

# A series of metal–organic coordination polymers assembled with disulfide ligand involving *in situ* cleavage of S–S under co-ligand intervention†

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A series of new metal–organic coordination complexes,  $[\text{Zn}(\text{cpds})(\text{H}_2\text{O})_2]_n$  (**1**),  $\{[\text{Zn}(\text{cpds})(4,4'\text{-bipy})] \cdot 6\text{H}_2\text{O}\}_n$  (**2**),  $\{[\text{Zn}(\text{cpds})(\text{bpe})]_2 \cdot 0.5(\text{bpe}) \cdot 4\text{H}_2\text{O}\}_n$  (**3**),  $[\text{Cu}(\text{cpds})(2,2'\text{-bipy})(\text{CH}_3\text{OH})]_2 \cdot 2\text{H}_2\text{O}$  (**4**),  $\{[\text{Cu}(\text{cpds})(4,4'\text{-bipy})(\text{H}_2\text{O})_2] \cdot 2.24\text{H}_2\text{O}\}_n$  (**5**),  $\{[\text{Cu}(6\text{-sinic})(4,4'\text{-bipy})_{0.5}] \cdot \text{CH}_3\text{OH} \cdot \text{H}_2\text{O}\}_n$  (**6**),  $[\text{Cd}_2(6\text{-mna})_2(\text{phen})]_n$  (**7**), and  $\{[\text{Cd}(\text{cpds})(\text{bpe})] \cdot 2.2\text{H}_2\text{O}\}_n$  (**8**) were prepared by self-assembly of disulfide derivative of the nicotinate, 6,6'-dithiodinicotinic acid ( $\text{H}_2\text{cpds}$ ) with transition metal ions in the absence of different N-donor ligands (4,4'-bipy = 4,4'-bipyridine, 2,2'-bipy = 2,2'-bipyridine, phen = 1,10-phenanthroline, bpe = 1,2-bis(4-pyridyl)ethene, 6-sinic = 6-sulfinto-nicotinate, 6-mna = 6-mercaptanicotinic acid). X-Ray structure analyses of **1–8** reveal their structure ranging from the discrete unit (0D) (**4**), one-dimensional (1D) (**1**, **5**), two-dimensional (2D) (**7**), non-interpenetrating 3D porous coordination polymers (**6**, **8**), 2-fold interpenetrated structure (**2**) to a 5-fold interpenetrating framework (**3**), which mainly due to the differences in the bridging modes of  $\text{cpds}^{2-}$  and the effect of the secondary ligands. Interestingly, in the complexes **6** and **7**, the starting  $\text{H}_2\text{cpds}$  reagent is converted into new ligands (6-sinic in **6** and 6-mna in **7**) under solvothermal condition *via in situ* cleavage of S–S bond. In addition, thermogravimetric analyses, X-ray powder diffractions and the fluorescent properties of complexes **1**, **2**, **3**, **7**, **8** have been investigated.

## Introduction

In recent years, the design and construction of metal–organic frameworks (MOFs) has attracted considerable attention in supramolecular and material chemistry due to the potential applications as catalysis, optoelectronic, magnetic, porous materials, as well as their intriguing variety of architectures and topologies.<sup>1</sup> Several rational synthetic strategies have been proposed to achieve the metallosupramolecular arrays, and the most effective one is to employ appropriate bridging building blocks capable of binding metal centers through direct dative bonds.<sup>2a</sup> It is well-known that the nature of organic ligands plays crucial roles in the design and construction of desirable supramolecular frameworks. The changes in flexibility, length, and symmetry of organic ligands can result in a remarkable class of materials bearing diverse architectures and functions. Thus, the construction of target MOF with properties mentioned above is a challenge for synthetic chemists.<sup>2b</sup> To date, many studies have been focused on the use of flexible bridging ligands to build coordination architectures.<sup>3</sup> The flexible spacer allows ligands to bend or rotate when coordinating to metal centers to conform to the coordination geometries of the metal ions.<sup>4</sup> The reactions of

such ligands (especially those containing S, N, or O donors) with appropriate metal ions under the proper synthetic conditions have led to many kinds of structures, such as discrete cycles, chains, or helices.<sup>4,5</sup> On that basis, flexible disulfide derivatives bearing –S–S– spacers can afford rich structure information compared with rigid ligands. An extensive amount of literature about the disulfide derivatives reported to date, however, are based on dipyridyldisulfide ligands.<sup>6</sup> In our previous work, we have also reported 4,4'-dipyridyldisulfide (dpds) reagent which can be used as a good flexible bridging ligand to assemble complexes and converted into dps ligand *via in situ* cleavage of both S–S and S–C bonds and temperature-dependent *in situ* ligand rearrangement of dpds.<sup>7</sup> Whereas, there have been few reports of studies on flexible disulfide derivatives of carboxylates. In this report, we focus on 6,6'-dithiodinicotinic acid ( $\text{H}_2\text{cpds}$ ) not only because of its twist conformation with a C–S–S–C torsion angle of *ca.* 90° and axial chirality that potentially generate the *M*- and *P*-enantiomers in chiral crystal engineering, but also the easy cleavage of the S–S bond. And the bridging S atom has coordination ability, which may lead to a unique network structures because of its bonding ability to soft metal ions.<sup>6b</sup> Moreover,  $\text{H}_2\text{cpds}$  not only has hard-only (carboxylate-*O*) but also has soft-only (pyridine-*N*) donor sets presenting versatile coordination modes to connect metal ions into higher-dimensional structures.<sup>8</sup>

On the other hand, the prospect of introducing the secondary organic ligands into a reaction system offers tremendous impetus for research on metal–organic supramolecular frameworks. However, due to the presence of many subtle interactions and limitations in self-assembly process as well as difficult prediction of the resulting products, the formation of extended solids based

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