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Synthesis of Oligodiacetylene Derivatives from Flexible Porous Coordination Frameworks

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Oligodiacetylene, Porous Coordination Polymer, Thermal Expansion, and Cross Linking

ABSTRACT: Oligodiacetylenes (ODAs) with alternating ene-yne conjugated structure is one of the significant materials for optical and electronic properties. Due to the low solubility of ODAs in common solvents, the synthetic approaches are limited. Here we disclose a new synthetic approach of ODAs without side alkyl chain using porous coordination polymer (PCP) as a sacrificial template. 1,2-bis(4-pyridyl)butadiyne which work as a monomer were embedded in the flexible framework of PCP, and ODAs were synthesized via utilization of the anisotropic thermal expansion (ATE) of PCP crystal. The oligomeric state of ODAs depends on the metal ion and co-ligand of the precursor.

INTRODUCTION

Since Wegner discovered the 1,4-diacetylene polymerization in solid state via topochemical reaction,¹ polydiacetylenes have been studied extensively owing to the unique alternating ene-yne conjugated structure.² In this research field, control of the molecular structure is important for design of the optical and electronic properties.3 Oligodiacetylenes (ODAs) with the welldefined conjugated structure has also been the significant synthesis target.⁴ Engineered crystalline hosts with hydrogen- or halogen-bonding are useful host for polydiacetylene synthesis,⁵ whereas ODAs with low polymerization degree are typically synthesized by using Sonogashira-Glaser coupling reaction4b,4c,6 or co-micellar strategy⁷. One of the issues with the sequential synthetic approaches is the difficulty to synthesize the structures without alkyl side chain due to the low solubility in organic solvents. Those alkyl chain sacrifices good conductive properties derived from the conjugated structure. Therefore new routes are demanded for the synthesis of ODAs without alkyl side chain.

In recent years, remarkable numbers of the preparation of functional solids such as porous carbon, metal nanoparticle, and organic polymer are reported by use of porous coordination polymers (PCPs) or metal organic frameworks (MOFs) as sacrificial precursor.⁸ They are also useful platform for the molecular synthesis. Sequential dimerization via the [2+2] cycloaddition, [2+2+2] cyclotrimerization, and the formation of an anhydride bridge between free carboxylic groups are the examples.⁹ These topochemical reactions were conducted by use of the robust crystal structure of PCP/MOFs, and this is not applicable for the various oligomer formations. This is because of the difficulty for the preparation of such topotactic reaction environment for oligomers. Development of the synthetic route of organic oligomers such as ODA without side alkyl chain by use of PCP/MOFs is therefore of general importance and challenge. For the synthesis of oligomer, we focused on the anisotropic thermal expansion (ATE) of the flexible PCP/MOFs derived from vibration of the ligands and the metal nodes.10 Topochemical oligomer synthesis requires the appropriate positioning of several monomers in the crystal structure. The ATE property of PCP/MOF would provide such a situation at a certain temperature as shown in Scheme 1.1 Here, we demonstrated the synthesis of various ODAs without alkyl side chain by use of the PCP/MOFs having two dimensional (2D) structures.

Scheme 1. Schematic illustration of the oligomer synthesis via ATE property of PCP/MOFs.



RESULTS AND DISCUSSION

We synthesized a bipyridyl ligand having butadiyne unit for the monomer as shown in Scheme S1. We denote it as bpb (bpb = 1,2-bis(4-pyridyl)butadiyne). We first investigated the oligomerization of bpb under conventional route such as UV irradiation and thermal treatment. However we recovered bpb, which means the oligomerization does not proceed in either route. We next synthesized a 2D interdigitated framework, [Zn(ip)(bpb)], which is denoted as ZnCID-24 (CID = coordination polymer with interdigitated structure, ip = isophthalate), as a template for preparation of ODAs. The crystal structure of ZnCID-24, which was determined by single crystal X-ray diffraction analysis at -120 °C, is shown in Figure 1. Each Zn²⁺ is in a distorted octahedral geometry, being coordinated by two nitrogen atoms of the bpb at the axial positions, two oxygen atoms from the chelating carboxylate groups of the ip in the equatorial plane. The Zn²⁺ and ip form a one dimensional (1D) double chain structures along the b axis and the further linkages of those chains via the bpb in the axial positions generate a two dimensional structure (Figure 1a, 1b). The 2D structures are interdigitated mutually to create a stable three dimensional (3D) assembled architecture from π - π interactions between the aryl planes of the ip (bond distance = 3.7 Å) (Figure 1c).



Figure 1. Crystal structure of ZnCID-24 showing: (a) 1D double chain of $[Zn(ip)]_n$, (b) 2D layer structure, and (c) 3D as-

sembled structure, where the gray, blue, red, and green colors denote C, N, O, and Zn, respectively, and H atoms are omitted.

Existence of guest DMF in crystal structure was confirmed by 'H NMR and thermogravimetric analysis (TGA). In the crystal structure, the guest DMF molecules are disordered even at –120 °C, therefore the positions of the guest molecules are not determined. Degas treatment of the single crystal of ZnCID-24 with guest gave the crystal structure of guest-free ZnCID-24. The crystal structure shows only a small difference of the assembled structure when compared to the ZnCID-24 with guest, and therefore the ZnCID-24 is regarded as a robust structure upon the guest adsorption/desorption (Table S2).

In order to investigate the thermal expansion property of the ZnCID-24, we performed variable temperature single crystal X-ray diffraction analysis over the temperature range of between –120 and 26 °C.



Figure 2. ZnCID-24; (a) Temperature-dependence unit cell parameters from -120 °C values determined by single crystal XRD for *a* (red) and *b* (blue) axis, *c* axis (black). (b) PXRD patterns from 25 to 300 °C. (c) Temperature-dependence unit cell parameters determined by PXRD for *c* axis. (d) TG/DTA profile.

As shown in Figure 2a, unit cell of the ZnCID-24 shows anisotropic thermal expansion (ATE) behavior. Thermal vibration of aryl plane of ip give the expansion along the b axis, and negative expansion along the a axis is caused by

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59 60 slipping of the assemble layer derived from repulsion between aryl planes of ip. The expansion along the *c* axis is indicative of the dynamic nature of bpb and it exhibits the highest expansion behavior. The coefficient of thermal expansion (α) over the temperature of between –120 and $26 \, ^{\circ}\text{C}$ are $\alpha_a = +44 \times 10^{-6}$, $\alpha_b = -20 \times 10^{-6}$ and $\alpha_c = +110 \times 10^{-6}$ K⁻¹, respectively. The coefficient of thermal expansion along the c axis is comparable to that of Nylon-6." We measured variable temperature powder X-ray diffraction (PXRD) of ZnCID-24 in the temperature range of 28-300 °C (Figure 2b). The reflection from the *c* axis shifts toward lower angle of 2 theta, suggesting a gradual structural transformation caused by the heating. The unit cell parameters of the *c* axis are calculated by the fitting analysis of PXRD patterns. As shown in Figure 2c, the unit cell parameters along the *c* axis in the ZnCID-24 exhibit even more expansion behavior over the temperature range of 28–300 °C. The α parameter indicates higher thermal expansion behavior (+479×10⁻⁶ K⁻¹) compared with the temperature range below 28 °C. Therefore the ZnCID-24 exhibits specific thermal expansion behavior along the c axis, where indicates the dynamic nature of bpb, according to the heating.

We performed TGA coupled with the differential thermal analysis (DTA) for the ZnCID-24 as shown in Figure 2d. TGA shows weight loss of 4% at 290 °C, and then weight loss of 35% at the temperature of 380-450 °C. From mass spectrometry and 'H NMR analyses, the first weight loss (4% at 230-300 °C) for the ZnCID-24 is the release of bpb, and the second weight loss suggests the decomposition of ip and oligomeric bpb compounds (Figure S2). On the other hand, DTA exhibits a clear exothermic peak at 300 °C. Each H₂ip, bpb and analogous interdigitated framework with 4, 4'-bipyridyl ligand, $[Zn(ip)(bpy)]_n$, ^{inc} does not show an exothermic peak as heating (Figure S₃). The exothermic event at 300 °C for the ZnCID-24 implies cross-linking of bpb in the structure due to the heating. For the cross linking of diacetylene moiety, repeated distance of 4.9 Å are required.^{3a} According to the thermal stimulation to the ZnCID-24, the distance between bpb get close to that distance, and then cross linking reaction would proceed in the framework as illustrated in Scheme 1.

To elucidate the oligomer formation in the framework, we conducted heat treatment of the ZnCID-24 at the temperature of 320 °C, where it is above the temperature of exhibits exothermic peak from TG/DTA profile. The heated ZnCID-24 is denoted as H-ZnCID-24, where H indicates heat treatment has completed. Elemental analysis of the H-ZnCID-24 shows the component derived from the releasing of bpb from the ZnCID-24 PXRD pattern of the H-ZnCID-24 shows no significant diffraction peaks because of the loss of crystallinity (Figure S4). We performed solid state NMR measurements with ¹³C Dipolar Decoupling Magic Angle Spinning (DDMAS) for the ZnCID-24 and the H-ZnCID-24 (Figure 3a).



Figure 3. (a) ¹³C DDMAS spectra of ZnCID-24 (grey), H-ZnCID-24 (black). (b) CO_2 adsorption (solid circles) and desorption (open circles) isotherms of ZnCID-24 (grey), H-ZnCID-24 (black). (c) MALDI-TOF-MS spectrum of EH-ZnCID-24. (d) Schematic view of cross linking behavior of bpb in the ZnCID-24.

A single peak at 78 ppm corresponding to adjacent C–C triple bonds in bpb is observed in the ZnCID-24, whereas the H-ZnCID-24 does not have the peak, because all the adjacent C-C triple bonds of bpb reacted as heating. The peaks from the generated C-C triple and double bonds in the H-ZnCID-24 are at the aromatic region of 110-160 ppm due to the change of bond environment. To observe the porous structure of the framework after the thermal treatment, we performed CO₂ adsorption measurement of the H-ZnCID-24 at -78 °C. The adsorption isotherm in Figure 3b shows a gradual rise from the low relative pressure region, which suggests the presence of microporous structure. The adsorbed amount of CO₂ in the H-ZnCID-24 is 42 mL g⁻¹. On the other hand, although the ZnCID-24 also shows similar adsorption behavior, the adsorbed amount of CO_2 is 33 mL g⁻¹. The deference of adsorbed amount between the H-ZnCID-24 and the ZnCID-24 would result from the increase of the adsorbed site of CO₂ molecules due to the structure transformation of bpb.

We etched the H-ZnCID-24 with EDTA·4Na solution (EDTA = ethylenediamine tetraacetic acid) to remove Zn and ip. The etched sample is denoted as EH-ZnCID-24. Matrix Assisted Laser Desorption Ionization-Time of Flight-Mass (MALDI-TOF-MS) spectrum of the EH-ZnCID-24 is shown in Figure 3c. The EH-ZnCID-24 shows the repeated peaks of m/z = 204.1, which corresponds to the molecular weight of bpb. On the other hand, the EH-ZnCID-24 does not show the peak of m/z = 204.1 derived from bpb monomer and dimer in the mass spectra below

m/z = 300 measured by APCI–MS (Figure S8g). As a further characterization, we conducted elemental analysis for the EH-ZnCID-24, and the result matched with protonated bpb oligomer (Table S1). Thus, it proves the cross linking reaction of bpb in the ZnCID-24 occurs upon heating to create the ODA without side alkyl chain as shown in Figure 3d. Both ionization profiles of the MALDI and the APCI suggest trimer is the dominant product for this case. On the other hand, 20 unit oligomer as a maximum cross linking product is also observed. The oligomer with long unit would be formed from small crystal particles, which are able to transfer the heat quickly.

We studied the mechanism of the preference trimer formation. To investigate the effect of reaction temperature for the oligomerization behavior, we heated the ZnCID-24 at the temperature of 200, 250, and 300 °C, and characterized the oligomerization by APCI-MS measurements (Figure S8d-f). The oligomer formation (trimer dominant) is only observed for the reaction at 300 °C, and the products prepared at 200 and 250 °C do not contain any oligomer species. We next changed heating rate from $5 \,^{\circ}\text{C} \,^{\text{min}^{-1}}$ to 1 and 15 $\,^{\circ}\text{C} \,^{\text{min}^{-1}}$ to study the influence of the heating rate to the formation of oligomer. The products are same as those obtained from 5 °C min⁻¹, and the oligomerization is independent on the heating rate (Figure S11). From the results ¹H NMR, TGA-MS, and the reactions under different temperatures or heating rates, the cross linking happens due to ATE along the release of partial bpb in the structure, and is under the thermodynamic process.

In order to determine the growth direction of the oligomer, we prepared other interdigitated framework with naphthalene dicarboxylate instead of ip, $[Zn(ndc)(bpb)]_n$ which is denoted as ZnCID-25 (Figure 4, ndc = naphthalene 2,7-dicarboxylate).



Figure 4. (a) The 1D double chain of $[Zn(ip)]_n$ from ZnCID-24 and $[Zn(ndc)]_n$ from ZnCID-25. (b) MALDI-TOF-MS spectrum of EH-ZnCID-25.

ZnCID-25 is constructed from 1D ribbon chains with an eight-membered ring of Zn²⁺, two ndc moieties, and bpb coordinating to Zn²⁺, which forms the 2D layers, and the layers are also interdigitated to create a 3D assembled structure. As shown in Figure 4a, the distance of between

bpb along the *b* axis is 2.4 Å larger than that of the ZnCID-24. We heated the ZnCID-25 at 320 °C for 15 min, and then etched the heated sample by using EDTA·4Na solution in the same manner with the case of the ZnCID-24. As shown in Figure 4b, MALDI–TOF–MS spectrum of the EH-ZnCID-25 shows the repeated peaks, and the trimer formation are dominant. The results suggest that the elongation of the *b* axis by applying ndc instead of ip in the structure does not affect the formation of ODA and they grow along the *a* axis, which is the inter-layer direction.

We further investigated the effect of the metal ion in the interdigitated PCP structure for the formation of ODA. We synthesized different metal derivatives of the ZnCID-24; CoCID-24 and CuCID-24. Both of the crystal structures show analogous interdigitated motif, whereas they exhibit the differences of bond distance and angle (Table S2). Both of the TG/DTA profiles exhibit exothermic peaks attributed from the oligomerization at the temperature of 330 °C and 260 °C, respectively (Figure S14c, S14d). Accordingly, we characterized the oligomerization of the etched samples by MALDI–TOF–MS measurements (Figure 5a).



Figure 5. (a) MALDI-TOF-MS spectra of the (left) EH-CuCID-24 and (right) EH-CoCID-24. (b) Emission spectra of EH-ZnCID-24 (black), EH-CoCID-24 (blue), EH-CuCID-24 (red), and EH-ZnCID-25 (green) in water.

Etched product from H-CoCID-24 (EH-CoCID-24) provides mainly trimer molecules which is similar with that of the EH-ZnCID-24, whereas the EH-CuCID-24 provides dimer dominantly. The ATE property of PCP/MOFs are influenced by the metal ions (Figure Sıb and Figure Sı4c, Sı4d),¹³ and the observed distinct formation of ODAs would be derived from the different ATE property of each interdigitated structure. The extent of cross-linking process in ODAs was monitored by recording emission profile of etched products. As shown in Figure 5b, the EH-CuCID-24, in which dimer formation is dominant, exhibits the emission band at 420 nm. On the other hand, the emission band of the EH-ZnCID-24, the EH-CoCID-24 and the EH-ZnCID-25, in which trimer formation are dominant, red shifted around 570 nm suggesting increased conjugation. These fluorescence properties also support the emission behavior from the oligomer state.⁷

CONCLUSION

In this work, we employed ATE property of the flexible PCP/MOFs for the topochemical synthesis of ODAs without alkyl side chain. ZnCID-24 having 2D structure expands the crystallographic unit cell along the *c* axis due to the heating. It is accompanied with the releasing of bpb, and then bpb forms oligomer in the framework at the temperature above 300 °C. The oligomeric unit of the products depend on the metal ions in frameworks, where Zn^{2+} and Co^{2+} show trimer formation and Cu^{2+} shows dimer formation dominantly. The ATE property is often observed in PCP/MOFs, but no attempt is reported for the synthesis of functional molecules so far. The proposed approach in this work would inspire the new route of synthesizing of various functional oligomers.

EXPERIMENTAL SECTION

Synthesis of ZnCID-24. $Zn(NO_3)_2 \cdot 6H_2O$ (298 mg, 1.0 mmol), isophthalic acid (166 mg, 1.0 mmol), bpb (204 mg, 1.0 mmol), DMF (40 mL), and MeOH (10 mL) were added to a 150 mL screw glass vial, then heated at 80 °C for 24 h. Pale yellow crystals thus produced were washed with DMF (50 mL × 2) and MeOH (20 mL × 1). In order to remove the guest solvent, the crystals were immersed in deoxidized MeOH (50 mL) for overnight, and then degassed under vacuum at 80 °C for 12 h. Synthetic procedures of ZnCID-25, CuCID24, and CoCID-24 were mentioned in the supporting information.

Heat treatment of CID-derivatives. Degassed sample (100 mg) was homogenously placed on a ceramic boat (16 \times 12 \times 80 mm), and then heated up to the targeted temperature with heating rate of 5 °C min⁻¹ under a flow of nitrogen (0.5 L min⁻¹). After the holding for 15 min at target temperature, H-CID-derivative was obtained. As a target temperature, ZnCID-24, ZnCID-25, CuCID-24, and CoCID-24 were adopted at 320, 320, 290, and 380 °C, respectively.

Etching of H-CID-derivatives. EH-CID-derivatives were prepared by etching of H-CID-derivative with 0.05 M EDTA solution. Typically, H-ZnCID-24 (30 mg) was stirred in 0.05 M EDTA solution (5 mL) for overnight, and then insoluble residue, which is EH-CID-derivative, was washed repeatedly with distillation water (5 mL \times 2) and MeOH (5 mL \times 1). For the MALDI-TOF-MS and the Fluorescence measurements, EH-CID-derivative was further dissolved in 3 M HCl solution, and then a solution was evaporated.

Single Crystal X-ray Diffraction Analyses. Single crystal X-ray diffraction measurements were performed with a Rigaku AFC10 diffractometer with Rigaku Saturn Kappa CCD system equipped with a MicroMax-007 HF/VariMax rotating-anode X-ray generator with confocal monochromated MoKa radiation. The structures were solved by a direct method (SHELXT-2014) and refined by full-matrix least-squares procedures on F2 for all reflections (SHELXL-2017). The hydrogen atoms were positioned geometry and refined using a riding model. In the crystal structures of ZnCID-24, CuCID-24, and CoCID-24, guest DMF is highly disordered and the SQUEEZE function of PLATON were used to eliminate the contribution of the electron density in the solvent region from the intensity data, and the solvent-free model was employed for the final refinement. For the refinement of the crystal structure of ZnCID-24, we removed 97 electrons by using SQUEEZE command. This corresponds to one DMF which was confirmed by 'H NMR, and TGA. We estimated the percentage of solvent accessible voids (SAVs) by using PLATON software and these are 32 % for guest-free ZnCID24.14

General Methods. Variable temperature PXRD data were collected on a Rigaku SmartLab multi-purpose diffractometer (Cu Ka radiation) equipped with temperature changer attachment. The unit cell parameters of *a*, *b*, and c axis were calculated by the fitting analysis of PXRD patterns using PDXL software from Rigaku. TG/DTA was performed using a Rigaku Thermo plus TG 8120 at the temperature range from 30 to 500 °C under N₂ gas flowing atmosphere with the ramping rate of 5 °C min⁻¹. TG-MS was performed with a Rigaku Thermo plus EVO II equipped with ThermoMass Photo/S by using electron impact ionization method. FT-IR were performed with Thermo Fisher Scientific Nicolet iS5. Liquid ¹H NMR spectra were recorded on a JEOL JNM-ECS400. Solid-state ¹³C DDMAS NMR spectra were recorded on a Bruker Biospin, ADVANCE III 400 NMR spectrometer. The spinning rate for DDMAS spectra was 12 kHz. MALDI-TOF-MS were performed with Bruker Daltonics ultraflex. As a matrix molecule, we used 2,5-dihydroxybenzoic acid. APCI-MS were performed with Thermo Fisher Scientific EXACTIVE. CO₂ adsorption isotherms were measured at -78 °C by BELSORP-mini with dry ice and MeOH dewar. PCP samples were activated by heating at 120 °C under reduced pressure (< 10⁻² Pa) for 12 h prior to the measurement. The excitation and emission spectra for the etched compounds were measured using Horiba FluoroLog-3 instrument.

ASSOCIATED CONTENT

Supporting Information. Experimental details and additional characterizations (PXRD, TG/DTA, TG–MS, FT–IR, ¹H NMR, CO₂ adsorption, MALDI–TOF–MS, APCI–MS, fluorescence, and crystallographic data). Crystallographic data in CIF format, CCDC reference numbers 1520515–152519. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors.

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REFERENCES

(1) Wegner, G., Z. Naturforschung B 1969, 24, 824.

(2) (a) Sarkar, A.; Okada, S.; Matsuzawa, H.; Matsuda, H.; Nakanishi, H., *J. Mater. Chem.* **2000**, *10*, 819. (b) Zhou, W.; Li, Y.; Zhu, D., *Chem. Asian J.* **2007**, *2*, 222. (c) Yoon, B.; Lee, S.; Kim, J.-M., *Chem. Soc. Rev.* **2009**, *38*, 1958. (d) Lee, S.; Kim, J.-Y.; Chen, X.; Yoon, J., *Chem. Commun.* **2016**, *52*, 9178.(e) Jelinek, R.; Ritenberg, M., *RSC Adv.* **2013**, *3*, 21192.

(3) (a) Reppy, M. A.; Pindzola, B. A., *Chem. Commun.* 2007, 4317. (b) Sun, X.; Chen, T.; Huang, S.; Li, L.; Peng, H., *Chem. Soc. Rev.* 2010, 39, 4244. (c) Chen, X.; Zhou, G.; Peng, X.; Yoon, J., *Chem. Soc. Rev.* 2012, 41, 4610. (d) Yarimaga, O.; Jaworski, J.; Yoon, B.; Kim, J.-M., *Chem. Commun.* 2012, 48, 2469.

(4) (a) Ottonelli, M.; Musso, G.; Comoretto, D.; Dellepiane, G., Phys. Chem. Chem. Phys. 2002, 4, 2754. (b) Pilzak, G. S.; van Lagen, B.; Hendrikx, C. C. J.; Sudhölter, E. J. R.; Zuilhof, H., Chem. Eur. J. 2008, 14, 7939. (c) Pilzak, G. S.; van Gruijthuijsen, K.; van Doorn, R. H.; van Lagen, B.; Sudhölter, E. J. R.; Zuilhof, H., Chem. Eur. J. 2009, 15, 9085.

(5) (a) Lauher, J. W.; Fowler, F. W.; Goroff, N. S., Acc. Chem. Res. 2008, 41, 1215. (b) Fowler, F. W.; Lauher, J. W., J. Phys. Org. Chem., 2000, 13, 850. (c) Wilhelm, C.; Boyd, S. A.; Chawda, S.; Fowler, F. W.; Goroff, N. S.; Halada, G. P.; Grey, C. P.; Lauher, J. W.; Luo, L.; Martin, C. D.; Parise, J. B.; Tarabrella, C.; Webb, J. A., J. Am. Chem. Soc., 2008, 130, 4415. (d) Curtis, S. M.; Le, N.; Fowler, F. W.; Lauher, J. W., Cryst. Growth Des., 2005, 5, 2313.

(6) (a) Pilzak, G. S.; Baggerman, J.; van Lagen, B.; Posthumus, M. A.; Sudhölter, E. J. R.; Zuilhof, H., *Chem. Eur. J.* 2009, *15*, 2296.
(b) Polhuis, M.; Hendrikx, C. C. J.; Zuilhof, H.; Sudhölter, E. J. R., *Tetrahedron Lett.* 2003, *44*, 899.

(7) Zhu, L.; Trinh, M. T.; Yin, L.; Zhang, Z., Chem. Sci. 2016, 7, 2058.

(8) (a) Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L., Acc. Chem. Res. **1998**, *31*, 474. (b) Kitagawa, S.; Kitaura, R.; Noro, S.-i., Angew. Chem. Int. Ed. **2004**, *43*, 2334. (c) Chaikittisilp, W.; Ariga, K.; Yamauchi, Y., J. Mater. Chem. A **2013**, *1*, 14. (d) Li, S.-L.; Xu, Q., Energy Environ. Sci. **2013**, *6*, 1656. (e) Zhao, Y.; Song,

Z.; Li, X.; Sun, Q.; Cheng, N.; Lawes, S.; Sun, X., *Energy Storage Mater.* **2015**, *2*, 35. (f) Xia, W.; Mahmood, A.; Zou, R.; Xu, Q., *Energy Environ. Sci.* **2015**, *8*, 1837. (g) Sun, J.-K.; Xu, Q., *Energy Environ. Sci.* **2014**, *7*, 2071. (h) Lux, L.; Williams, K.; Ma, S., Cryst. Eng. Comm. **2015**, *17*, 10. (i) Uemura, T.; Yanai, N.; Kitagawa, S., *Chem. Soc. Rev.* **2009**, *38*, 1228. (j) Distefano, G.; Suzuki, H.; Tsujimoto, M.; Isoda, S.; Bracco, S.; Comotti, A.; Sozzani, P.; Uemura, T.; Kitagawa, S., *Nat. Chem.* **2013**, *5*, 335. (k) Furukawa, Y.; Ishiwata, T.; Sugikawa, K.; Kokado, K.; Sada, K., *Angew. Chem. Int. Ed.* **2012**, *51*, 10566. (l) Ishiwata, T.; Furukawa, Y.; Sugikawa, K.; Kokado, K.; Sada, K., *J. Am. Chem. Soc.* **2013**, *135*, 5427. (m) Allen, C. A.; Cohen, S. M., *Inorg. Chem.* **2014**, **53**, 7014.

(9) (a) Medishetty, R.; Park, I.-H.; Lee, S. S.; Vittal, J. J., Chem. Commun. 2016, 52, 3989. (b) Mir, M. H.; Koh, L. L.; Tan, G. K.; Vittal, J. J., Angew. Chem. Int. Ed. 2010, 49, 390. (c) Sato, H.; Matsuda, R.; Mir, M. H.; Kitagawa, S., Chem. Commun. 2012, 48, 7919. (d) Hu, F.-L.; Wang, H.-F.; Guo, D.; Zhang, H.; Lang, J.-P.; Beves, J. E., Chem. Commun. 2016, 52, 7990. (e) Park, I.-H.; Chanthapally, A.; Zhang, Z.; Lee, S. S.; Zaworotko, M. J.; Vittal, J. J., Angew. Chem. Int. Ed. 2014, 53, 414. (f) Park, I.-H.; Medishetty, R.; Lee, H.-H.; Mulijanto, C. E.; Quah, H. S.; Lee, S. S.; Vittal, J. J., Angew. Chem. 2015, 127, 7421. (g) Ragon, F.; Campo, B.; Yang, Q.; Martineau, C.; Wiersum, A. D.; Lago, A.; Guillerm, V.; Hemsley, C.; Eubank, J. F.; Vishnuvarthan, M.; Taulelle, F.; Horcajada, P.; Vimont, A.; Llewellyn, P. L.; Daturi, M.; Devautour-Vinot, S.; Maurin, G.; Serre, C.; Devic, T.; Clet, G., J. Mater. Chem. A 2015, 3, 3294. (h) Wei, Y.-S.; Zhang, M.; Liao, P.-Q.; Lin, R.-B.; Li, T.-Y.; Shao, G.; Zhang, J.-P.; Chen, X.-M., Nat. Comm. 2015, 6, 8348.

(10) (a) Dubbeldam, D.; Walton, K. S.; Ellis, D. E.; Snurr, R. Q., Angew. Chem. 2007, 46, 4496. (b) Wu, Y.; Kobayashi, A.; Halder, G. J.; Peterson, V. K.; Chapman, K. W.; Lock, N.; Southon, P. D.; Kepert, C. J., Angew. Chem. 2008, 47, 8929. (c) Yang, C.; Wang, X.; Omary, M. A., Angew. Chem. 2009, 48, 2500. (d) Walker, A. M.; Civalleri, B.; Slater, B.; Mellot-Draznieks, C.; Corà, F.; Zicovich-Wilson, C. M.; Román-Pérez, G.; Soler, J. M.; Gale, J. D., Angew. Chem. Int. Ed. 2010, 49, 7501. (e) DeVries, L. D.; Barron, P. M.; Hurley, E. P.; Hu, C.; Choe, W., J. Am. Chem. Soc. 2011, 133, 14848. (f) Grobler, I.; Smith, V. J.; Bhatt, P. M.; Herbert, S. A.; Barbour, L. J., J. Am. Chem. Soc. 2013, 135, 6411. (g) Henke, S.; Schneemann, A.; Fischer, R. A., Adv. Funct. Mater. 2013, 23, 5990. (h) Lock, N.; Christensen, M.; Wu, Y.; Peterson, V. K.; Thomsen, M. K.; Piltz, R. O.; Ramirez-Cuesta, A. J.; McIntyre, G. J.; Noren, K.; Kutteh, R.; Kepert, C. J.; Kearley, G. J.; Iversen, B. B., Dalton Trans. 2013, 42, 1996. (i) Cai, W.; Katrusiak, A., Nat. Comm. 2014, 5, 4337. (j) Wu, Y.; Peterson, V. K.; Luks, E.; Darwish, T. A.; Kepert, C. J., Angew. Chem. Int. Ed. 2014, 53, 5175. (k) Zhou, H. L.; Zhang, Y. B.; Zhang, J. P.; Chen, X. M., Nat. Comm. 2015, 6, 6917.

(11) (a) Li, D.; Kaneko, K., *Chem. Phys. Lett.* **2001**, *335*, 50. (b) Kitaura, R.; Seki, K.; Akiyama, G.; Kitagawa, S., *Angew. Chem. Int. Ed.* **2003**, *42*, *428*. (c) Horike, S.; Tanaka, D.; Nakagawa, K.; Kitagawa, S., *Chem. Commun.* **2007**, *3395*.

(12) Segal, L., Polym. Eng. Sci. 1979, 19, 365.

(13) (a) Zhao, T.-M.; Chen, S.; Shang, R.; Wang, B.-W.; Wang, Z.-M.; Gao, S., *Inorg. Chem.* **2016**, 55, 10075. (b) Breeze, M. I.; Clet,

G.; Campo, B. C.; Vimont, A.; Daturi, M.; Grenèche, J.-M.; Dent,

A. J.; Millange, F.; Walton, R. I., *Inorg. Chem.* 2013, 52, 8171.
 (14) Spek, A. L, *Acta. Cryst.* 2009, D65, 148.

