

Rational Design of Coordination Polymers with Flexible Oxyethylene Side Chains

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We rationally designed and synthesized metallopolymers with organic 1,4-benzenedicarboxylic acid (BDC) linkers with different lengths of oxyethylene side chains in order to examine the influence of side chains on the coordination characteristics. While in a previous report the BDC linkers with alkyl side chains were found to form three-dimensional (3D) isorecticular metal-organic framework (IRMOF) structures or one-dimensional (1D) coordination polymeric structures with short $-\text{O}(\text{CH}_2)_6\text{CH}_3$ or long $-\text{O}(\text{CH}_2)_9\text{CH}_3$ side chains, respectively, new BDC linkers with oxyethylene side chains of the same lengths, $-(\text{OCH}_2\text{CH}_2)_2\text{CH}_3$ and $-(\text{OCH}_2\text{CH}_2)_3\text{CH}_3$, form only 3D IRMOF structures. This result is attributed to the higher flexibility and smaller volume of oxyethylene side chains compared to alkyl side chains.

Key Words : Metallopolymers, Metal-organic framework, Coordination polymers

Introduction

Metallopolymers consisting of organic molecules and metal coordination sites are very attractive materials for various applications.¹⁻³ Porous three-dimensional (3D) coordination polymers, the so-called metal-organic frameworks (MOFs), exhibit high performance in the separation and storage of gases and high catalytic activities due to their regular porosity.⁴⁻⁹ However, 3D MOFs are not very processable, because they are insoluble and infusible, like conventional organic cross-linked polymers.^{10,11} On the other hand, linear one-dimensional (1D) coordination polymers are often soluble in solvent or fusible and they therefore are solution- or melt-processable, like conventional organic polymers without cross-linking.^{1-3,10,11}

In solvothermal reactions with identical metal salts and binding parts in the organic molecules, the resulting coordination polymers often exhibit different coordination characteristics, including either 1D or 3D coordination, and these characteristics strongly depend on the side chains of the organic linkers.^{10,11} Organic 1,4-benzenedicarboxylic acid (BDC) linkers with methylene side chains react with zinc salt to form either porous 3D isorecticular MOF (IRMOF) structures¹² or linear 1D coordination polymers. For example, ZnC7 metallopolymers synthesized from an organic linker of C7-acid (2,5-bis(heptyloxy)terephthalic acid; see Figure 1) with relatively short $-\text{O}(\text{CH}_2)_6\text{CH}_3$ side chains exhibit the IRMOF-5 structure, while ZnC10 metallopolymers synthesized from C10-acid (2-(decyloxy)-5-undecylterephthalic acid) with relatively long $-\text{O}(\text{CH}_2)_9\text{CH}_3$ side chains are processable 1D polymers, in which the long alkyl chains prevent the formation of the IRMOF structure *via* a large steric hindrance.^{10,11} Therefore, understanding the influence

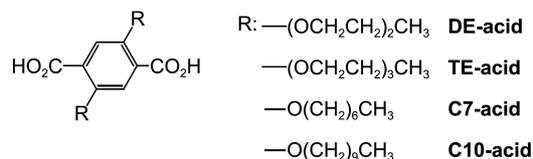


Figure 1. Chemical structure of 1,4-benzenedicarboxylic acid (BDC) derivatives with side chains.

of side chains on the coordination characteristics is important for obtaining the desired processability and physical properties of coordination polymers.

In this work, we rationally designed and synthesized new organic 1,4-benzenedicarboxylic acid (BDC) linkers with oxyethylene side chains (see Figure 1) in order to examine the influence of side chains on the coordination characteristics of metallopolymers. In a previous report in which BDC linkers with side chains were studied, the linkers with short $-\text{O}(\text{CH}_2)_6\text{CH}_3$ side chains that form ZnC7 metallopolymers with 3D IRMOF coordination and the linkers with long $-\text{O}(\text{CH}_2)_9\text{CH}_3$ side chains that form ZnC10 metallopolymers with linear 1D coordination. By contrast, in this study, both of the new BDC linkers have the same number of atoms (*i.e.*, C and O atoms) in their side chains but have different characteristics due to their oxyethylene units, $-(\text{OCH}_2\text{CH}_2)_2\text{CH}_3$ and $-(\text{OCH}_2\text{CH}_2)_3\text{CH}_3$ and form only the 3D IRMOF structures. This result is attributed to the higher flexibility and smaller volume of the oxyethylene side chains compared to those of the alkyl side chains.

Experimental

Synthesis of Organic Linkers. The newly designed BDC linkers were synthesized as described in the literature.^{10,13,14}

2,5-Bis(2-(2-methoxyethoxy)ethoxy)terephthalic acid (DE-acid): Diethyl 2,5-dihydroxyterephthalate (10 g, 39.3 mmol) and K_2CO_3 (27.18 g, 196.7 mmol) were dissolved in

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acetonitrile (150 mL). After 2-(2-methoxyethoxy)ethyl *p*-toluenesulfonate (31.31 g, 90.4 mmol) was added, the mixture was refluxed for 24 hr. Water was added to terminate the reaction. The solution was extracted with dichloromethane and concentrated *via* rotary evaporation. The resulting material was dissolved in THF, and then NaOH solution was added. The mixture was stirred at 50 °C to perform hydrolysis. The solution was extracted to remove the water layer and then treated with 1 *N* HCl. The solution was extracted with dichloromethane several times, and the solvent was subsequently evaporated *via* rotary evaporation to give the final product. Yield: 76%. ¹H NMR (CDCl₃, δ) 7.83 (s, 2H), 4.41 (t, 4H), 3.69 (t, 4H), 3.57 (t, 4H), 3.36 (s, 6H).

2,5-Bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)terephthalic acid (TE-acid): TE-acid was prepared in a manner similar to that used for DE-acid. Yield: 73%. ¹H NMR (CDCl₃, δ) 7.80 (s, 2H), 4.39 (m, 4H), 3.90 (m, 4H), 3.54–3.73 (m, 16H), 3.37 (s, 6H).

Synthesis of Metallopolymers. Solvothermal reactions were performed in a convection oven. The solvothermal reactions of DE-acid (0.125 mmol, 50.3 mg) and zinc nitrate hexahydrate (0.25 mmol, 74.4 mg) in diethylformamide (DEF; 2–16 mL) at 80 °C gave ZnDE metallopolymers with cubic-shaped crystal morphologies. In addition, the reactions in various mixed solvents (dimethylformamide (DMF)/ethanol (EtOH) (3/1) or DEF/EtOH (3/1)) or at a reaction temperature of 100 °C also gave ZnDE crystals. The metallopolymer ZnTE was synthesized in a manner similar to that used for ZnDE. ZnTE crystals were prepared using solvothermal reactions of zinc nitrate hexahydrate (0.25 mmol, 74.4 mg) and TE-acid (0.125 mmol, 61.3 mg) in 6–8 mL of DEF solvent. The final products were filtered and washed with DMF and acetone.

Results and Discussion

Design of Organic Linkers. Figure 1 shows the newly designed 1,4-benzenedicarboxylic acid (BDC) linkers. In order to investigate the influence of the characteristics of the side chains on the coordination of the metallopolymers, we introduced oxyethylene $-(\text{OCH}_2\text{CH}_2)_n-$ units; DE-acid (2,5-bis(2-(2-methoxyethoxy)ethoxy)terephthalic acid) possesses two oxyethylene units, and TE-acid (2,5-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)terephthalic acid) possesses three oxyethylene units. The lengths of the side chains in these acids are practically identical to those of the C7-acid with $-\text{OC}_7\text{H}_{13}$ side chains and the C10-acid with $-\text{OC}_{10}\text{H}_{21}$ side chains, respectively.^{10,11} The synthesis of DE-acid and TE-acid was performed as described in the literature.^{10,13,14}

Supramolecular Ordering of Organic Linkers. To investigate the characteristics of the oxyethylene unit compared to those of the methylene unit in the supramolecular ordering, BDC linkers were measured using the powder X-ray diffraction (PXRD) patterns, as shown in Figure 2(a). The carboxylic acids of the BDC linkers form strong, symmetric hydrogen bonds with other BDC linkers and form

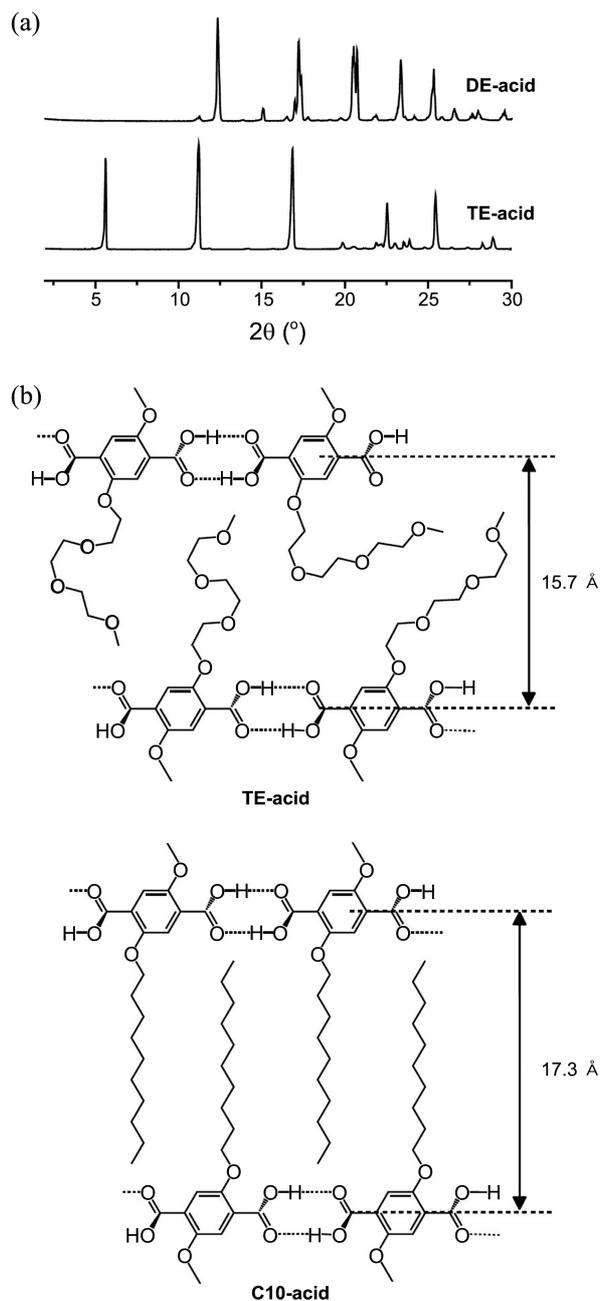


Figure 2. (a) Powder X-ray diffraction patterns of DE-acid and TE-acid. (b) Schematic illustration of the mesophase structure of TE-acid and C10-acid from Ref. [10 and 11].

polymer-like chains (see Figure 2(b)).^{10,11,14} Compared to the BDC linkers with methylene units, the BDC linkers with oxyethylene side chains have a smallest-angle diffraction peak (*i.e.*, longest distance of ordering) shifted to higher angles (*i.e.*, shorter distances) in the PXRD patterns: the peak was at 5.59° for TE-acid versus 5.16° for C10-acid¹⁰ and at 11.2° for DE-acid versus 10.18° for C7-acid.¹⁰ In C10-acid, the peak at 5.16° (17.3 Å) corresponds to the layer distance between hydrogen-bonded chains (see Figure 2(b)) when the methylene units are in a fully extended con-

formation. However, the distance of 15.7 Å (5.59°) in TE-acid is shorter than the length of the oxyethylene $-(\text{OCH}_2\text{CH}_2)_3\text{CH}_3$ side chains in their extended conformation. Therefore, in contrast to C10-acid, which shows an extended conformation of the alkyl side chains, TE-acid does not show the extended conformation, and it is rather slightly bent, as shown in Figure 2(b). Therefore, in contrast to the extended conformation of alkyl side chains,^{10,11} a non-extended conformation of oxyethylene side chains may appear in the coordination polymers.

Metallopolymers with Oxyethylene Side Chains. The coordination polymers ZnDE and ZnTE were prepared *via* solvothermal reactions between zinc nitrate and DE-acid and TE-acid, respectively. The $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and BDC derivatives bearing oxyethylene side chains were reacted in DMF, DEF, or a mixed solvent with ethanol.

The structures of ZnDE and ZnTE were confirmed *via* infrared (IR) absorption spectra, powder X-ray diffraction patterns, and thermal gravimetric analysis (TGA). In the IR spectra, the peaks of the symmetric (γ_{sym}) and asymmetric (γ_{asym}) stretching vibrations of carboxylate (COO^-) in ZnDE and ZnTE are shifted to lower wavenumbers than those obtained from DE-acid and TE-acid: $\gamma_{\text{sym}} = 1596 \text{ cm}^{-1}$ and $\gamma_{\text{asym}} = 1412 \text{ cm}^{-1}$ for ZnDE while $\gamma_{\text{sym}} = 1683 \text{ cm}^{-1}$ and $\gamma_{\text{asym}} = 1468 \text{ cm}^{-1}$ for DE-acid, and $\gamma_{\text{sym}} = 1598 \text{ cm}^{-1}$ and $\gamma_{\text{asym}} = 1417 \text{ cm}^{-1}$ for ZnTE, while $\gamma_{\text{sym}} = 1674 \text{ cm}^{-1}$ and $\gamma_{\text{asym}} = 1456 \text{ cm}^{-1}$ for TE-acid. The shift of the carboxylate group peaks in the IR absorption spectra to lower wavenumbers, which is a unique characteristic of coordinated carboxylate,^{7c,10,11} confirms that in ZnDE and ZnTE metallopolymers, carboxylate groups are coordinated with Zn.

The crystal structure of metallopolymers was analyzed by X-ray diffraction experiments. Yagi *et al.* reported on the crystal structure of IRMOF-5 synthesized with C5-acid (2,5-bis(pentyloxy)terephthalic acid) consisting of 1,4-benzenedicarboxylic acid and the $-(\text{OCH}_2)_4\text{CH}_3$ alkyl side chains, which is shorter than that of C7-acid, C10-acid, DE-acid and TE-acid studied in this work. They collected single crystal data and refined the backbone framework, but not refined the positions of flexible side chain and obtained relatively high error index (*i.e.*, high *R* value in the crystallographic data).^{12b} We also tried to analyze the crystal structure of metallopolymers having longer side chain than IRMOF-5 with $-(\text{OCH}_2)_4\text{CH}_3$ by single crystal X-ray diffraction experiments. However, compared to IRMOF-5 with the $-(\text{OCH}_2)_4\text{CH}_3$,^{12b} we obtained the refined position only of backbone framework with higher *R* value or could not solve the single crystal data. It may be due to very disordered positions of the long side chains in the cage. In order to interpret the crystals structure of metallopolymers, powder X-ray diffraction experiments were performed. Figure 3 shows the powder X-ray diffraction patterns of the ZnDE and ZnTE metallopolymers. For comparison, calculated diffraction pattern of IRMOF-5 structure¹² is also shown in Figure 3. The PXRD patterns of both ZnDE and ZnTE metallopolymers are similar with IRMOF-5 structure. The powder X-ray diffraction pattern of ZnTE is slightly shifted

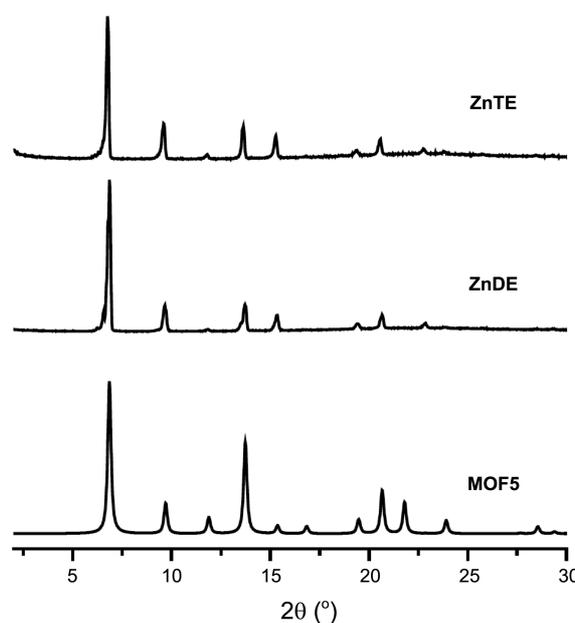


Figure 3. Powder X-ray diffraction patterns of ZnDE and ZnTE coordination polymers from DE-acid and TE-acid, respectively and calculated X-ray diffraction patterns of IRMOF-5.¹²

to lower angles compared to IRMOF-5 structure and that of ZnDE is much closer to IRMOF-5. The shift of ZnTE having longer side chains is much larger than that of ZnDE: for example, the lowest-angle diffraction peak for 2 theta value in Figure 3 is 6.767, 6.864 and 6.860° for ZnTE, ZnDE and IRMOF-5,¹² respectively. It is noticeable that the cell parameters of ZnTE (13.06 Å) slightly increase due to the effect of long oxyethylene side chains compared to those of ZnDE (12.89 Å) and IRMOF-5 (12.88 Å).¹² Therefore, while the ZnC7 metallopolymers with $-(\text{O}(\text{CH}_2)_6\text{CH}_3)$ and ZnC10 metallopolymers with $-(\text{O}(\text{CH}_2)_9\text{CH}_3)$ exhibit IRMOF-5 and 1D polymer structures, respectively,^{10,11} both the ZnDE metallopolymers with $-(\text{OCH}_2\text{CH}_2)_2\text{CH}_3$ and the ZnTE metallopolymers with $-(\text{OCH}_2\text{CH}_2)_3\text{CH}_3$ form 3D IRMOF structures.

TGA curves also confirmed that both ZnDE and ZnTE exhibit the IRMOF-5 structure. After the two metallopolymers were heated to 500 °C under air, the amount of residual ZnO was 24% for ZnDE and 19% for ZnTE, which is in good agreement with the values calculated assuming IRMOF-5 structures: 22% and 19%, respectively.^{10,11} The crystal shape of the synthesized ZnDE and ZnTE is cubic, as is that of conventional MOFs (see Figure 4).

Although ZnTE and ZnC10 have the same side chain lengths (*i.e.*, the same number of C and O atoms), ZnTE has a 3D IRMOF structure and ZnC10 has a 1D coordination structure. Moreover, in contrast to the extended conformation of the alkyl side chain observed in ZnC10,^{10,11} the conformation of the oxyethylene side chains $-(\text{OCH}_2\text{CH}_2)_3\text{CH}_3$ was not extended, because the length of the fully extended oxyethylene side chains is longer than the pore diameter (12.9 Å) in the IRMOF-5 structure. The only differences between the two metallopolymers are the characteristics of

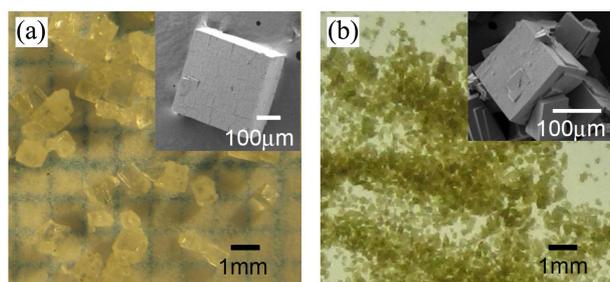


Figure 4. Photographs and scanning electron microscopy (SEM) images for (a) ZnDE and (b) ZnTE.

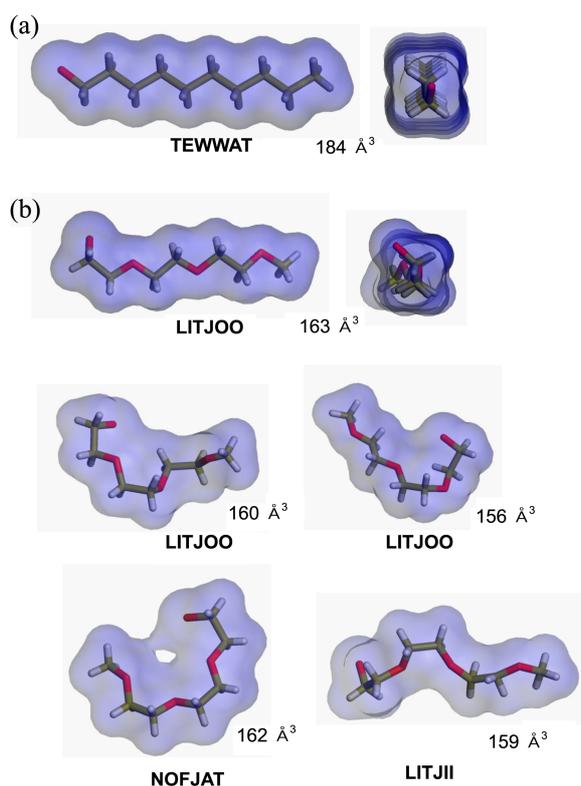


Figure 5. Connolly surfaces of selected conformations of side-chain fragments: (a) $-\text{O}(\text{CH}_2)_9\text{CH}_3$ and (b) $-(\text{OCH}_2\text{CH}_2)_3\text{CH}_3$. The fragments are detached from the reported structures in the CSD¹⁵ (reference codes: TEWWAT,¹⁷ LITJOO,¹⁸ NOFJAT,¹⁹ and LITJII²⁰).

the side chains; one has oxyethylene side chains and the other has alkyl side chains.

In order to investigate the reason for the different coordination structures, we surveyed the crystal structures of molecules with the side-chain fragments $-\text{O}(\text{CH}_2)_9\text{CH}_3$ and $-(\text{OCH}_2\text{CH}_2)_3\text{CH}_3$, which have same chemical structure as the side chains in ZnC10 and ZnTE, respectively using the CSD (Cambridge Structural Database).¹⁵ The conformations and Connolly surfaces¹⁶ of the side-chain fragments are shown in Figure 5. The survey showed that most of the alkyl side chain fragments $-\text{O}(\text{CH}_2)_9\text{CH}_3$ have fully extended structures, as shown in Figure 5(a).¹⁷ However, Figure 5(b) shows that many oxyethylene $-(\text{OCH}_2\text{CH}_2)_3\text{CH}_3$ side chains exhibit non-stretched or balled-up conformations,¹⁸⁻²⁰ which are attributed to the higher flexibility of the oxyethylene unit.

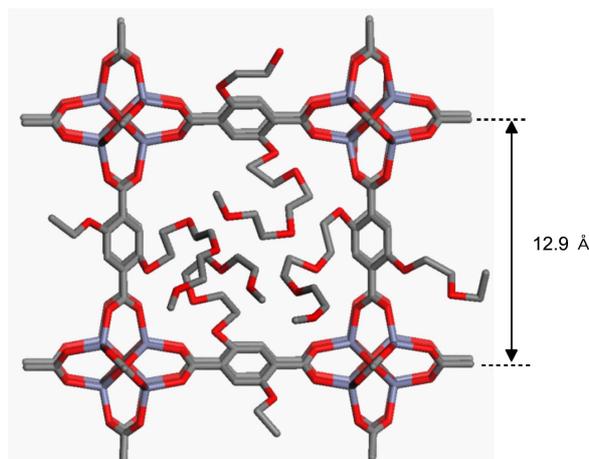


Figure 6. Expected model of ZnTE metallopolymers, where the coordination structure is sketched partially based on those of MOF5 from Ref. [12a].

Moreover, the volume occupied by the $-(\text{OCH}_2\text{CH}_2)_3\text{CH}_3$ fragment is about 160 \AA^3 , which is much smaller than that occupied by the $-\text{O}(\text{CH}_2)_9\text{CH}_3$ fragment (183 \AA^3). The occupied volume of 48 $-(\text{OCH}_2\text{CH}_2)_3\text{CH}_3$ fragments is about 45% of the cage volume of IRMOF-5 structure, which is much smaller than that of 48 $-(\text{CH}_2)_9\text{CH}_3$ fragments (52%) and maximum accessible volume (55-61%).^{10,12a} Therefore, compared to alkyl side chains, oxyethylene side chains with their non-stretched conformations and smaller occupied volumes provide less steric hindrance to the formation of porous IRMOF structures (see Figure 6).

Conclusion

We have designed and synthesized new organic 1,4-benzenedicarboxylic acid (BDC) linkers with oxyethylene side chains in order to examine the influence of side chains on the coordination characteristics of metallopolymers. In contrast to in previous reports, BDC linkers with alkyl side chains, *i.e.*, the C7-acid linkers with short $-\text{O}(\text{CH}_2)_6\text{CH}_3$ side chains that form ZnC7 metallopolymers with 3D IRMOF coordination and the C10-acid linkers with long $-\text{O}(\text{CH}_2)_9\text{CH}_3$ side chains that form ZnC10 metallopolymers with linear 1D coordination, the new DE-acid and TE-acid linkers have the same side-chain lengths if stretched but different characteristics due to their oxyethylene units, $-(\text{OCH}_2\text{CH}_2)_2\text{CH}_3$ and $-(\text{OCH}_2\text{CH}_2)_3\text{CH}_3$: they form only 3D IRMOF structures. This result is attributed to the higher flexibility and smaller volume of oxyethylene side chains compared those of to alkyl side chains.

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References

1. George, R. W.; Manner, I. *Adv. Mater.* **2007**, *19*, 3439.
2. Kurth, D. G. *Sci. Technol. Adv. Mater.* **2008**, *9*, 014103.
3. Soto Bustamantea, E. A.; Galyametdinovb, Y. G.; Griesar, K.; Schuhmacher, E. Haase, W. *Macromol. Chem. Phys.* **1998**, *199*, 1337.
4. (a) Chen, B.; Eddaoudi, M.; Hyde, S. T.; O'Keeffe, M.; Yaghi, O. M. *Science* **2001**, *291*, 1021. (b) Meek, S. T.; Greathouse, J. A.; Allendorf, M. D. *Adv. Mater.* **2011**, *23*, 249. (c) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem. Int. Ed.* **2004**, *43*, 2334.
5. Long, J. R.; Yagi, O. M. *Chem. Soc. Rev.* **2009**, *38*, 1312-1504 (2009 Metal-organic frameworks issue).
6. Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surblé, S.; Margiolaki, I. *Science* **2005**, *309*, 2040.
7. (a) Choi, E.-Y.; Barron, P. M.; Novotney, R. W.; Hu, C.; Kwon, Y.-U.; Choe, W. *Cryst. Eng. Comm.* **2008**, *10*, 824. (b) Xu, L.; Choi, E.-Y.; Kwon, Y.-U. *Inorg. Chem. Commun.* **2008**, *11*, 1190. (c) Xu, L.; Choi, E.-Y.; Kwon, Y.-U. *Inorg. Chem.* **2007**, *46*, 10670.
8. (a) Yang, Q.; Zhong, C. *J. Phys. Chem. B* **2006**, *110*, 655. (b) Frost, H.; Snurr, R. Q. *J. Phys. Chem. C* **2007**, *111*, 18794. (c) Lee, T. B.; Kim, D.; Jung, D. H.; Choi, S. B.; Yoon, J. H.; Kim, J.; Choi, K.; Choi, S.-H. *Catal. Today* **2007**, *120*, 330. (d) Belof, J. L.; Stern, A. C.; Eddaoudi, M.; Space, B. J. *Am. Chem. Soc.* **2007**, *129*, 15202. (f) Kuc, A.; Enyashin, A.; Seifert, G. *J. Phys. Chem. B* **2007**, *111*, 8179.
9. Ko, N.; Kim, J. *Bull. Korean Chem. Soc.* **2011**, *32*, 2705.
10. Choi, E.-Y.; Gao, C.; Lee, H.-J.; Kwon, O.-P.; Lee, S.-H. *Chem. Commun.* **2009**, 7563.
11. Choi, E.-Y.; Lee, H.-J.; Gao, C.; Kwon, O.-P.; Lee, S.-H. *Macromol. Chem. Phys.* **2010**, *211*, 1955.
12. (a) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276. (b) Eddaoudi, M. *et al. Science* **2002**, *295*, 469. (c) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2003**, *300*, 1127. (d) Mulder, F.; Dingemans, T.; Wagemaker, M.; Kearley, G. *Chem. Phys.* **2005**, *317*, 113.
13. Kwon, O. P.; Lee, S. H.; Montemezzani, G.; Gunter, P. *Adv. Funct. Mater.* **2003**, *13*, 434.
14. (a) Yuan, Z.; Lee, C.-W.; Lee, S.-H. *Angew. Chem., Int. Ed.* **2004**, *43*, 4197. (b) Lee, S.-H.; Yuan, Z.; Lee, C.-W. *Adv. Mater.* **2003**, *15*, 251.
15. www.ccdc.cam.ac.uk (CSD version 5.32).
16. Connolly surfaces are constructed using Materials Studio (version 4.3.0.0), Accelrys Software Inc., 2008.
17. Keegstra, E. M. D.; van der Mieden, V.; Zwikke, J. W.; Jenneskens, L. W.; Schouten, A.; Kooijman, H.; Veldman, N.; Spek, A. L. *Chem. Mater.* **1996**, *8*, 1092.
18. Meudtner, R. M.; Ostermeier, M.; Goddard, R.; Limberg, C.; Hecht, S. *Chem. Eur. J.* **2007**, *13*, 9834.
19. Pollard, K. D.; Vittal, J. J.; Yap, G. P. A.; Puddephatt, R. J. *J. Chem. Soc. Dalton Trans.* **1998**, 1265.
20. Meudtner, R. M.; Ostermeier, M.; Goddard, R.; Limberg, C.; Hecht, S. *Chem. Eur. J.* **2007**, *13*, 9834.