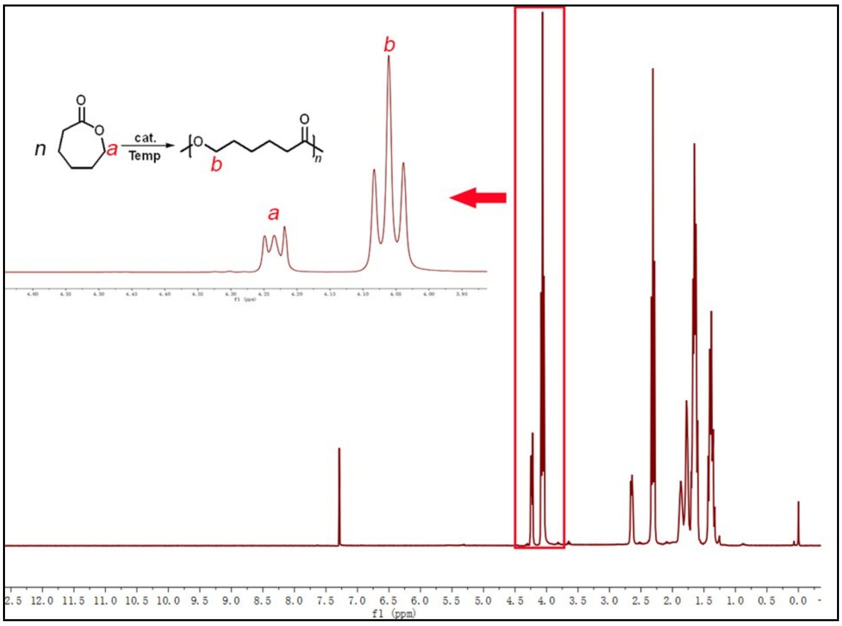

Fig. S3 [1]H NMR of the resluting PCL obtained by the solvent-free ROP of CL over CZU-5 catalyst.

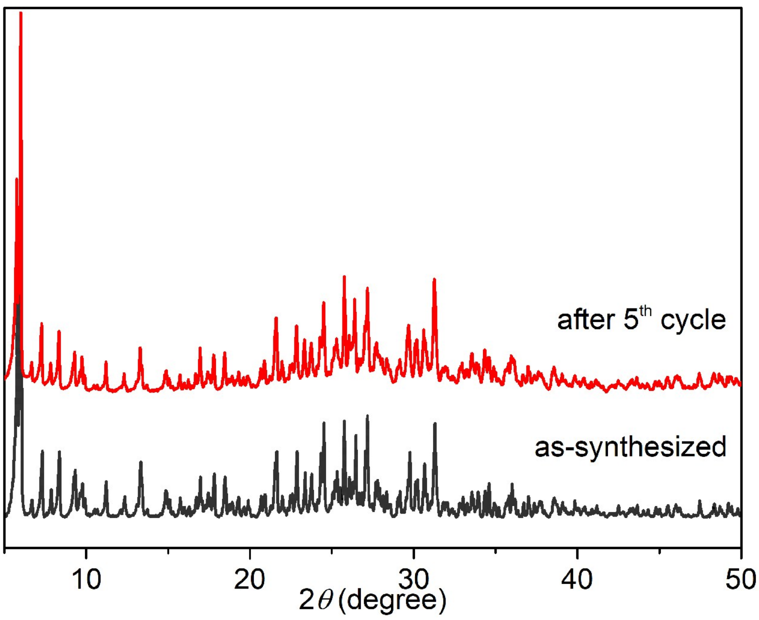

Fig. S4 [1] PXRD patterns of CZU-5 after cycling experiments of solvent-free ROP of CL.

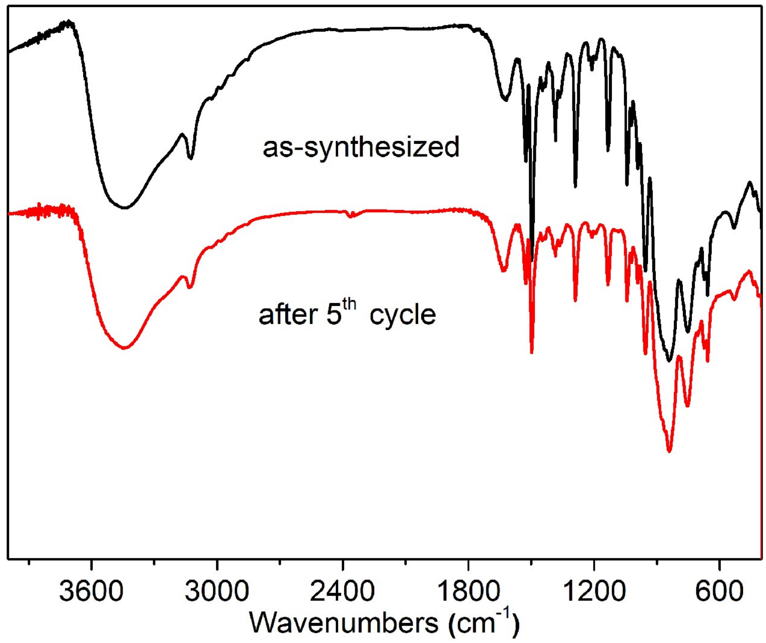

Fig. S5 FT-IR spectra of CZU-5 after cycling experiments of solvent-free ROP of CL.

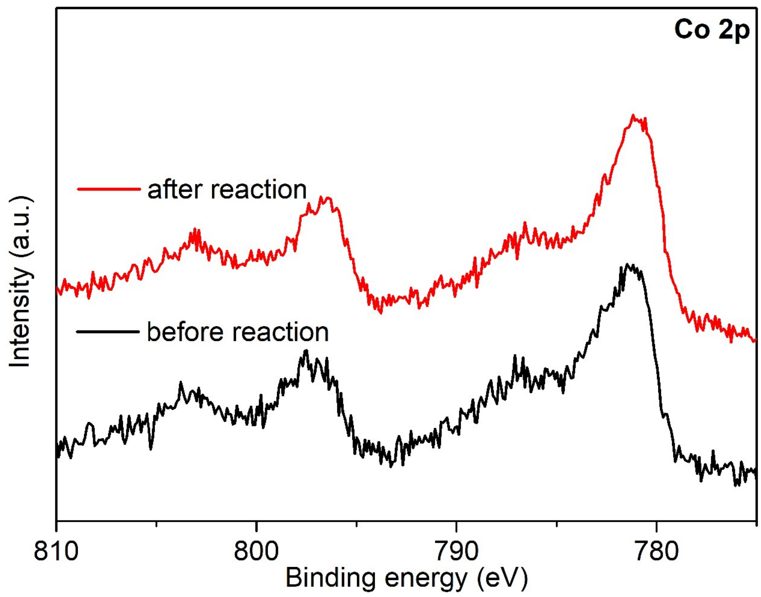

Fig. S6 XPS spectra showing the oxidation states of Co in CZU-5 after cycling experiments of solvent-free ROP of CL.

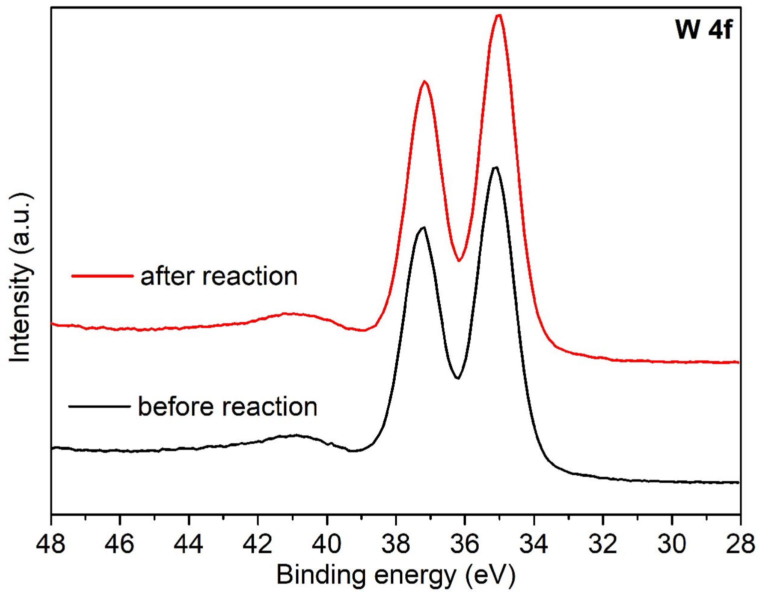

Fig. S7 XPS spectra showing the oxidation states of W in CZU-5 after cycling experiments of solvent-free ROP of CL.

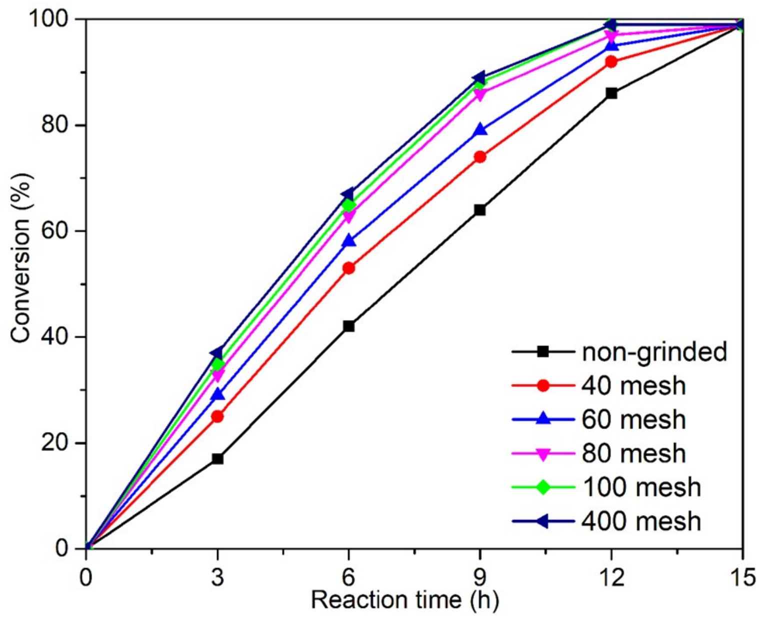

Fig. S8 The effect of particle size of the grinded CZU-5 samples on the bulk ROP reaction.

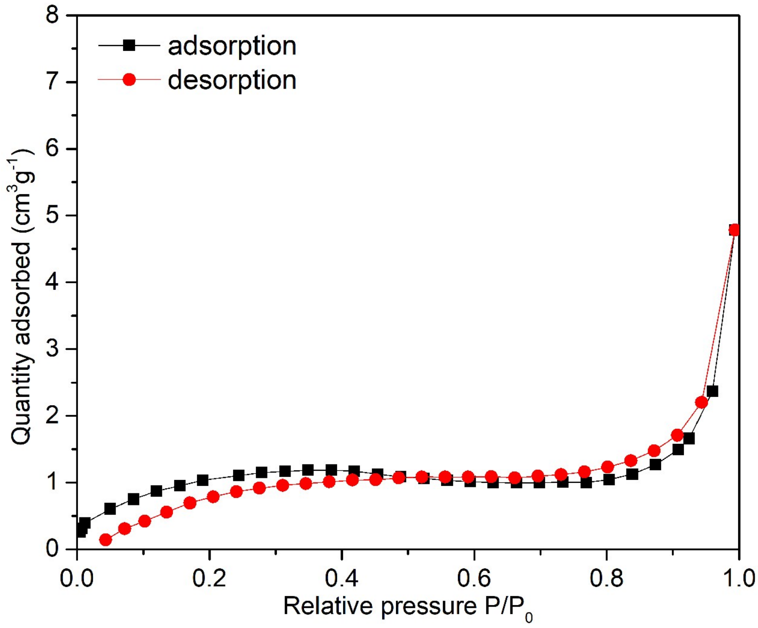

Fig. S9 Nitrogen sorption isotherm (77 K) for CZU-5.

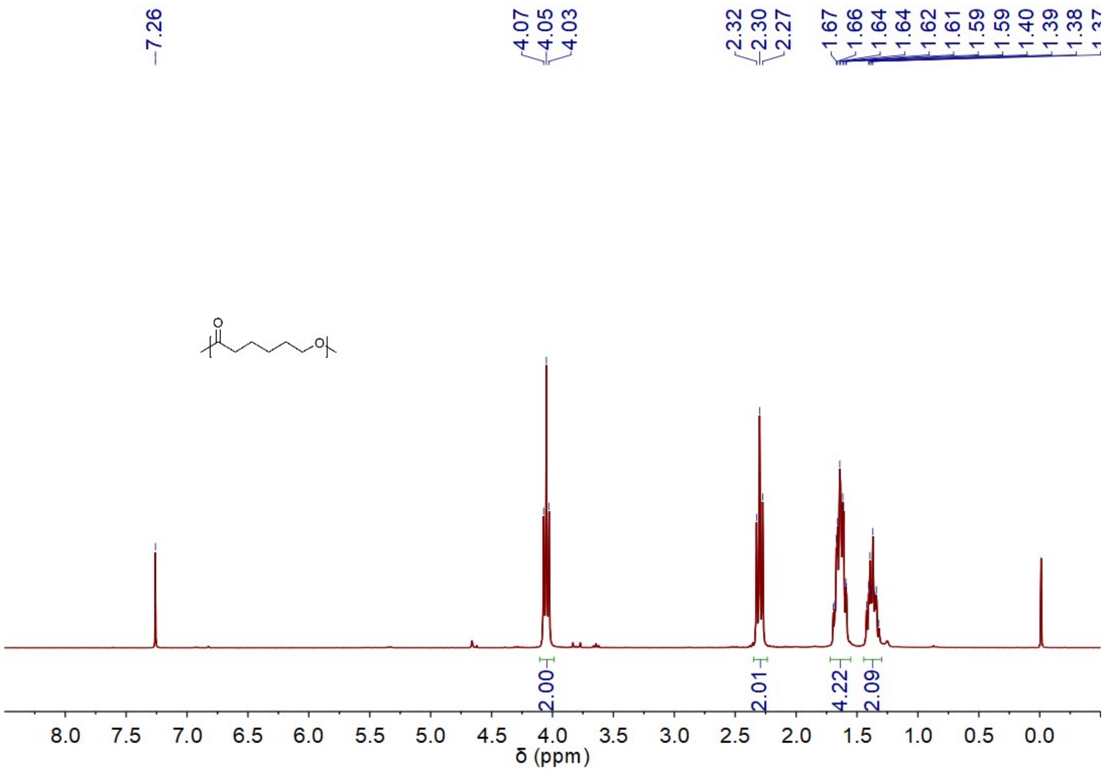

Fig. S10 ^1H NMR of PCL produced by the solvent-free ROP of CL over CZU-5 catalyst.

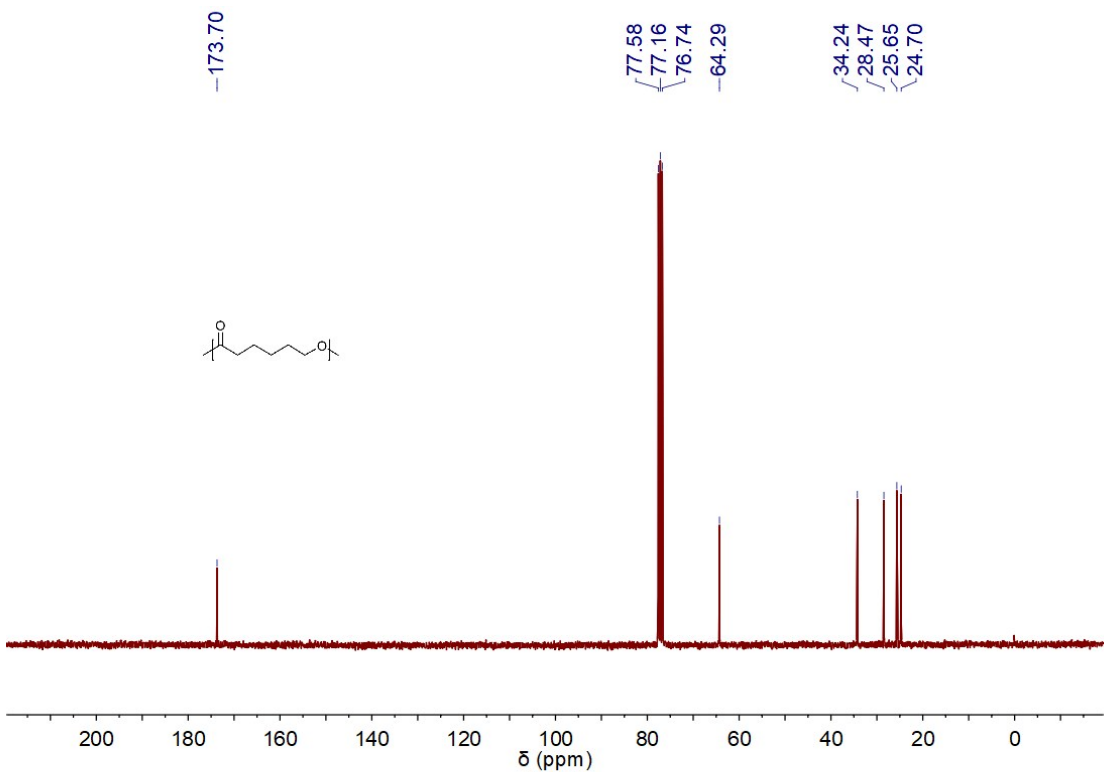

Fig. S11 ^{13}C NMR of PCL produced by the solvent-free ROP of CL over CZU-5 catalyst.