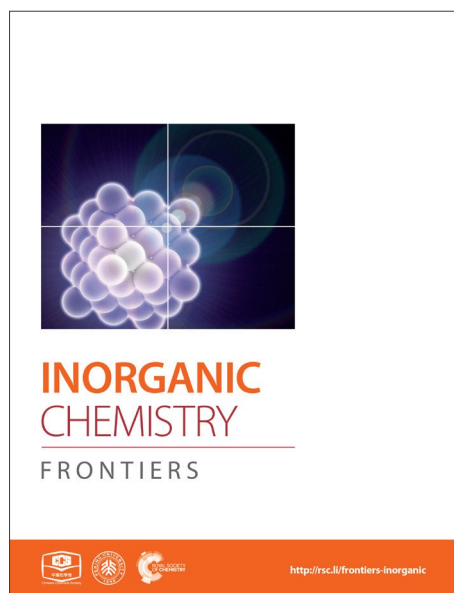
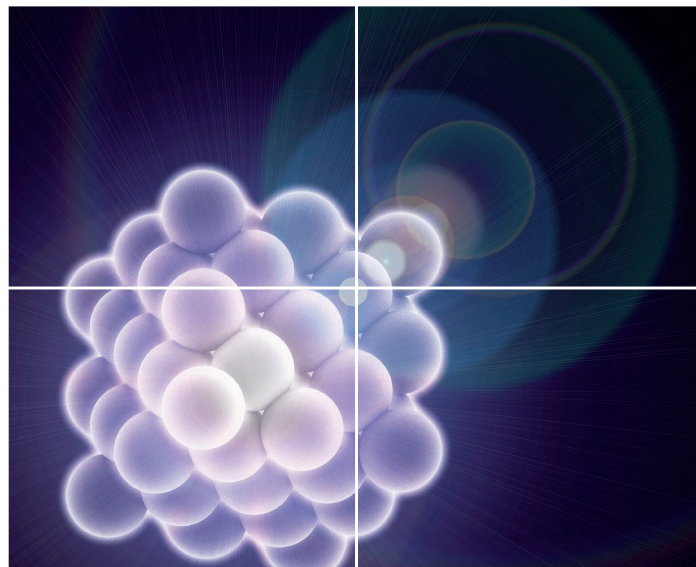


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## Construction of a series of zero-dimensional / one-dimensional crystalline Zn-S clusters – effect of the character of bridging organic ligands on structural diversity†

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**ABSTRACT:** A series of chalcogenide compounds with various compositions, i.e., octanuclear or tetranuclear Zn-S cluster have been achieved in a feasible way. Different fused-ring aromatic ligands were used as capping ligands and corresponding zero-dimensional (0D) products were obtained. Whereas bridging ligands led to a family of one-dimensional (1D) coordination polymers and *in situ* ligand reaction has been observed in  $[\text{Zn}_8\text{S}(\text{SC}_6\text{H}_5)_{13}\text{L}_1(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$  (L = 3-carboxypyridyl) due to the hydrolysis of cyano group of 3-Pyridinecarbonitrile. A very rare 1D helical-chain structure was observed in  $[\text{Zn}_4(\text{SC}_6\text{H}_5)_8\text{L}_1]_2$  (L = 4,4'-Bipyridyl), providing evidence of the character of bridging organic ligands on corresponding crystalline materials. First-principles calculations of  $[\text{Zn}_4(\text{SC}_6\text{H}_5)_8\text{L}_1]_2$  (L = 4,4'-Bipyridyl) further reveal that the two cluster units could rotate freely along the C-C single bond in a broad range, eventually leading to the formation of one-dimensional helical structure.

Hybrid inorganic-organic framework materials have potential application in many areas such as chiral separations, asymmetric catalysis<sup>1</sup>, ion exchange<sup>2</sup>, adsorption-desorption<sup>3</sup>, gas storage<sup>4</sup>, non-linear optics<sup>5</sup>, molecular magnetism<sup>6</sup> and ferroelectric<sup>7</sup>, therefore brought new development opportunities for those multifunctional materials. In comparison with “metal-organic frameworks (MOFs)”, “porous coordination polymers (PCPs)” which constructed by metal atoms and organic ligands, the synergistic interactions between metal clusters and bridging organic ligands make the assembly and topological control of corresponding crystalline materials a challenge task. The aim is to construct crystalline frameworks with intriguing topologies and it is important to systematically investigate the relationship between the intrinsic characters of bridging ligands and the specific framework materials to fully understand supramolecular assembly.<sup>8</sup> By using the identical metal clusters as building blocks, structural diversity could be observed by virtue of different bridging ligands through modification of the length and the shape of the linkers.<sup>9</sup> In this aspect, chalcogenide clusters with well-defined molecular structures and interesting electrical/optical properties are promising building blocks. Vaqueiro has summarized a number of hybrid materials featuring chalcogenide clusters as inorganic units which linked by organic ligands.<sup>10</sup> Recently, Feng and co-workers reported the precise doping of Mn<sup>2+</sup> ion into coreless supertetrahedral chalcogenide nanoclusters could induce unusual red shift, demonstrated its potential application for photonic devices and bio-imaging.<sup>11</sup> By using the “bottom-up” synthetic strategy, herein we report nine chalcogenide compounds showing versatile structure characters including zero-dimensional (0D) clusters and one-dimensional (1D) coordination polymers. It is demonstrated in this communication that various compositions, by using the deliberately capping ligands or bridging ligands, can be made in a feasible way.

It is well known that zinc sulfide clusters exhibiting different isomers based upon the sphalerite (cubic ZnS) and wurtzite (hexagonal ZnS) phases.<sup>12</sup> The sphalerite (or zinc blende) structure has an expanded face-centered cubic (*fcc*) anion lattice, whereas the wurtzite structure is derived from an expanded hexagonally closed-packed (*hcp*) anion array. We have recently described the synthetic entry to a class of individual zinc sulfide clusters based upon the wurtzite-like Zn<sub>8</sub>S cores.<sup>13</sup> This simple and efficient synthetic method could achieve clusters containing Zn<sub>8</sub>S(SC<sub>6</sub>H<sub>5</sub>)<sub>14</sub>L<sub>2</sub> (L = substituted organic ligands) and a recent example has shown that this class of Zn-S

cluster could help to inhibit the photobleaching of fluorescent dye in a certain degree,<sup>14</sup> establishing them as a new promising platform for future application.

Complexes **1** ~ **8** were obtained by hydrothermal synthesis and their structures were determined from single-crystal X-ray diffraction (Table 1).<sup>15-16</sup> Unlike the previous research by using substituted pyridine ligands, fused-ring aromatic ligands such as 3-Methylquinoline, 5-Aminoquinoline, 3-(2-Thienyl)pyridine, 4,7-Phenanthroline were used as capping ligands and corresponding zero-dimensional (0D) products were  $\text{Zn}_8\text{S}(\text{SC}_6\text{H}_5)_{14}[\text{3-H}_3\text{CC}_9\text{H}_6\text{N}]_2$  (**1**),  $\text{Zn}_8\text{S}(\text{SC}_6\text{H}_5)_{14}[\text{5-H}_2\text{NC}_9\text{H}_6\text{N}]_2$  (**2**),  $\text{Zn}_8\text{S}(\text{SC}_6\text{H}_5)_{14}[\text{C}_4\text{H}_3\text{SC}_5\text{H}_4\text{N}]_2$  (**3**) and  $\text{Zn}_8\text{S}(\text{SC}_6\text{H}_5)_{14}[\text{NC}_{12}\text{H}_8\text{N}]_2$  (**4**) (Fig. 1), respectively. The  $\text{Zn}_8\text{S}$  cores of neutral clusters display significant thermodynamic stability when different capping ligands are present, therefore could generate a large number of individual clusters upon using numerous capping ligands.

The results of photoluminescence properties of **2** ( $c = 2.5 \times 10^{-6}$  M in DMSO) at room temperature are shown in Fig. S1a. The fluorescence emission of **2** occurs at 476 nm due to excitation at  $\lambda_{\text{ex}}$  370 nm, compared to the typical absorption maximum at about 260 nm of  $\text{Zn}_8\text{S}(\text{SC}_6\text{H}_5)_{14}[\text{phenanthridyl}]_2$  in previous report,<sup>13a</sup> suggesting that there is relationship between the terminal capping ligands and their corresponding spectral properties. Excitation of **3** at  $\lambda_{\text{ex}}$  296 nm leads to a prominent emission peak at 350 nm (fwhm ~ 50 nm) with a blue shift compared to that of compound **2**, presumably due to the perturbation of ion electronic state induced by terminal 3-(2-Thienyl)pyridyl ligands (Fig. S1b, ESI†). Surprisingly, there are no observable fluorescence emissions of compounds **1** and **4**, indicating that the photoluminescence of overall clusters was very hard to tune by simply changing the surface-capping ligands.

Apart from using the capping ligands to get the zero-dimensional nanoclusters **1** ~ **4**, it is highly desirable to use bridging ligands to link chalcogenide clusters which behave like large “artificial atoms”. The aim is to organize uniform molecular-level integration of crystalline frameworks using chalcogenide clusters as building blocks.<sup>17</sup> To our best knowledge however, only a few hybrid materials featuring similar compositions as building blocks that linked by organic ligands have been reported.<sup>17b,18</sup> Extended targeted synthesis of 1D coordination polymers have successfully led to **5** ~ **8** when bridging ligands link clusters together. Using 3-Pyridinecarbonitrile, 2,5-Bis(4-pyridyl)-1,3,4-thiadiazole, *trans*-1,2-Bis(4-pyridyl)ethylene, 4,4'-Bipyridyl as bridging ligands led to

$[\text{Zn}_8\text{S}(\text{SC}_6\text{H}_5)_{13}\text{L}_1(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$  ( $\text{L} = 3\text{-carboxypyridyl}$ ) (**5**),  $[\text{Zn}_8\text{S}(\text{SC}_6\text{H}_5)_{14}\text{L}_1]$  ( $\text{L} = 2,5\text{-Bis}(4\text{-pyridyl})\text{-}1,3,4\text{-thiadiazole}$ ) (**6**),  $[\text{Zn}_4(\text{SC}_6\text{H}_5)_8\text{L}_1]$  ( $\text{L} = \textit{trans}\text{-}1,2\text{-Bis}(4\text{-pyridyl})\text{ethylene}$ ) (**7**) and  $[\text{Zn}_4(\text{SC}_6\text{H}_5)_8\text{L}_1]$  ( $\text{L} = 4,4'\text{-Bipyridyl}$ ) (**8**), respectively. Compounds **5** ~ **7** displayed 1D zig-zag chain (Fig. 2) whereas a very rare 1D helical-chain structure was observed in compound **8** (Fig. 3).

Under similar conditions to get zero-dimensional compounds, the cyano group in 3-Pyridinecarbonitrile was hydrolysed to obtain 3-carboxypyridyl in compound **5** and consequently, 1D zig-zag chain was achieved by virtue of the bridging ligand 3-carboxypyridyl (Fig. 2a). The observation of *in situ* ligand reaction further demonstrated its importance to construct functional crystalline clusters.<sup>13a</sup>

Interestingly, in the absence of thiourea, T2 clusters (supertetrahedral clusters are denoted by  $T_n$  where  $n$  is the number of metal layers in each cluster) in **7/8** have evolved and are linked by ditopic ligands. Compared to 1D zig-zag chain in **7**, the intriguing character of **8** is its helical-chain structure, which is very rare in the family of hybrid materials with chalcogenide clusters as fundamental building blocks.<sup>18,19</sup> As demonstrated in Fig. 3, structure of **8** shows the fragment of the sphalerite (cubic ZnS) phase and two crystallographically independent adamantane-type  $\text{Zn}_4\text{S}_8\text{N}_2$  clusters are linked by two independent 4,4'-bipyridyl ligands in an asymmetric unit. The bond lengths of Zn-S range from 2.2501(17) to 2.4236(14) Å and the Zn-N bond lengths vary from 2.041(4) and 2.060(4) Å, respectively. Of particular note is the twist character of the two pyridine rings in 4,4'-bipyridyl, i.e., the dihedral angle between the ring of N1, C51 ~ C55 atoms and the ring of N2, C56 ~ C60 atoms is 32.0°, whereas the angle between the ring of N3A, C49A, C50A, C114 ~ C116 atoms and the ring of N4, C109 ~ C113 atoms is 35.4°. This distorted character of bridging ligands may be the basis of the observation of  $2_1$  helix along the  $b$  axis. The pitch range of each chain is 31.625 Å, which is equal to the unit cell parameter along the  $b$  axis and that increases to 31.993 Å which is derived from its room temperature structure (**8RT**).<sup>20</sup> Although it is not uncommon to integrate right-handed helix and left-handed helix into an overall achiral structure in **8**, the exploration of ligands with greater flexibility will facilitate the discovery of more helical structures.<sup>21</sup>

To further understand the twist character of cluster units around the C-C single bond in 4,4'-bipyridyl ligand, a first-principle computational study was performed. The first-principle calculations based on density functional theory were carried out within the Vienna ab initio simulation package.<sup>22,23</sup> The electron-ion interaction was

described by the projected augmented wave (PAW) potentials<sup>24</sup> and the plane-wave basis set, with the local density approximation (LDA) exchange-correlation functional.<sup>25</sup> The kinetic energy cutoff was set as 400 eV. The Hellmann–Feynman forces acting on each atom were less than 0.05 V/Å. To simplify the periodic structure to cluster model as shown in Fig. 4a, the dangling bonds were dealt with carbon rings, which were highlighted by green circles in Fig. 4a. We employed a supercell of  $25 \times 26 \times 41 \text{ \AA}^3$  for all calculations so that the interactions generated by the periodic boundary condition could be neglected. The built cluster model was first fully optimized without any symmetry constraint. Then we calculated the rotation energy of part A ( $\text{Zn}_4\text{S}_8\text{N}_2$  cluster) to part B (another  $\text{Zn}_4\text{S}_8\text{N}_2$  cluster) in the cluster model around the C-C single bond (schematic diagram shown in Fig. 4a) within 90 degrees and the results suggested that the two parts can rotate freely, of which the energy difference was relatively small in comparison with the initial position (Fig. 4b). As clearly shown in Fig. 4b, when the dihedral angle is  $32.0^\circ$  or  $35.4^\circ$  (crystallographic results), the rotation energies of part A to Part B along C-C single bond are rather small ( $\sim 0.04 \text{ eV}$ ). On the contrary, the energy difference is relatively high when the rotation angle is around 80 degree. This suggests that the two cluster units can freely rotated (from theoretical calculation). Thus, the theoretical study matches with the observed twist character, and we believe that crystal packing effect and intermolecular interactions play an important role in the formation of helical structure.

In summary, we have shown that a family of chalcogenide compounds with versatile characters (0D and 1D) has been constructed by rational combination of Zn-S clusters and capping / bridging ligands. The solution-state properties of compounds **1** ~ **8** could be measured by NMR and MS and reported elsewhere.<sup>26</sup> The observation of *in situ* ligand reaction in **5**, namely, the hydrolysis process of cyano group of 3-Pyridinecarbonitrile to make 3-carboxypyridyl bridging ligand help to construct  $[\text{Zn}_8\text{S}(\text{SC}_6\text{H}_5)_{13}\text{L}_1(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$  ( $\text{L} = 3\text{-carboxypyridyl}$ ). A rare 1D helical-chain structure in  $[\text{Zn}_4(\text{SC}_6\text{H}_5)\text{L}_1]_2$  ( $\text{L} = 4,4'\text{-Bipyridyl}$ )(**8**) has indicated that organic ligands play an important role in affecting the assembly of hybrid inorganic-organic materials. It is well-known that bridging ligands are called di-, tri-, tetratopic depending on the number of donor atoms and we believe that the bidentate bridging ligands such as those shown in this work are the first choice to link crystalline clusters to obtain one-dimensional coordination polymers and the rigidity/flexibility of ligands could be the

basis for the variation of structural topologies. Furthermore, the employment of tri-, tetratopic ligands may make it possible to get higher dimensional polymers.

**Acknowledgments**

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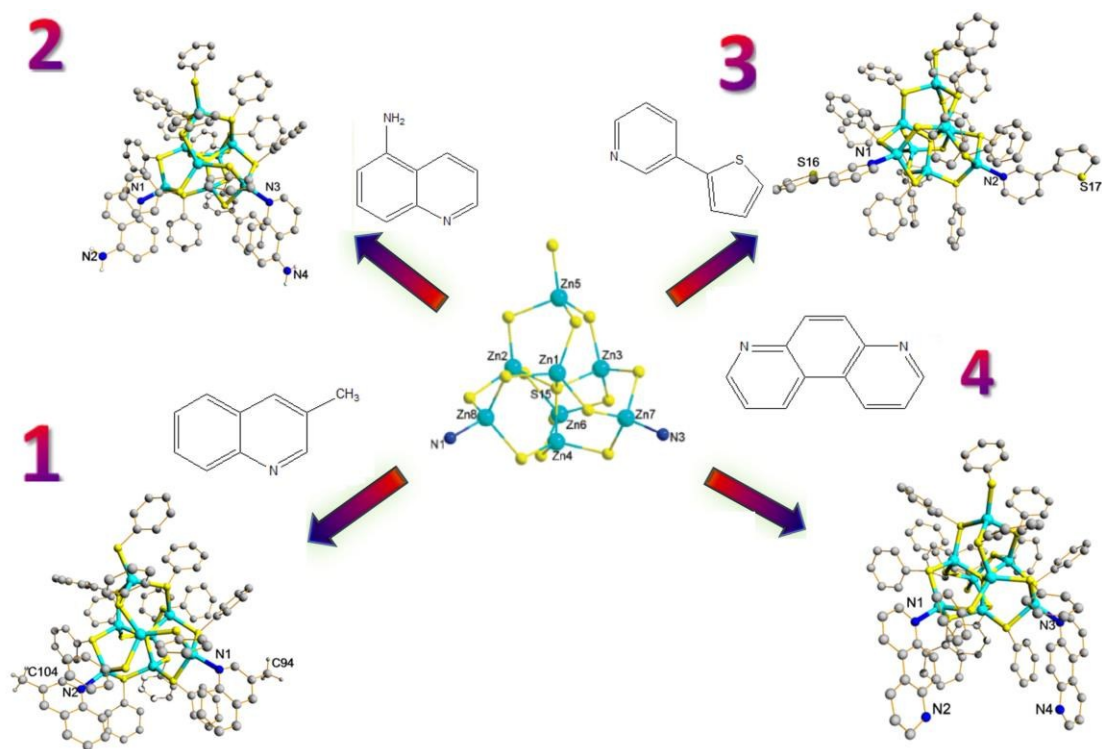
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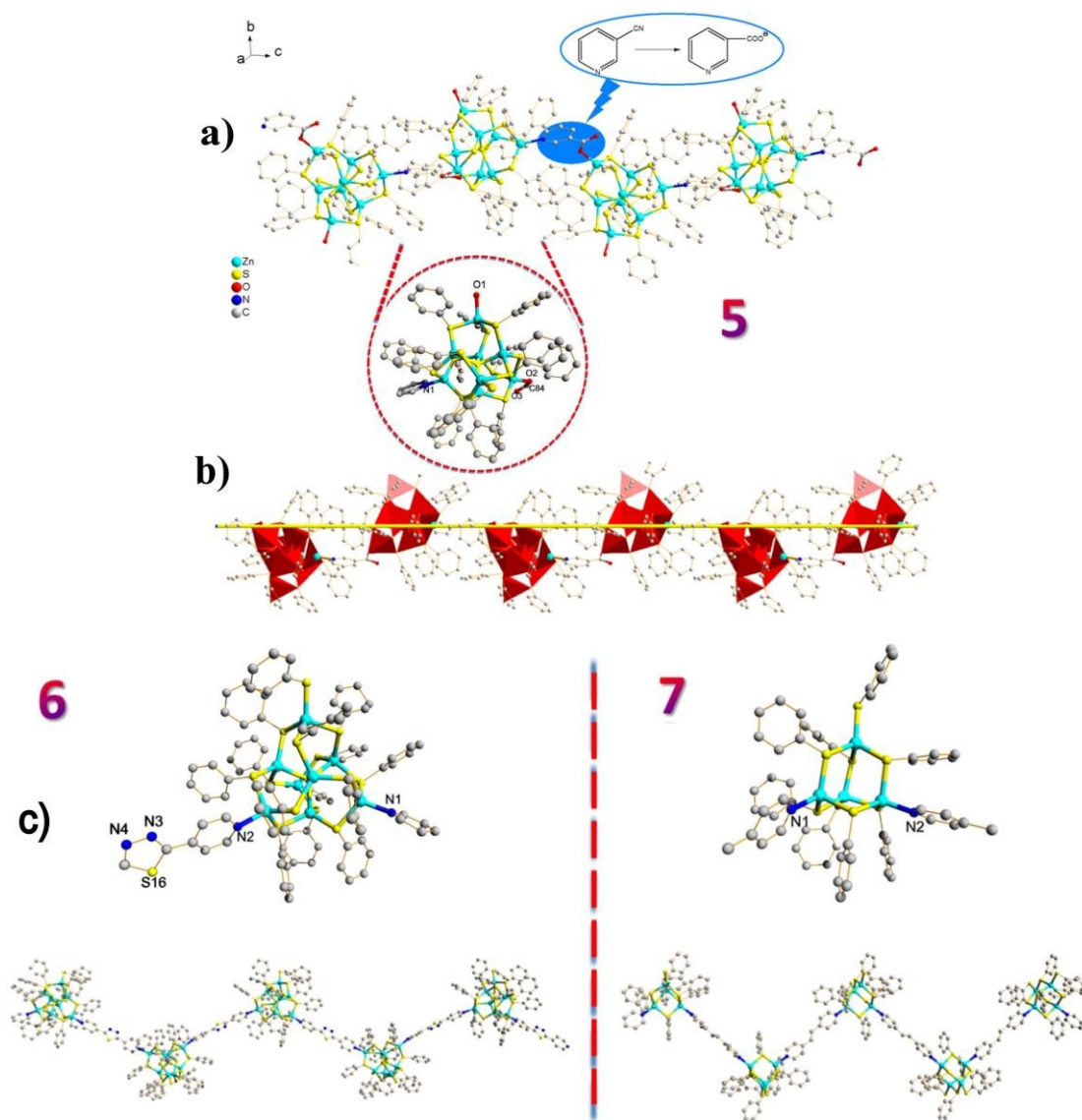
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- 20 Unit cell parameters of **8** at room temperature:  $a = 19.4573(4) \text{ \AA}$ ,  $b = 31.9930(6) \text{ \AA}$ ,  $c = 18.6800(4) \text{ \AA}$ ,  $\beta = 99.1590(10)^\circ$ ,  $V = 11480.0(4) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_c = 1.438 \text{ g cm}^{-3}$ , GOF = 1.018, Total of 88524 reflections (21822 unique) with  $R_{\text{int}} = 0.0452$ ,  $R_1 = 0.0708$ ,  $wR_2 = 0.1841$  ( $I > 2\sigma(I)$ ). CCDC 1012594.
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**Table 1** Crystal Parameters for Complexes **1 ~ 8**

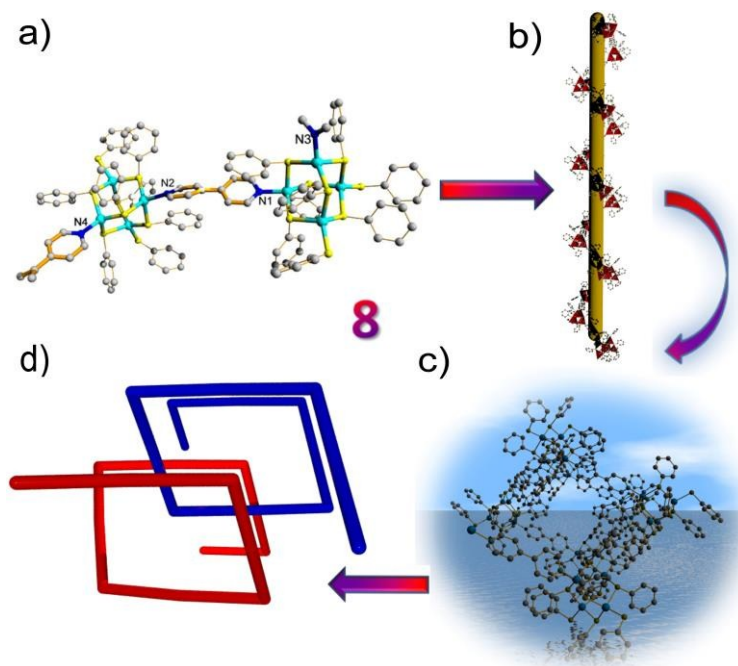
|  | <b>1</b>   | <b>2</b>   | <b>3</b>   | <b>4</b>   | <b>5</b>   | <b>6</b>  | <b>7</b>   | <b>8</b>   |
|--|--|--|--|--|--|---|--|--|
| formula  | C <sub>104</sub> H <sub>88</sub> N <sub>2</sub><br>S <sub>15</sub> Zn <sub>8</sub> | C <sub>102</sub> H <sub>86</sub> N <sub>4</sub><br>S <sub>15</sub> Zn <sub>8</sub> | C <sub>102</sub> H <sub>84</sub> N <sub>2</sub><br>S <sub>17</sub> Zn <sub>8</sub> | C <sub>108</sub> H <sub>86</sub> N <sub>4</sub><br>S <sub>15</sub> Zn <sub>8</sub> | C <sub>84</sub> H <sub>75</sub> NO <sub>5</sub><br>S <sub>14</sub> Zn <sub>8</sub> | C <sub>96</sub> H <sub>78</sub> N <sub>4</sub><br>S <sub>16</sub> Zn <sub>8</sub> | C <sub>60</sub> H <sub>50</sub> N <sub>2</sub><br>S <sub>8</sub> Zn <sub>4</sub> | C <sub>116</sub> H <sub>96</sub> N <sub>4</sub><br>S <sub>16</sub> Zn <sub>8</sub> |
| fw   | 2370.00  | 2371.98  | 2406.08  | 2444.05  | 2150.25  | 4477.831  | 1316.98  | 2581.89  |
| cryst syst   | Monoclinic   | Monoclinic   | Triclinic  | Monoclinic   | Monoclinic   | Monoclinic  | Monoclinic   | Monoclinic   |
| space group  | <i>P</i> 2 <sub>1</sub> / <i>c</i>   | <i>Cc</i>  | <i>P</i> 1   | <i>P</i> 2 <sub>1</sub> / <i>n</i>   | <i>Cc</i>  | <i>C</i> 2 <i>c</i>   | <i>P</i> 2 <sub>1</sub> / <i>n</i>   | <i>P</i> 2 <sub>1</sub> / <i>c</i>   |
| <i>a</i> / Å   | 25.9462(6)   | 25.4629(19)  | 13.3365(4)   | 13.0752(5)   | 16.951(2)  | 53.269(3)   | 13.3661(2)   | 19.3609(10)  |
| <i>b</i> / Å   | 13.3330(2)   | 13.3084(10)  | 13.4427(4)   | 25.2259(9)   | 20.589(3)  | 13.3807(3)  | 24.0675(3)   | 31.6252(18)  |
| <i>c</i> / Å   | 28.9328(5)   | 29.022(2)  | 29.4227(9)   | 31.8774(13)  | 25.375(4)  | 38.045(2)   | 19.0210(4)   | 18.4565(9)   |
| $\alpha$ / °   | 90   | 90   | 90.982(2)  | 90   | 90   | 90  | 90   | 90   |
| $\beta$ / °  | 98.500(2)  | 98.821(4)  | 91.336(2)  | 96.401(2)  | 96.243(2)  | 133.037(9)  | 105.480(2)   | 99.136(2)  |
| $\gamma$ / °   | 90   | 90   | 106.792(3)   | 90   | 90   | 90  | 90   | 90   |
| <i>V</i> / Å <sup>3</sup>                            | 9899.1(3)  | 9718.3(13)   | 5047.0(3)  | 10448.7(7)   | 8804(2)  | 19820(3)  | 5896.87(17)  | 11157.4(10)  |
| <i>Z</i>   | 4  | 4  | 2  | 4  | 4  | 4   | 4  | 4  |
| <i>d</i> <sub>calc</sub> / g cm <sup>-3</sup>        | 1.590  | 1.621  | 1.583  | 1.498  | 1.622  | 1.501   | 1.483  | 1.537  |
| GOF  | 1.041  | 1.007  | 1.125  | 0.889  | 1.026  | 1.010   | 1.032  | 1.029  |
| <i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )]   | 0.0740   | 0.1046   | 0.1373   | 0.0663   | 0.0694   | 0.0939  | 0.0334   | 0.0569   |
| w <i>R</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )] | 0.1789   | 0.3357   | 0.3721   | 0.1610   | 0.1661   | 0.2469  | 0.0641   | 0.1284   |



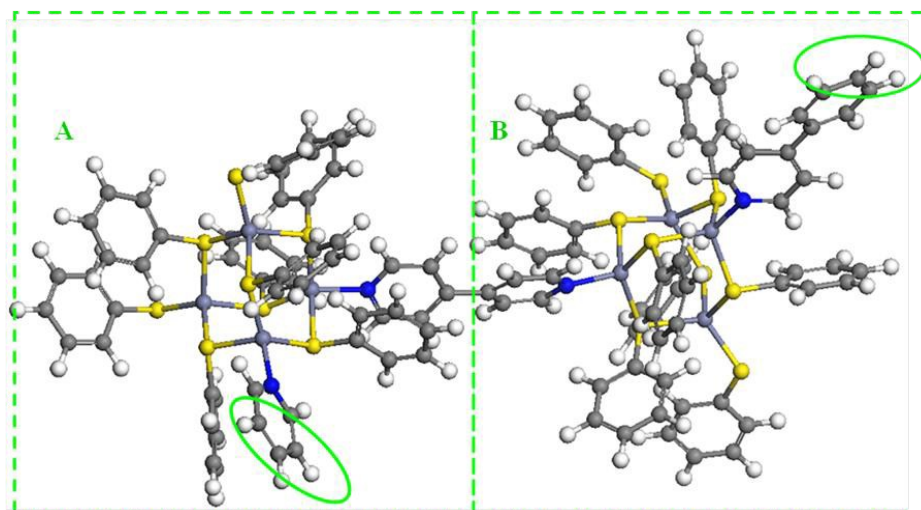
**Fig. 1** Structures of zero-dimensional (0D) products:  $\text{Zn}_8\text{S}(\text{SC}_6\text{H}_5)_{14}[\text{3-H}_3\text{CC}_9\text{H}_6\text{N}]_2$  (**1**),  $\text{Zn}_8\text{S}(\text{SC}_6\text{H}_5)_{14}[\text{5-H}_2\text{NC}_9\text{H}_6\text{N}]_2$  (**2**),  $\text{Zn}_8\text{S}(\text{SC}_6\text{H}_5)_{14}[\text{C}_4\text{H}_3\text{SC}_5\text{H}_4\text{N}]_2$  (**3**) and  $\text{Zn}_8\text{S}(\text{SC}_6\text{H}_5)_{14}[\text{NC}_{12}\text{H}_8\text{N}]_2$  (**4**).



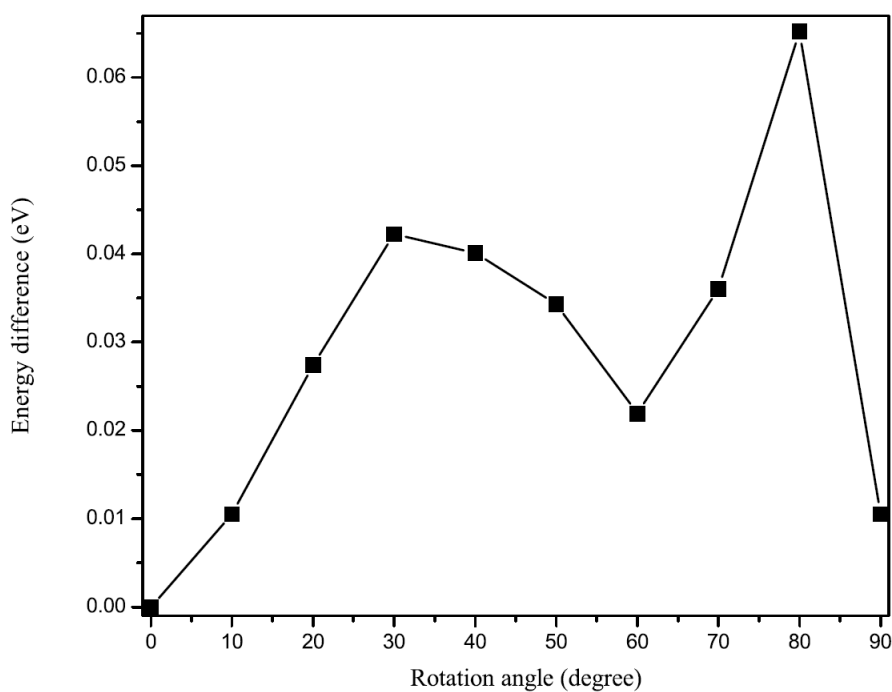
**Fig. 2** (a) 1D polymeric chain of compound **5**  $[\text{Zn}_8\text{S}(\text{SC}_6\text{H}_5)_{13}\text{L}_1(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$  ( $\text{L} = 3\text{-carboxypyridyl}$ ) with the formation of 3-carboxypyridyl ligand. (b) 1D zig-zag chain of **5**. (c) 1D zig-zag polymeric chain of **6**:  $[\text{Zn}_8\text{S}(\text{SC}_6\text{H}_5)_{14}\text{L}_1]$  ( $\text{L} = 2,5\text{-Bis}(4\text{-pyridyl})\text{-}1,3,4\text{-thiadiazole}$ )(left) and **7**:  $[\text{Zn}_4(\text{SC}_6\text{H}_5)_8\text{L}_1]$  ( $\text{L} = \text{trans-}1,2\text{-Bis}(4\text{-pyridyl})\text{ethylene}$ ) (right).



**Fig. 3** (a) Molecular structure of  $[Zn_4S(SC_6H_5)_8L_1]$  (L = 4,4'-Bipyridyl) (**8**). (b) 1D helical structure. (c) Integration of right-handed helix and left-handed helix. (d) Schematic representation of overall achiral structure (viewed along  $b$ -axis).



(a)



(b)

**Fig. 4** (a) The cluster model for rotation calculations in **8**. (b) The calculation results of energy difference vs rotation angle (from 0° to 90°).