Supporting Information

Transformation of Framework Solids into Processible Metallo-polymers

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Experimental materials

Characterizations: FT-IR spectra were obtained on a NICOLET 800 spectrometer with sample powders in the range of 4000–550 cm^{-1}. Thermogravimetric (TG) analyses were carried on a TGAQ5000IR instrument in flowing O_2 with a heating rate of 10 °C·min^{-1}. X-ray powder diffraction data were recorded on a Rigaku D/max-2500V/PC diffractometer at 30 KV, 40 mA for Cu*Kα*, (λ = 1.5406 Å) with a scan speed of 2 °min^{-1} and a step size of 0.02 ° in 2θ. SEM images of compounds were obtained with JEOL JSM-7401F and S-3000H. ^{1}H NMR spectra were recorded on a Varian 200 at 300MHz. The chemical shifts are reported in ppm (δ) relative to $(CH_3)_4Si$.

Materials: Zinc acetate dihydrate $(Zn(OAC)_2 \cdot 2H_2O)$ was purchased from Aldrich. *N,N*-dimethylformamide (DMF) was purchased from Junsei. All materials were used without further purification. Seven derivatives of 1,4-benzene dicarboxylic acid (BDC) were synthesized according to the following method.

The synthesis of 3,6-di-dodecyloxy-1,4-benzenedicarboxylic acid (C12-Acid)
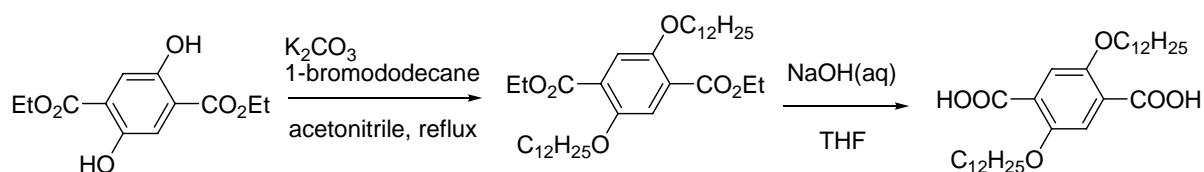
Diethyl 2,5-dihydroxyterephthalate (10 g, 39.33 mmol) and K_2CO_3 (27.18 g, 196.65 mmol) were dissolved in acetonitrile (200 mL). To this solution 1-bromododecane (23.6 mL, 98.33 mmol) was added and the mixture was refluxed for 24 hrs. After the reaction mixture was cooled to room temperature and was filtered to remove K_2CO_3. The filterate was concentrated under the reduced pressure. The resulting white powder was dissolved in THF (200 mL) and then NaOH solution (10 %, 200 mL) was added, and the mixture was stirred at 50 °C for 24 hrs. The resulting mixture was extracted to remove water layer and then treated with 1N HCl (200 ml) and filtered to get product. The final white solid C12-acid (20 g, 37.40 mmol, 95%) was obtained by washing with dichloromethane and ethanol. ^{1}H NMR ($CDCl_3$): δ 11.25(s, 2H), 7.88(s, 2H), 4.30(t, J=6.60Hz, 4H), 1.96~1.87(m, 4H), 1.56~1.26(m, 44H), 0.87(t, J=6.78 Hz, 6H).

The remaining six Cn-acid monomers were obtained by the same synthetic method with that of C12-acid. **C14-acid** (16.83 g, 35.16 mmol, 89%): ^{1}H NMR ($CDCl_3$): δ 11.18(s, 2H), 7.88(s, 2H), 4.30(t, J=6.60Hz, 4H), 1.96~1.87(m, 4H), 1.62~1.27(m, 28H), 0.88(t, J=6.78, 6H); **C10-acid** (16.83 g, 35.16 mmol, 89%): ^{1}H NMR ($CDCl_3$): δ 11.25(s, 2H), 7.88(s, 2H), 4.30(t, J=6.60Hz, 4H), 1.96~1.87(m, 4H), 1.56~1.27(m, 28H), 0.88(t, J=6.78Hz, 6H); **C9-acid** (13.26 g, 29.43 mmol, 75%): ^{1}H NMR ($CDCl_3$): δ 11.25(s, 2H), 7.88(s, 2H), 4.30(t, J=6.60Hz, 4H), 1.95~1.90(m, 4H), 1.48~1.28(m, 24H), 0.90(t, J=6.78Hz, 6H); **C8-acid** (13.28 g, 31.46 mmol, 80%): ^{1}H NMR ($CDCl_3$): δ 11.25(s, 2H), 7.87(s, 2H), 4.30(t, J=6.67, 4H), 1.95~1.90(m, 4H), 1.46~1.31(m, 20H), 0.90(t, J=6.78Hz, 6H); **C7-acid** (15.00 g, 38.02 mmol, 97%): ^{1}H NMR ($CDCl_3$): δ 11.25(s, 2H), 7.87(s, 2H), 4.30(t, J=6.12, 4H), 1.95~1.90(m, 4H), 1.46~1.31(m, 16H), 0.90(6H, t, J=6.78Hz, 6H); **C6-acid** (10.4 g, 28.39 mmol, 72%): ^{1}H NMR ($CDCl_3$): δ 11.25(s, 2H), 7.87(s, 2H), 4.30(t, J=6.40Hz,4H), 1.95~1.90(m, 4H), 1.49~1.36(m, 12H), 0.91(t, J=6.78Hz, 6H).
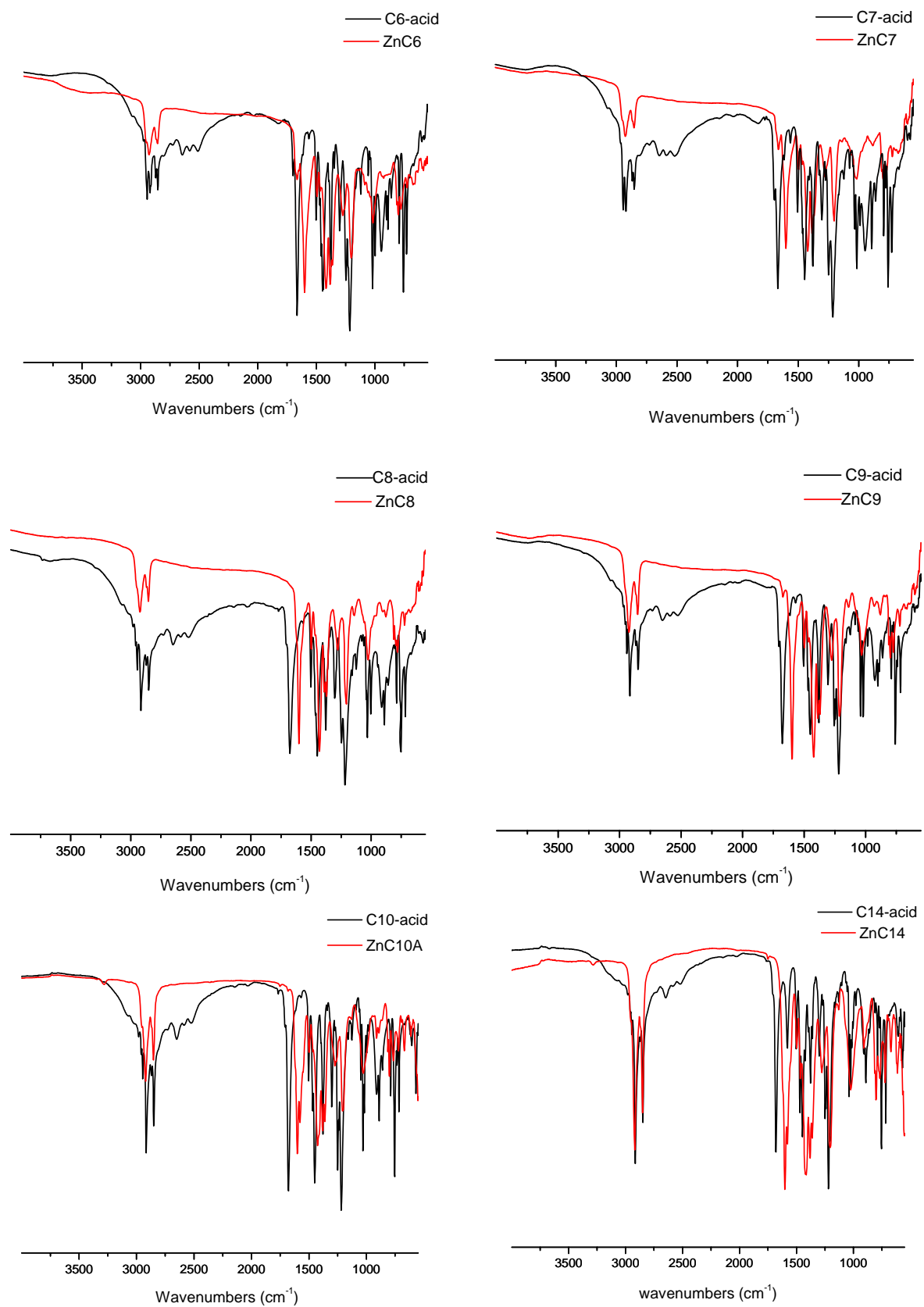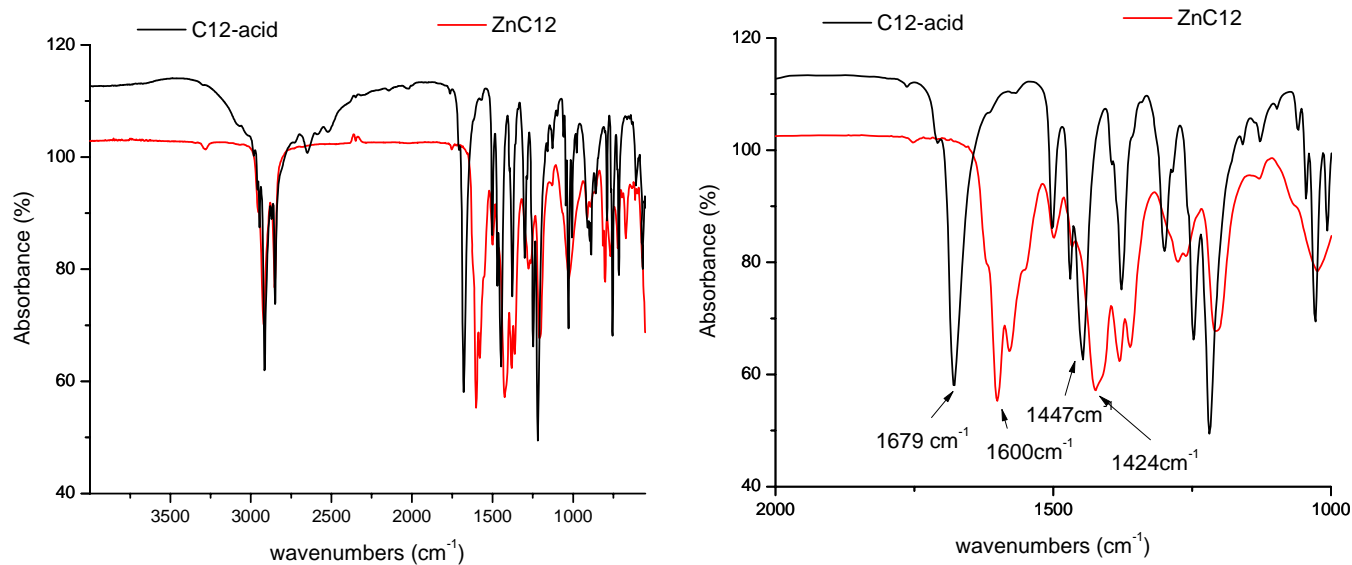
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Figure S1. IR spectra of monomers Cn-acid and polymers ZnCn.

Table S1. Main IR Characteristic Absorption Peaks for monomer (Cn-acid) and polymer (ZnCn)

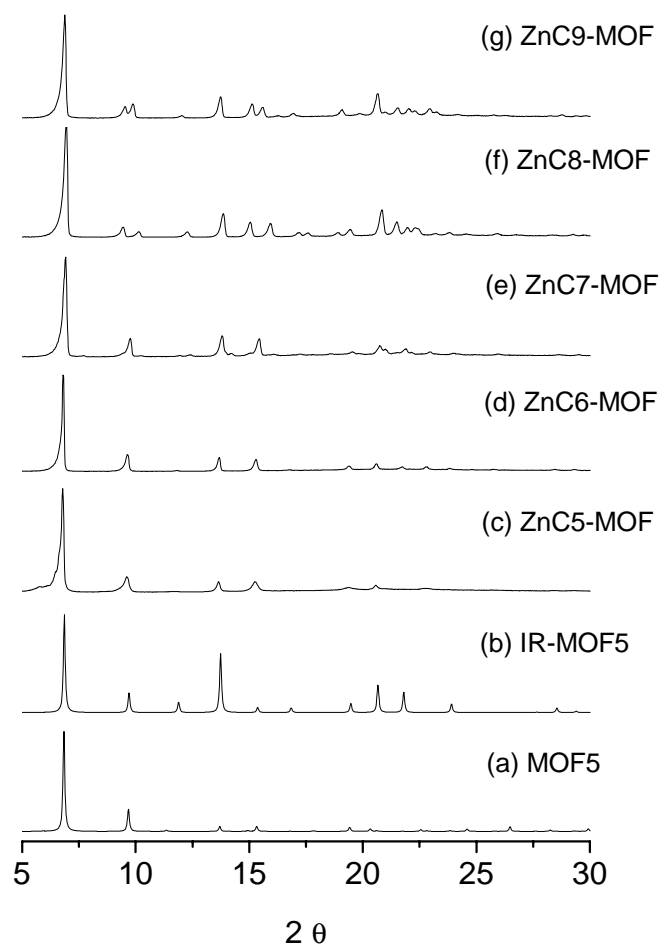|	Monomer, Cn-acid			Layered Polymer, ZnCn		
	$\gamma_{as}(COO^-)$, cm^{-1}	$\gamma_s(COO^-)$, cm^{-1}	$\gamma_{as}(COO^-)$- $\gamma_s(COO^-)$, cm^{-1}	$\gamma_{as}(COO^-)$, cm^{-1}	$\gamma_s(COO^-)$, cm^{-1}	$\gamma_{as}(COO^-)$-$\gamma_s(COO^-)$, cm^{-1}
C6	1664	1441	223	1599	1416	183
C7	1664	1445	219	1599	1420	179
C8	1676	1447	229	1599	1428	171
C9	1678	1450	228	1597	1421	176
C10	1678	1451	227	1599	1423	176
C12	1679	1447	232	1600	1424	177
C14	1681	1448	233	1602	1423	179

Figure S2. X-ray powder diffractions simulated from single crystal data of (a) MOF-5[1], $Zn_4O(BDC)_3$, and (b) IRMOF-5[1] having pentyloxy side chain and (c-f) X-ray powder diffraction of synthesized ZnCn (n=5~9) showing that their structures are identical that of three dimensional MOF-5.[1]

(a) MOF-5 (from Zinc acetate)
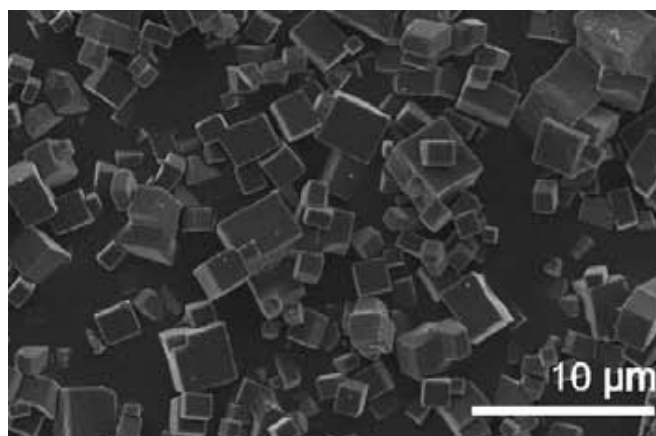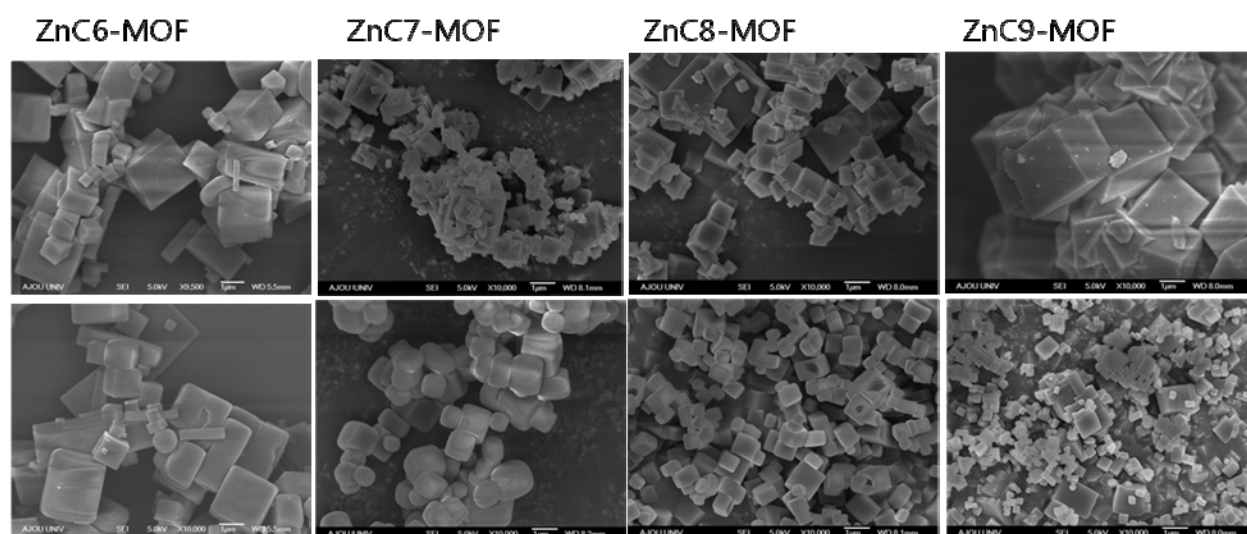

(b) ZnCn-MOF (n =6~9)

Figure S3. Scanning electron microscopy (SEM) image of (a) MOF-5[2] synthesized from zinc

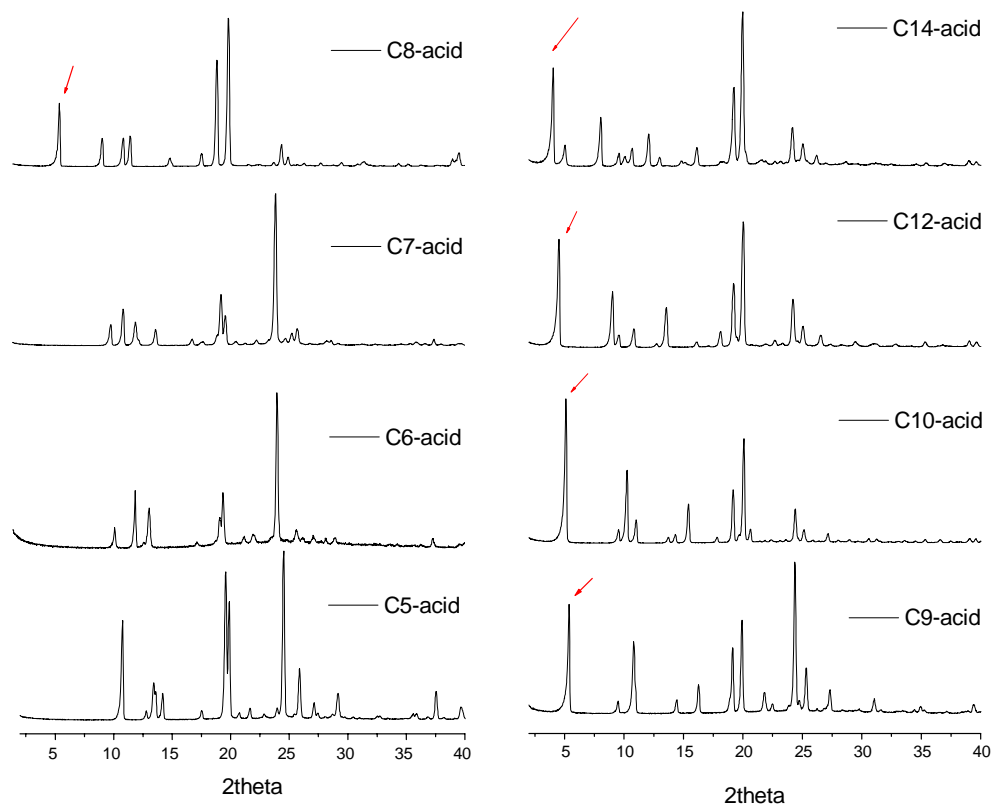acetate and (b) ZnCn (n=6~9)-MOF showing cubic morphology identically.

Figure S4. X-ray powder diffraction of Cn-acid showing self-layering tendency from C8-acid.

Table S2. Comparison in layer distances (Å) between monomers and polymers based on XRPD.

n^a	8	9	10	12	14
Cn-acid	14.93	16.43	17.26	19.55	21.88
ZnCn	17.8	19.0	20.34	22.87	25.66

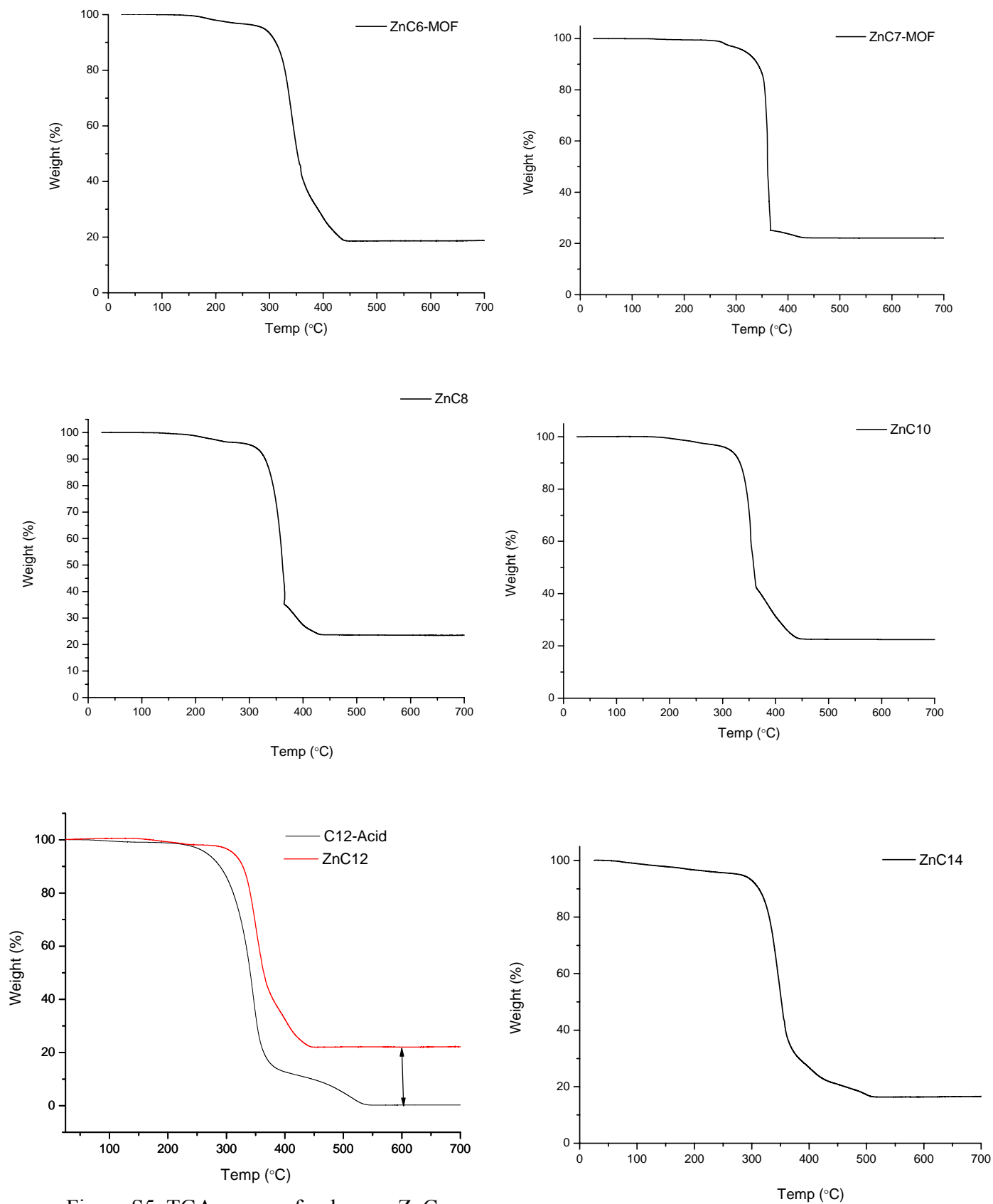[a]The number of methylene unit of side chains

Figure S5. TGA curves of polymers ZnCn.

Table S3. Comparison between remaining ZnO amount after TGA and calculated value.

		ZnO % (exp)	[a]ZnO % (CAL)	Expected Structure
MOF	ZnC6	23%	23.8%	$Zn_4O(C_{20}H_{28}O_6)_3$
	ZnC7	22%	22.4%	$Zn_4O(C_{22}H_{32}O_6)_3$
Polymer	ZnC8	24%	24.3%	$Zn_2(C_{24}H_{36}O_6)(CH_3COO)_2$
	ZnC10	22.4%	22.5%	$Zn_2(C_{28}H_{44}O_6)(CH_3COO)_2$
	ZnC12	22.0%	20.9%	$Zn_2(C_{32}H_{52}O_6)(CH_3COO)_2$
	ZnC14	17%	19.5%	$Zn_2(C_{36}H_{60}O_6)(CH_3COO)_2$

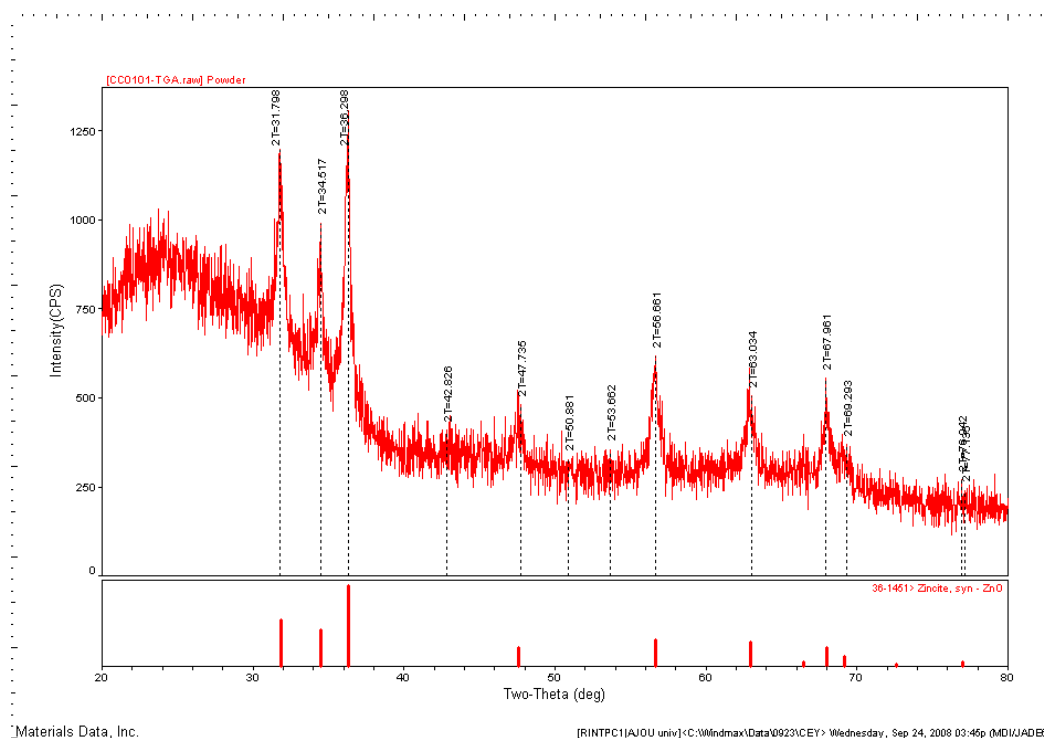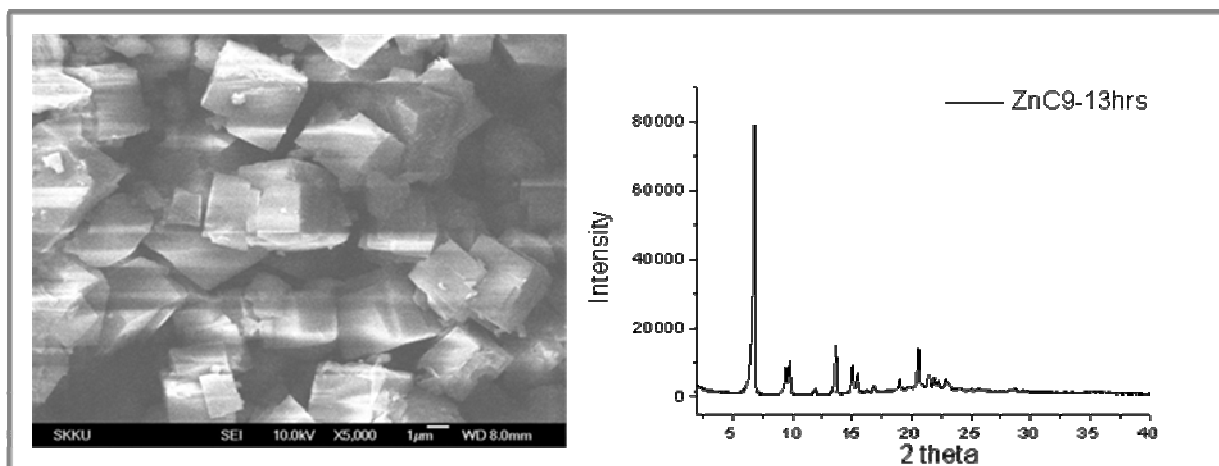[a]Calculated Value based on the expected structure

Figure S6. XRPD of the remaining material after TGA of ZnCn, showing that the remaining material is ZnO compound.
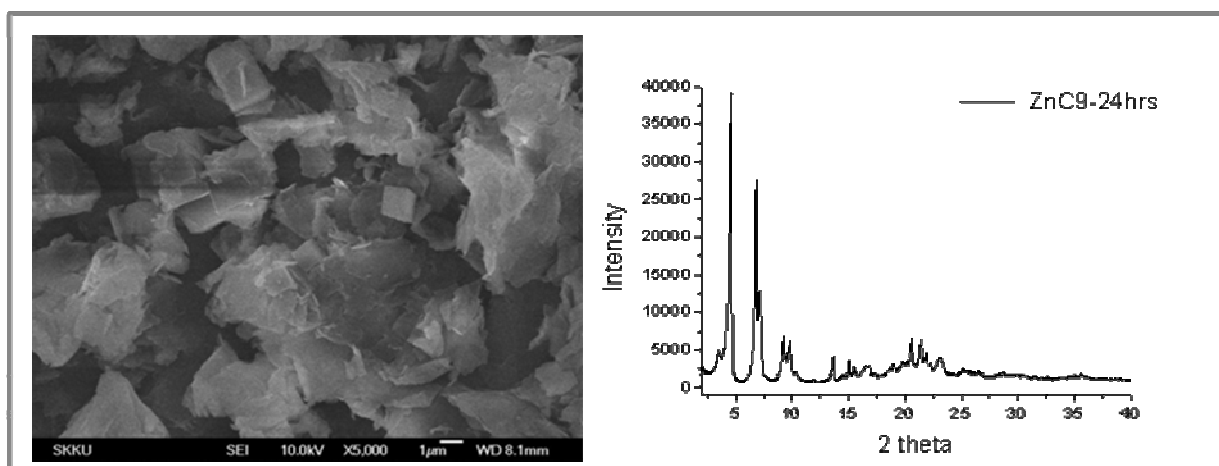
ZnC9-13hrs

ZnC9-1d

Figure S7. SEM images and XRPD showing transformation from MOF to polymer (ZnC9), in which some extents of MOF still exist.
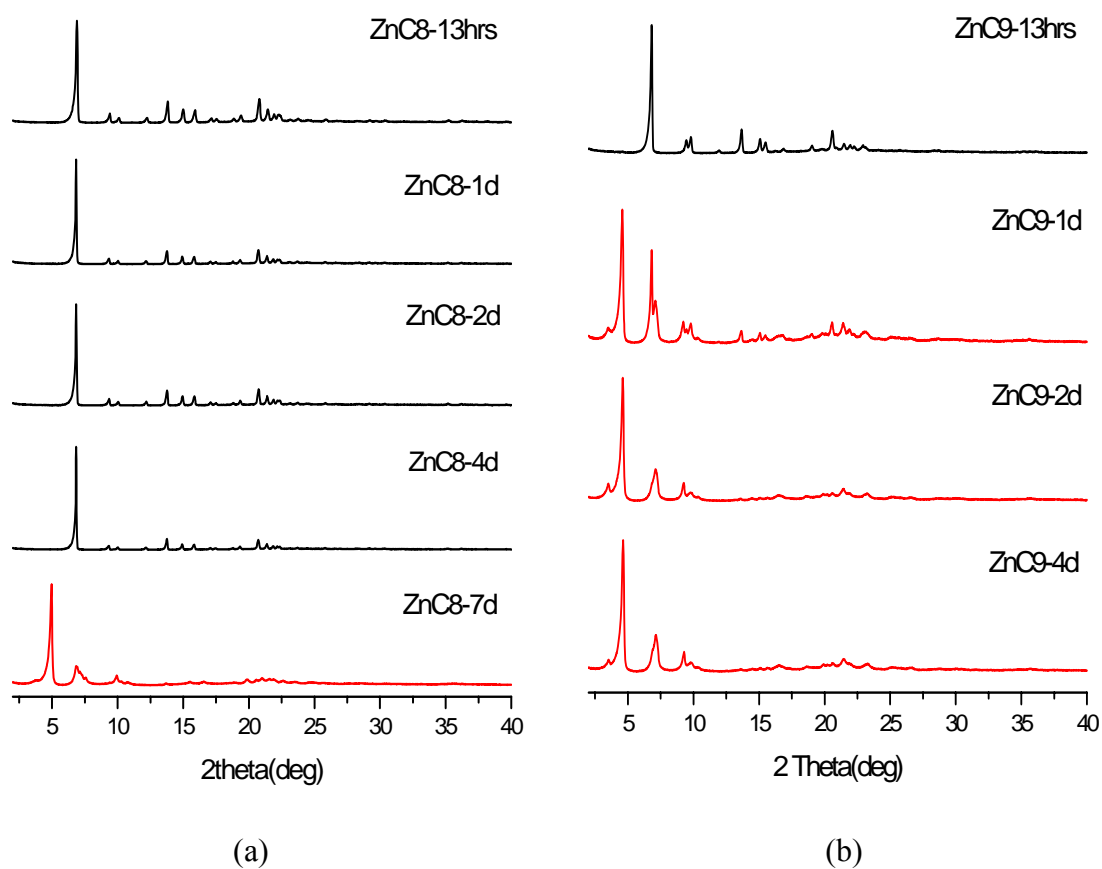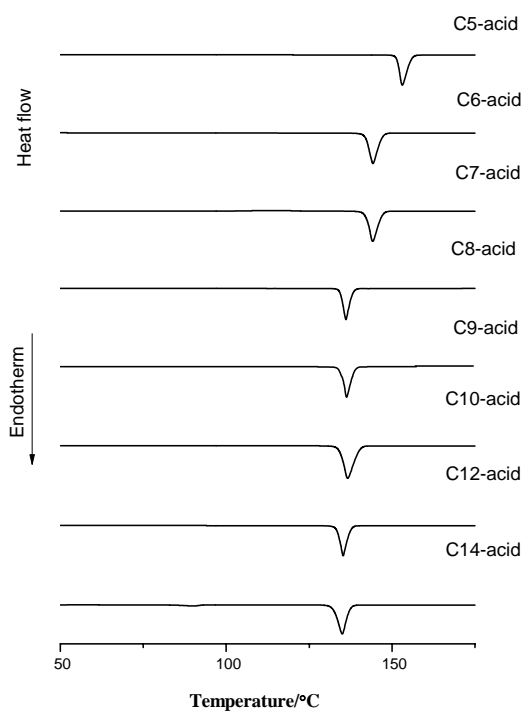
(a)

(b)

Figure S8. XRPD showing transformation of (a) ZnC8 and (b) ZnC9 from 3D MOF (black line) to 1D polymer (red line) by external factor[2], time (at constant temperature 100 °C)
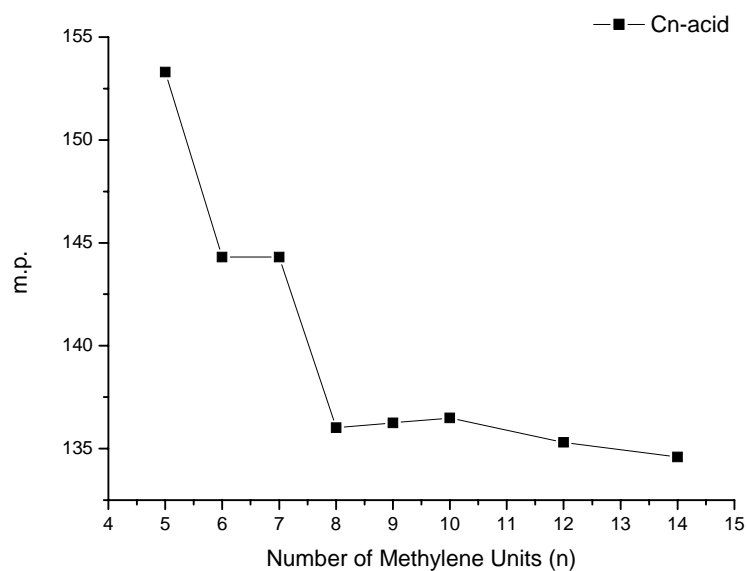
(a)

(b)

Figure S9. (a) DSC heating curve (heating rate 10 °C/min) of Cn-acids bearing side chains and (b) plot of melting point versus the lengths of the aliphatic side chains. Note that

attaching a longer side chain greater than C7 showed a pronounced reduction of the melting point of Cn-acid monomers by 10°C: m.p. of C6 and C7-acids were measured at ca 145°C and m.p. of C8 ~C14 at around 135°C. The longer side chains of C8~C14 have a greater tendency to act independently, and thus the solubilization effect is dominant. It seems to be this length that plays an important role in determining the boundary of the transitional properties from MOFs to the metallo-backbone polymers.

Reference

1. (a) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science*, **2002**, *295*, 469; (b) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature*, 1999, **402**, 276-279.

2. (a) E. Biemmi, S. Christian, N. Stock, T. Bein, *Micropor. Mesopor. Mater.* 2009, **117**, 111-117; (b) D. J. Tranchemontagne, J. R. Hunt, O.M. Yaghi, *Tetrahedron*, 2009, **64**, 8553-8557.

3. In our system, there can be internal and external parameters for the formation of product. Internal parameter is the length of side chain and external parameter can be reaction time, temperature, solvent etc.