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### Introduction

An intriguing issue in the domain of coordination networks is the construction of an attractive topology, preferably with practical task-specific roles.<sup>1-9</sup> Some functional coordination networks have been widely synthesized by self-assembly of metal ions and polydentate ligands in consideration of various factors such as anions, mole ratios, reaction temperature, and reaction solvents.<sup>10–14</sup> Among diverse coordination networks, three-connected open-skeletons are promising candidates as structural models for scaffolding-like functional materials<sup>15–19</sup> that can serve as alternatives to four-connected diamonoid skeletons.<sup>20,21</sup> Thus, some metal coordination networks have been used as practical solid catalysts for organic reactions.<sup>22–31</sup> The transesterification reaction, for example, is a basic, fundamentally important process for mass-production of bio-diesel

## Enantiomeric two-fold interpenetrated 3D zinc(II) coordination networks as a catalytic platform: significant difference between water within the cage and trace water in transesterification<sup>†</sup>

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Self-assembly of  $Zn(ClO_4)_2$  with 1,1,2,2-tetramethyl-1,2-di(pyridin-3-yl)disilane (L) as a bidentate N-donor gives rise to 3D coordination networks,  $[Zn(\mu-OH)(L)]_3(ClO_4)_3$ .5H<sub>2</sub>O (**1**·5H<sub>2</sub>O), of unique,  $10^3$ -*a srs* net topology. An important feature is that two enantiomeric 3D frameworks,  $4^1$ - and  $4^3$ - $[Zn(\mu-OH)(L)]_3(ClO_4)_3$ .5H<sub>2</sub>O, are interpenetrated to form a racemic two-fold 3D network with cages occupied by two water molecules. Another structural characteristic is a  $C_3$ -symmetric planar  $Zn_3(\mu-OH)_3$  6-membered ring with tetrahedral Zn(n) ions. The steric hindrance of substrates and trace water effects on transesterification catalysis using the network have been scrutinized. The coordination network acts as a remarkable heterogeneous transesterification catalytic system that shows both the significant steric effects of substrate alcohols and momentous water effects. The substrate activity is in the order ethanol > *n*-propanol > *n*-butanol > iso-propanol > 2-butanol > *tert*-butanol. For the reaction system, solvate water molecules within the cages of the interpenetrated 3D frameworks do not decrease the transesterification activity, whereas the trace water molecules in the substrate alcohols act as obvious obstacles to the reaction.

from any fat or soybean oil; and indeed, the synthesis of biodiesel from renewable biological sources has advantages both environmentally and with respect to sustainable production.<sup>33,34</sup> Furthermore, such a transesterification is more efficient for the formation of esters than esterification reaction from carboxylic acids and alcohols, presumably owing to solubility and molecular structure behaviors. General transesterifications often have been catalyzed, and thus are sensitive to catalysts, moisture, pressure, and other factors.<sup>32–34</sup> Zn( $\pi$ ) species such as zinc ( $\pi$ ) oxide and zinc( $\pi$ ) coordination polymers have been used effectively as esterification and transesterification catalysts.<sup>35,36</sup>

In this context, systematic research on the specific influence on transesterification *via* a unique racemic crystal of two enantiomeric two-fold 3D zinc(II) networks,  $[Zn(\mu-OH)$ (L)]<sub>3</sub>(ClO<sub>4</sub>)<sub>3</sub>·5H<sub>2</sub>O, as a solid catalyst, has been carried out. The two aims of this research were to explore the steric effects of substrate alcohols as well as the trace water effects on solid transesterification catalysis. Notably, significantly different effects between trace water molecules in reactant alcohols and isolated water molecules within the cages of the network are reported herein. Generally, zinc(II) complexes have been investigated and deemed to be appropriate for tetrahedral-binding Lewis acidity, metallo-enzymes, zinc finger proteins, transmetallation, and homogeneous catalysis<sup>37–43</sup> in the transesterification of a wide range of esters with alcohols.<sup>35,36</sup>

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<sup>†</sup> Electronic supplementary information (ESI) available: TGA and DSC curves, <sup>1</sup>H NMR spectra, FT-IR spectra, ICP-OES data and powder X-ray diffraction patterns of the present zinc( $\pi$ ) compounds, ORTEP drawing of [Zn( $\mu$ -OH)(L)](ClO<sub>4</sub>), crystal structures of [ZnBr<sub>2</sub>L], and <sup>1</sup>H NMR spectra for the procedure of transesterification using [Zn( $\mu$ -OH)(L)](ClO<sub>4</sub>). CCDC 1522055 and 1522056. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7dt00217c

### **Experimental**

### Materials and methods

All chemicals including zinc( $\pi$ ) bromide, zinc( $\pi$ ) perchlorate hexahydrate, *n*-butyllithium, 3-bromopyridine, and 1,2-dichlorotetramethyldisilane were purchased from Sigma-Aldrich and used without further purification. 1,1,2,2-Tetramethyl-1,2-di(pyridin-3-yl)disilane (L) was prepared by our previously reported method.<sup>44</sup> Elemental analyses (C, H, N) were performed on crystalline samples at the KBSI Pusan Center using a Vario-EL III analyzer. <sup>1</sup>H (300 MHz) and <sup>13</sup>C (75 MHz) NMR spectra were obtained on a Varian Mercury Plus 300. Infrared spectra were recorded on a Nicolet 380 FT-IR spectrophotometer using samples prepared as KBr pellets. Thermal analyses were undertaken under a nitrogen atmosphere at a scan rate of 10 °C min<sup>-1</sup> using a Labsys TGA-DSC 1600. ICP-OES data were recorded using a PerkinElmer Optima 8300 model.

#### Syntheses

[Zn(μ-OH)(L)]<sub>3</sub>(ClO<sub>4</sub>)<sub>3</sub>·5H<sub>2</sub>O (1·5H<sub>2</sub>O). An acetonitrile solution (3 mL) of zinc(II) perchlorate hexahydrate (3.7 mg, 0.01 mmol) was carefully layered onto a tetrahydrofuran solution (3 mL) of L (2.7 mg, 0.01 mmol). The reaction mixture was slowly evaporated to obtain yellow crystals suitable for X-ray single crystallography in 7 days (7.4 mg, 52%). Mp 294 °C (dec.). Elemental Anal. Calcd Found: C, 34.60; H, 5.12; N, 5.84. Calc. for C<sub>42</sub>H<sub>61</sub>N<sub>6</sub>O<sub>15</sub>Si<sub>6</sub>Zn<sub>3</sub>Cl<sub>3</sub>·5H<sub>2</sub>O: C, 34.71; H, 5.06; N, 5.78%. FT-IR  $\nu_{max}/cm^{-1}$ : 1595s, 1411m, 1253m, 1108s, 1061s, 1030w, 825w, 800s, 769w, 705m, 622m, 585m.

[ZnBr<sub>2</sub>(L)] (2). An acetone solution (3 mL) of zinc(II) bromide (3.4 mg, 0.015 mmol) was carefully layered onto an acetonitrile solution (1 mL) of L (4.1 mg, 0.015 mmol), resulting in the formation of yellow crystals suitable for X-ray single crystallography in 4 days (4.9 mg, 65%). Mp 281 °C (dec.). Elemental Anal. Found: C, 33.50; H, 4.19; N, 5.55. Calc. for C<sub>14</sub>H<sub>20</sub>N<sub>2</sub>Si<sub>2</sub>ZnBr<sub>2</sub>: C, 33.78; H, 4.05; N, 5.63%. FT-IR  $\nu_{max}/cm^{-1}$ : 1587s, 1471w, 1402m, 1333w, 1252m, 1201w, 1128w, 1057m, 835m, 789s, 769s, 704s, 656m.

#### Transesterification catalysis

Phenyl acetate (0.13 mL, 1 mmol) was dissolved in each of the alcohols (7.5 mL), and to each the catalyst (0.05 mmol,  $45.4 \text{ mg } 1.5\text{H}_2\text{O}$ ) was added. All of the catalysis reactions were stirred at 50 °C. In the case of the ethanolysis, the catalytic reactions were carried out according to the quantity of water in ethanol (commercially available 99.9%, 98%, and 95% ethanol). Conversion yields were monitored by using <sup>1</sup>H NMR spectra. All of the reactions were run at least three times, and their average conversion yields were recorded.

### Crystal structure determination

X-ray data were collected on a Bruker SMART automatic diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) and a CCD detector at -25 °C. Thirty-six frames of 2D diffraction images were collected and processed to obtain

Table 1 Crystallographic data for  $[Zn(\mu\text{-}OH)(L)]_3(ClO_4)_3\cdot 5H_2O$  (1.5H\_2O) and  $[ZnBr_2(L)]$  (2)

	1.5H2O	2
Formula	C42H73N6O20Si6Zn3Cl3	C14H20N2Si2ZnBr2
$M_{\rm w}$ (g mol <sup>-1</sup> )	1453.06	497.69
Crystal sys.	Cubic	Orthorhombic
Space group	Ia3d	Pnna
a (Å)	30.7561(2)	13.6038(4)
b (Å)	30.7561(2)	25.6130(7)
c (Å)	30.7561(2)	11.8630(3)
$V(Å^3)$	29 093.4(6)	4133.5(2)
$\sigma (g \text{ cm}^{-3})$	1.327	1.599
Z	16	8
$\mu ({\rm mm}^{-1})$	1.252	5.166
F(000)	12 032	1968
R <sub>int</sub>	0.0771	0.0443
Completeness (%)	100.0	100.0
GoF on $F^2$	1.228	1.095
$R_1 \left[ I > 2\sigma(I) \right]^a$	0.0940	0.0298
$wR_2$ (all data) <sup>b</sup>	0.2630	0.0710
${}^{a}R_{1} = \sum   F_{0}  -  F_{c}  /\sum$	$\sum  F_{\rm o} . \ ^{b} wR_{2} = \left(\sum [w(F_{\rm o}^{2} - F_{\rm c}^{2})]\right)$	$^{2}]/\sum[w(F_{o}^{2})^{2}])^{1/2}.$

the cell parameters and orientation matrix. The data were corrected for Lorentz and polarization effects. The absorption effects were corrected using the multi-scan method (SADABS).<sup>45</sup> The structures were resolved using direct methods (SHELXS 2013/1) and refined by full-matrix least squares techniques (SHELXL 2014/7).<sup>46</sup> The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions and refined only for the isotropic thermal factors. The crystal parameters and procedural information corresponding to the data collection and structure refinement are listed in Table 1.

### **Results and discussion**

### Synthesis

The overall synthetic procedure is summarized in Scheme 1. Self-assembly of Zn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O with 1,1,2,2-tetramethyl-1,2-di (pyridin-3-yl)disilane (L) afforded two-fold interpenetrated 3D coordination frameworks of unusual topology, namely the two enantiomers  $4^{1}$ - and  $4^{3}$ -[Zn( $\mu$ -OH)(L)]<sub>3</sub>(ClO<sub>4</sub>)<sub>3</sub>·5H<sub>2</sub>O, in the solvent system (Scheme 1). The structure consists of 6-membered hydrolyzed  $Zn_3(\mu$ -OH)<sub>3</sub> moieties. The formation of the  $Zn_3(\mu$ -OH)<sub>3</sub> skeletal ring can be explained similarly to the account that is available in the literature.47 The reaction of ZnBr<sub>2</sub> with L as an N-donor produced zigzag 1D coordination polymers, [ZnBr<sub>2</sub>(L)], which subsequently were used for the catalysis comparison. These reactions were originally treated at the 1:1 mole ratio of Zn(II): L, but the products were not significantly affected by either the mole ratio or the concentrations, which indicated their thermodynamic stability. The colorless crystalline products,  $[Zn(\mu-OH)(L)]_3(ClO_4)_3 \cdot 5H_2O$  $(1.5H_2O)$  and  $[ZnBr_2(L)]$  (2), are air-stable and insoluble in water, chloroform, and acetone. The products are easily dissociated in N,N-dimethylformamide and dimethylsulfoxide



Scheme 1 Synthetic scheme for 4<sup>1</sup>- and 4<sup>3</sup>-[Zn( $\mu$ -OH)(L)]<sub>3</sub>(ClO<sub>4</sub>)<sub>3</sub>·5H<sub>2</sub>O and catalytic effects.

(Fig. S1<sup>†</sup>); 1·5H<sub>2</sub>O is slightly soluble even in methanol. They were characterized in this study by microanalyses, IR, thermal analyses, and X-ray single crystallography, as will be explained in detail. The decomposition temperature of 2 was 281 °C, and that of 1·5H<sub>2</sub>O was 294 °C (Fig. S2<sup>†</sup>). Their IR spectra were determined to be consistent with their structures (Fig. S3<sup>†</sup>).

#### Crystal structures

The relevant bond lengths and angles are listed in Table 2. 1·5H<sub>2</sub>O has a bridged bidentate L, a 6-membered cyclic  $Zn_3(\mu$ -OH)<sub>3</sub> motif (Zn…Zn = 3.50(1) Å), and the tetrahedral

Table 2 Selected bond distances and bond angles for  $[Zn(\mu\text{-}OH)\ (L)]_3(ClO_4)_3\cdot 5H_2O\ (1\cdot 5H_2O)\ and\ [ZnBr_2(L)]\ (2)$ 

1·5H <sub>2</sub> O		2	
Zn(1)-O(1)	1.924(3)	Zn(1)-N(1)	2.056(2)
$Zn(1) - O(1)^{\#3}$	1.924(3)	Zn(1) - Br(1)	2.3464(4)
$Zn(1)^{\#5} - O(1)$	1.924(3)	Zn(2) - N(2)	2.035(2)
Zn(1)-N(1)	2.027(7)	Zn(2) - Br(2)	2.3475(4)
$Zn(1) - N(1)^{#4}$	2.027(7)		
$O(1) - Zn(1) - O(1)^{\#3}$	109.2(4)	$N(1)-Zn(1)-N(1)^{\#1}$	97.0(1)
O(1) - Zn(1) - N(1)	111.5(2)	$Br(1)-Zn(1)-Br(1)^{\#1}$	124.63(3)
$O(1)^{\#3}$ -Zn(1)-N(1)	106.9(2)	$N(2) - Zn(2) - N(2)^{\#2}$	99.5(1)
$O(1) - Zn(1) - N(1)^{\#4}$	106.9(2)	$Br(2)-Zn(2)-Br(2)^{#2}$	118.46(3)
$O(1)^{\#3}$ -Zn(1)-N(1) <sup>#4</sup>	111.5(2)		
$N(1) - Zn(1) - N(2)^{\#4}$	110.9(4)		

 $^{\#1}-x + 1/2, -y - 1, z, ^{\#2}x, -y + 1/2, -z - 1/2, ^{\#3}z, x, y, ^{\#4}-z + 1/4, -y + 1/4, -x + 1/4, ^{\#5}-y + 1/4, -x + 1/4, -z + 1/4.$ 

zinc(II) ion (Zn–N = 2.027(7) Å; Zn–O = 1.924(3) Å), and thus forms a three-connected 3D network of the  $10^{3}$ -*a* topology type. The distortion of the tetrahedral Zn(II) ion was confirmed by the O(1)–Zn(1)–N(1) bond angles, which ranged from 106.9(2)– 111.5(2)°. The *C*<sub>3</sub>-symmetric Zn<sub>3</sub>(µ-OH)<sub>3</sub> ring adopts a plane (Zn–O–Zn = 130.8(4)°; O–Zn–O = 109.2(4)°) (Fig. S4†), which is in contrast to the known Zn<sub>3</sub>(µ-OH)<sub>3</sub> species.<sup>47</sup> A significant feature is that the two enantiomeric (4<sup>1</sup> and 4<sup>3</sup>) 3D frameworks interpenetrate to form racemic crystals (Fig. 1). The interpenetration of the two enantiomeric bowl parts forms unique cages (3.3 × 3.3 × 5.0 Å<sup>3</sup>) that are occupied by two H<sub>2</sub>O molecules (Fig. 2). The volume of 1.5H<sub>2</sub>O occupying solvate molecules was 19.7% (5740.9/29 093.4 Å) as detected on the basis of PLATON/SOLV calculation.<sup>48</sup> The perchlorate anions act as counteranions rather than ligands.

The structure of 2 is, for catalytic comparison, a 1D sinusoidal coordination polymer (Zn–N = 2.035(2)–2.056(2) Å) for 2



**Fig. 1** Packing structures of  $1.5H_2O$  in a (100) direction (top), and in a (111) direction with highlighted cage moieties (bottom) (red and green indicate interpenetrated 3D coordination polymers, curved arrows indicate the chirality).



Fig. 2 Top views (top) and side view (bottom) for bowl-like cage moieties of  $[Zn(\mu\text{-}OH)(L)]_3.$ 

(Fig. S5†). Each L connects two zinc( $\pi$ ) ions in a  $\mu^2$ -fashion. The geometry of zinc( $\pi$ ) is tetrahedral (N–Zn–N = 97.0(1)–99.5(1)°; Br–Zn–Br = 118.46(3)–124.63(3)°). A period of sinusoidal coordination polymers consists of four zinc( $\pi$ ) halides and four ligands.

#### **Construction principle**

The reaction of  $Zn(ClO_4)_2$  with L afforded three-connected 3D coordination polymeric structures. The bridged-hydroxo zinc(II) network, 1.5H<sub>2</sub>O, was characterized by X-ray crystallography as consisting of enantiomeric  $(4^1 \text{ and } 4^3)$  two-fold 3D coordination polymers; the  $Zn_3(\mu$ -OH)<sub>3</sub> moieties possess a  $C_3$ symmetry, with each hydroxo group bridging to zinc centers. What is the critical driving force behind the formation of bridged-hydroxo species? The bridged-hydroxo moiety probably is formed through hydrolysis of trace water molecules in the reaction system.<sup>47</sup> For instance, in the present study, the addition of trace NaOH in the reaction system accelerated the formation of the product. The structure was favorably selfassembled irrespective of concentrations and mole ratios, indicating that the skeleton is thermodynamically stable. The appropriate torsion angles of the Py-Si-Si-Py ligand might play a significant role in the construction of the topological network. The size of the halide or perchlorate anion seems to partially contribute to the formation of the skeletal network. Rational construction of the desirable, interpenetrated topology would be a challenging issue. In fact, for the  $10^3$  srs net topology, the two enantiomers can elegantly interpenetrate (Fig. 1), as was already known to the Ciani group.<sup>17,49,50</sup>

#### Transesterification catalytic efficiency

First of all, in order to elucidate the steric effects of the substrates on the heterogeneous catalytic activity, 1.5H<sub>2</sub>O was employed in a transesterification reaction of phenyl acetate with various alcohols<sup>51</sup> because, as stated in the introduction, not only are transesterifications carried out without side reactions, but also the reactions are very useful in the bio-fuels molecular system.<sup>33</sup> 1.5H<sub>2</sub>O (0.05 mmol) significantly catalyzed the reactions of phenyl acetate (1 mmol) with excess alcohols. The catalysis process was monitored by using <sup>1</sup>H NMR spectra (Fig. S6<sup>†</sup>). The catalytic yields at 60 min are shown in Tables S1-S3.† A control reaction without the catalysts, meanwhile, showed trace amounts of ester-converted product in 5% yield even for 3 days. The catalyst showed drastic alcohol related steric effects in the order EtOH > n-PrOH > n-BuOH > iso-PrOH > 2-BuOH > tert-BuOH, indicating, as depicted in Fig. 3, a strong dependency of the reaction rate on the bulkiness of alcohols. For the catalysis reaction of phenyl acetate with EtOH, comparable catalytic systems were compared, resulting in the order  $1.5H_2O > a$  mixture of  $Zn(ClO_4)_2$  and L > 2 (Fig. 4), which indicated that the present catalytic system,  $1.5H_2O_1$ , is a superior catalyst to the others. The catalytic reaction using a simple mixture of ZnClO<sub>4</sub> and L instead of the catalyst proceeded at a much slow rate, suggesting that the detailed structure of 1.5H2O is another important factor. The reaction rate of  $1.5H_2O > 2$  can be explained in terms of the difference in the nature of the OH and bulky Br moiety around the tetrahedral zinc(II) ion. This hydroxyl effect is consistent with both the esterification and transesterification activities of zinc hydroxy nitrate (Zn<sub>5</sub>(OH)<sub>8</sub>(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O).<sup>9,10</sup> Accordingly, the trace water molecules in each of the alcohols drastically decreased the reaction rates. For example, the reaction in general EtOH (95%) was much slower than that in absolute EtOH. The same reaction rate in 98% EtOH is the median value (Fig. 5), indicating that trace water is very sensitive to



**Fig. 3** Plot showing catalytic yields of transesterification of phenyl acetate using  $1.5H_2O$  in EtOH (red line), *n*-propanol (blue line), *n*-butanol (green line), iso-propanol (purple line), 2-butanol (orange line), and *tert*-butanol (pink line).

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Fig. 4 Plot showing catalytic yields of transesterification of phenyl acetate in 99.9% EtOH using  $1.5H_2O$  (solid red line),  $ZnClO_4 + L$  (solid blue line), and 2 (solid green line) under the same conditions described in the Experimental section.



Fig. 5 Plot showing catalytic yields of transesterification of phenyl acetate using  $1.5H_2O$  in 99.9% EtOH (solid red line), 98% EtOH (solid green line), and 95% EtOH (solid purple line), and 1 in 99.9% EtOH (dashed blue line) under the same conditions described in the Experimental section.

transesterification. The most significant result, however, was that the water solvate molecules within cages do not play any significant role in the reaction, indicating that they are safely nestled. In comparison of catalytic efficiency, the water-de-solvate species 1, which is prepared by heating at 50 °C under vacuum for 2 days, showed a similar result. The perchlorate groups were located in the vacant sites, and were not involved in the coordination of the Zn( $\pi$ ) cations. The alcohol substrate-approaching frequency to the Zn( $\pi$ ) center might be a key factor in transesterification. The solubility of  $1.5H_2O$  is an additional significant factor relevant to catalytic efficiency. For example, in MeOH, the catalyst was soluble, and thus, the reaction rate was very fast, and the reaction was carried out within



Fig. 6 Proposed mechanism for transesterification reaction.

20 min. Even though it is not easy to elucidate the exact mechanism of the catalysis at this stage, the mechanism of Zn(II)cation-catalyzed transesterification probably involves electrophilic activation of the carbon center of the carbonyl moiety by binding of the Zn(II) to the carbonyl oxygen.52,53 Thus, the vacant site and Lewis acidity of the zinc(II) center play important roles in this catalytic transesterification. Additionally, the skeletal structural collapse was prohibited by the chelate effect of tridentate ligands. Based on this idea, a possible mechanism for transesterification is shown in Fig. 6. No  $zinc(\pi)$ species was detected after the catalysis in absolute ethanol as shown in the ICP data (Table S4<sup>†</sup>).<sup>54</sup> When the catalyst amount was increased twice, the catalytic rates increased significantly. Such a fact suggests that the structures, including the surface properties of the present 3D porous materials, play an important role in catalysis. The recycled catalyst shows a similar efficiency even though the crystallinity of 1.5H<sub>2</sub>O decreases after catalytic reaction (Fig. S7 and S8<sup>†</sup>).

### Conclusions

Self-assembly of zinc( $\pi$ ) perchlorate with 1,1,2,2-tetramethyl-1,2-di(pyridin-3-yl)disilane (L) afforded two enantiomeric twofold 3D coordination networks, 4<sup>1</sup>- and 4<sup>3</sup>-1.5H<sub>2</sub>O, of unique 10<sup>3</sup>-*a srs* net topology. This system is a proof-of-experiment example of the development of 3D networks as a solid catalyst, demonstrating the direct structural effects, substituent bulkiness, and trace water effects. The significantly different effects between the water molecules inside and outside of the ovalshaped cage represent an important conceptual advance in the development of such a catalytic system. More systematic studies, for example on the synthesis of related ligands, are in progress. Further investigation of this series of coordination frameworks, including a new topology based on the N-donor tridentate ligand, also is underway.

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### Notes and references

- 1 A. Schoedel, M. Li, D. Li, M. O'Keeffe and O. M. Yaghi, *Chem. Rev.*, 2016, **116**, 12466–12535.
- 2 S. Horike, D. Umeyama and S. Kitagawa, Acc. Chem. Res., 2013, 46, 2376–2384.
- 3 C. B. Aakeröy, N. R. Champness and C. Janiak, *CrystEngComm*, 2010, **12**, 22–43.
- 4 C. Mellot-Drazniek, J. Dutour and G. Ferey, *Angew. Chem.*, *Int. Ed.*, 2004, **43**, 6290–6296.
- 5 T. H. Noh and O.-S. Jung, Acc. Chem. Res., 2016, 49, 1835-1843.
- 6 Y. Cho, T. H. Noh, J. G. Kim, H. Lee and O.-S. Jung, *Cryst. Growth Des.*, 2016, **16**, 3054–3058.
- 7 T. H. Noh, H. Lee, J. Jang and O.-S. Jung, *Angew. Chem., Int. Ed.*, 2015, **54**, 9284–9288.
- 8 J. G. Kim, T. H. Noh, Y. Cho, J. K. Park and O.-S. Jung, *Chem. Commun.*, 2016, 52, 2545–2548.
- 9 A. G. Slater and A. I. Cooper, Science, 2015, 348, 988.
- 10 G. R. Desiraju, The Crystal as a Supramolecular Entity: Perspectives in Supramolecular Chemistry, John Wiley & Sons, New York, 1996, vol. 2.
- 11 M. Du, X.-H. Bu, Z. Huang, S.-T. Chen and Y.-M. Guo, *Inorg. Chem.*, 2003, **42**, 552–559.
- 12 M. Du, X.-H. Bu, Y.-M. Cuo, J. Ribas and C. Diaz, *Chem. Commun.*, 2002, 2550–2551.
- 13 S. Y. Moon, E. Kim, T. H. Noh, Y.-A. Lee and O.-S. Jung, *Dalton Trans.*, 2013, 42, 13974–13980.
- 14 J. Jiang, Y. Zhao and O. M. Yaghi, J. Am. Chem. Soc., 2016, 138, 3255–3265.
- 15 F. Jiang, L. Dai, Y. Shi and Z. Wang, Acta Crystallogr., Sect. C: Cryst. Struct. Commun., 2013, 69, 1485–1487.
- 16 S. T. Hyde, M. O'Keeffe and D. M. Proserpio, Angew. Chem., Int. Ed., 2008, 47, 7996–8000.
- 17 L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *Chem. Commun.*, 1996, 1393–1394.
- 18 A. J. Nunez, L. N. Shear, N. Dahal, I. A. Ibarra, J. Yoon, Y. K. Hwang, J.-S. Chang and S. M. Humphrey, *Chem. Commun.*, 2011, 47, 11855–11857.
- 19 A. M. Bohnsack, I. A. Ibarra, V. I. Bakhmutov, V. M. Lynch and S. M. Humphrey, *J. Am. Chem. Soc.*, 2013, **135**, 16038– 16041.

- 20 A. M. Kirillov, S. W. Wieczorek, A. Lis, M. F. C. Guedes da Silva, M. Florek, J. Krol, Z. Staroniewicz, P. Smolenski and A. J. L. Pombeiro, *Cryst. Growth Des.*, 2011, **11**, 2711–2716.
- 21 M. J. Zaworotko, Chem. Soc. Rev., 1994, 23, 283-288.
- 22 J. Y. Lee, O. K. Farha, J. Rorberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, 38, 1450–1459.
- 23 N.-X. Zu, C.-W. Zhao, J.-C. Wang, Y.-A. Li and Y.-B. Dong, *Chem. Commun.*, 2016, 52, 12702–12705.
- 24 D. Kim, B. J. Kim, T. H. Noh and O.-S. Jung, *CrystEngComm*, 2015, **17**, 2583–2590.
- 25 M. Jacoby, Chem. Eng. News, 2013, 91, 34-35.
- 26 A. Henschel, K. Gedrich, R. Kraehnert and S. Kaskel, *Chem. Commun.*, 2008, 4192–4194.
- 27 Z. Wang and S. M. Cohen, *Chem. Soc. Rev.*, 2009, 38, 1315– 1329.
- 28 R. Yepez, S. Garcia, P. Schachat, M. Sanchez-Sanchez, J. H. Gonzalez-Estefan, E. Gonzalez-Zamora, I. A. Ibarra and J. Aguilar-Pliego, *New J. Chem.*, 2015, **39**, 5112.
- 29 A. Corma, H. Garcia and F. X. Llabres i Xamena, *Chem. Rev.*, 2010, **110**, 4606–4655.
- 30 A. M. Kirillov, Y. Y. Karabach, M. V. Kirillova, M. Haukka and A. J. L. Pombeiro, *Cryst. Growth Des.*, 2012, 12, 1069– 1074.
- 31 M. V. Kirillova, A. M. Kirillov, A. N. C. Martins, C. Graiff, A. Tiripicchio and A. J. L. Pombeiro, *Inorg. Chem.*, 2012, 51, 5224–5234.
- 32 J. Otera, Chem. Rev., 1993, 93, 1449-1470.
- 33 D. M. Reinoso, M. B. Fernandez, D. E. Damiani and G. M. Tonetto, Int. J. Low-Carbon Technol., 2012, 7, 348–356.
- 34 J. Romanski, P. Nowak, K. Kosinski and J. Jurczak, *Tetrahedron Lett.*, 2012, **53**, 5287–5289.
- 35 M. Kahnes, H. Gorls, L. Gonzalez and M. Westerhausen, *Organometallics*, 2010, **29**, 3098–3108.
- 36 A. Nagvenkar, S. Naik and J. Fernandes, *Catal. Commun.*, 2015, 65, 20–23.
- 37 A. W. Kleij, M. Kuil, D. M. Tooke, M. Lutz, A. L. Spek and J. N. H. Reek, *Chem. – Eur. J.*, 2005, **11**, 4743–4750.
- 38 J. W. Shin, J. M. Bae, C. Kim and K. S. Min, *Inorg. Chem.*, 2013, 52, 2265–2267.
- 39 S. P. Jang, J. I. Poong, S. H. Kim, T. G. Lee, J. Y. Noh and C. Kim, *Polyhedron*, 2012, 33, 194–202.
- 40 S. Enthaler, ACS Catal., 2013, 3, 150-158.
- 41 T. M. McCormick and S. Wang, *Inorg. Chem.*, 2008, 47, 10017–10024.
- 42 W. N. Lipscomb and N. Strater, *Chem. Rev.*, 1996, **96**, 2375–2434.
- 43 L. S. Felices, E. C. Escudero-Adan, J. Benet-Buchholz and A. W. Kleij, *Inorg. Chem.*, 2009, 48, 846–853.
- 44 E. Choi, H. Lee, T. H. Noh and O.-S. Jung, *CrystEngComm*, 2016, **18**, 6997–7002.
- 45 G. M. Sheldrick, *SADABS, A Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Germany, 1996.
- 46 G. M. Sheldrick, *SHELXL-2014/7: A Program for Structure Refinement*, University of Göttingen, Germany, 2014.

- 47 M. J. Plater, M. R. St., J. Foreman, T. Gelbrich and M. B. Hursthouse, *Dalton Trans.*, 2000, 1995–2000.
- 48 A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 1999.
- 49 S. W. Jaros, P. Smolenski, M. F. C. Guedes da Silva, M. Florek, J. Krol, Z. Staroniewicz, A. J. L. Pombeiro and A. M. Kirillov, *CrystEngComm*, 2013, 15, 8060–8064.
- 50 J.-Z. Gu, A. M. Kirillov, J. Wu, D.-Y. Lv, Y. Tang and J.-C. Wu, *CrystEngComm*, 2013, **15**, 10287–10303.
- 51 H. Kim, M. Park, H. Lee and O.-S. Jung, *Dalton Trans.*, 2015, 44, 8198-8204.
- 52 H. Lee, T. H. Noh and O.-S. Jung, *Dalton Trans.*, 2014, 43, 3842–3849.
- 53 H. Kwak, et al., Polyhedron, 2009, 28, 553-561.
- 54 E. Sánchez-González, A. López-Olvera, O. Monroy, J. Aguilar-Pliego, J. G. Flores, A. Islas-Jácome, M. A. Rincón-Guevara, E. González-Zamora, B. Rodríguez-Molina and I. A. Ibarra, *CrystEngComm*, 2017, DOI: 10.1039/C6CE02621D.