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A zinc-organic coordination polymer of glycine-functionalized naphthalenediimide ligand

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ABSTRACT

The first metal–organic coordination polymer of amino-acid functionalized naphthalenediimide (NDI) ligand, $[Zn(Gly\text{-}NDI)(DMF)_2]_n$ (**1**), has been synthesized and characterized. Single-crystal X-ray diffraction revealed that the Zn ions are linked by *anti*-conformational Gly-NDI ligands, and **1** displays a one-dimensional zigzag chain coordination polymer. These chains are cross-linked through strong π···π stacking interactions between NDI cores to give a three-dimensional supramolecular framework with square planar 4-connected $CdSO_4$ (**cds**) topology. The thermal stability and fluorescence emissions of **1** were also investigated.

The multifunctional coordination polymers with amazing structural versatility and potential applications in sensing, gas separation and catalysis have collected great attention in recent years [1–4]. A number of design strategies have been investigated in search of viable modes such as zigzags, helices, tubes, layers assemble and framework structures of the coordination polymers systems [5–7]. The ability to chemically modify the organic ligands is an important strategy to design coordination polymeric materials with new functionality [8]. Naphthalenediimides (NDI) are emerging both as a building block for organic supramolecular assembly due to their aromatic stacking ability and as a promising class of chromophores because of their strong absorption and fluorescent emission at visible and near IR wavelengths [9,10]. Recently, amino-acid functionalized NDI molecules self-assemble into hydrogen-bonded helical nano-tubes and supramolecular structures have been fabricated and found to act as receptors for fullerenes, condensed aromatic systems, and quaternary ammonium ions [12–27]. However, the metal–organic coordination assembly based on amino-acid functionalized NDI ligands has not been reported so far.

We consider that amino-acid functionalized NDI are excellent candidates of organic linkers to construct novel coordination polymers with the following advantages: (1) NDI presenting the nature of chemical robust plane which might produce stable metal–organic coordination polymers owning to strong π···π interactions among neighboring molecules; (2) NDI could act as a redox-active unit for possessing reversible electric reduction which gives the potential direction of designing photo-induced electron transfer materials; (3) NDI bearing electron-deficient aromatic core which is an attractive target for host–guest interactions, in particular donor–acceptor charge transfer type complexes; (4) amino acids and their derivatives cut a figure in biological activity and the function of beginning molecular recognition; (5) amino-acid based coordination polymers will provide an excellent platform for understanding the chirality transcription of amino acids to coordination polymers. Guided by these principles, our strategy is to construct a series of coordination polymers composed of the amino-acid functionalized NDI ligands. Herein, we wish to report the synthesis, crystal structure and physical properties of the first example of metal–organic coordination polymer with amino-acid functionalized NDI ligand, $[Zn(Gly\text{-}NDI)(DMF)_2]_n$ (**1**) (Gly-NDI = glycine-functionalized NDI, Scheme 1; DMF = dimethylformamide).

The organic ligand Gly-NDI was prepared according to literature [23]. The compound **1** was synthesized from the solvothermal reaction Gly-NDI (0.0387 g 0.1 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (0.0301 g 0.1 mmol) in 3 ml DMF at 120 °C for 72 h. The crude product was washed with DMF to give brown block single crystals of **1**. The yield of

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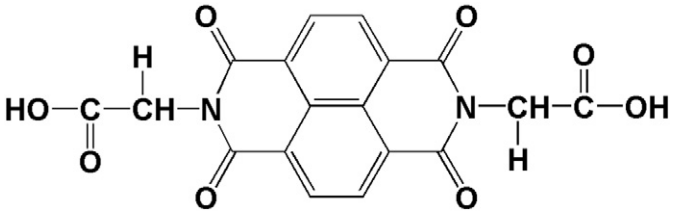

Scheme 1. The molecular structure of Gly-NDI.

1 is ca. 70 % based on $Zn(NO_3)_2 \cdot 6H_2O$. Anal. Calcd. For $ZnC_{24}H_{22}N_4O_{10}$ (%): C, 48.71; H, 3.75; N 9.47. Found (%): C, 48.62; H, 3.55; N 9.41. IR (KBr, ν/cm^{-1}): 3432(s), 1663(vs), 1453(w), 1384(s), 1292(s), 1246(s), 775(m).

Single-crystal X-ray diffraction analyses revealed that **1** crystallizes in monoclinic, space group $P2_1/c$ [28]. As shown in Fig. 1, each Zn(II) atom adopts distorted trigonal bipyramid coordination geometry through bonding to three oxygen atoms of two carboxylate groups and two oxygen atoms of two separated DMF molecules. The Zn – O bond distances present a broad region in range from 1.923(3) to 2.486(3) Å, in which the longest bond length is axial Zn1 – O2. In crystal structure of **1**, there are two crystallographic independent Gly-NDI ligands, two carboxylate groups in each Gly-NDI ligand are arranged in the *anti*-conformation with respect to the NDI core, and the carboxylate groups in two independent Gly-NDI ligands adopt different coordination modes as monodentate and chelating, respectively. All the Gly-NDI ligands are joined by $Zn(DMF)_2$ units to form a one-dimensional zigzag chain coordination polymer. The adjacent Zn1···Zn1A and Zn1···Zn1B distances are 15.195(3) Å and 16.153(3) Å, respectively, due to two independent Gly-NDI linkers. The dihedral angle of two independent NDI planes in chains is 15.714(1)°.

As known, NDI exhibits strong stacking ability in the solid state due to their planar aromatic nature [11]; thus the zigzag chains of **1** are cross-linked to a three-dimensional supramolecular framework through strong intrermolecular π···π stacking interactions with centroid-to-centroid distances of 3.604 Å (Fig. 2a and b). It has long been established that the order of stability in the interaction of two π systems is π-deficient···π-deficient > π-deficient···π-rich > π-rich···π-rich [29]. Therefore, this π-deficient functionality of NDI groups can be utilized to implement strong, directional π···π stacking interactions for crystal engineering. To clearly analyze the whole 3D supramolecular structure, the topology of **1** was studied and shown in Fig. 2c. If the intrermolecular π···π interaction were considered as a linker, each NDI core is linked to four other ones by $Zn(DMF)_2$ units and π···π interactions, which acts as a square planar 4-connected node. Therefore, the whole 3D framework can be simplified as a square planar 4-connected $CdSO_4$ (**cds**) topology [30,31]. To the best of our knowledge, the compound **1** is the first example of 3D framework with interesting **cds** topology involving both covalent and strong π···π interactions.

Powder X-ray diffraction (PXRD) was carried out to confirm the purity of **1**, and the experimental PXRD pattern perfectly match the simulated one based on the single-crystal X-ray data (Fig. 3a). Thermogravimetric analyses (TGA) of **1** were performed in an ambient atmosphere over a temperature range of 30–800 °C (Fig. 3b). The result shows that the weight loss in the range of 100–350 °C corresponds to the loss of coordinated DMF molecules, and the removal of the organic Gly-NDI occurs at 350 °C. Taking into account the excellent luminescent properties of d^{10} metal complexes [32–34] as well as the absorption and fluorescent emission at visible and near IR wavelengths of NDI [9–11], the photoluminescent spectra of powdered Gly-NDI ligand and compound **1** were measured and shown in Fig. 3c. The Gly-NDI ligand displays broad emission bands from 400 to 650 nm, and has emission peaks at 430, 457 and 525 nm under 320 nm light excitation, which come from to the π*–π transition of the aromatic organic ligands [12]. While **1** is of special interesting reviews that the maximal emission peaks at 458 nm under 320 nm light excitation, showing the seeds of blue-light-emitting materials for **1**. The luminescent mechanism of **1** could be attributed to metal-to-ligand charge transfer (MLCT) and ligand-to-ligand charge transfer (LLCT) supporting by intrermolecular π···π interactions [16,35].

In summary, the first metal–organic coordination polymer of amino-acid functionalized naphthalenediimide ligand, $[Zn(Gly\text{-}NDI)(DMF)_2]_n$ (**1**), has been synthesized and characterized. Compound **1** displays a 3D supramolecular framework with square planar 4-connected $CdSO_4$ (**cds**) topology, which formed from zigzag chains cross-linked through strong π···π stacking interactions. Additionally, **1** displays strong blue fluorescence emissions suggesting that it may be a jarless blue light-emitting material. The metal-assembly of Gly-NDI and other amino-acid functionalized naphthalenediimide ligands are under way, and the results will be reported in full papers.

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Appendix A. Supplementary material

Materials and physical measurements, Experimental procedures, CCDC No. 929820 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the

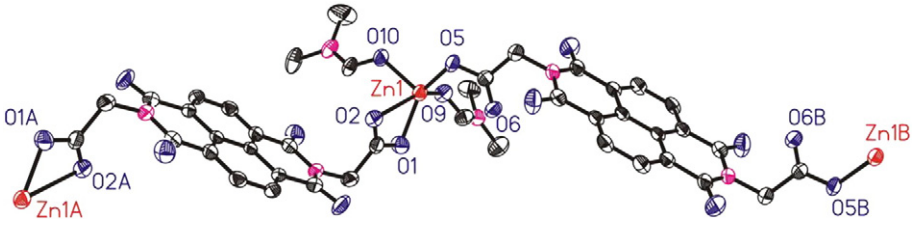

Fig. 1. View of the coordination environments of Zn(II) and Gly-NDI in **1** (symmetry code. A: $-x+1, -y, -z$; B: $-x, -y+1, -z+1$).