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Short communication

Synthesis, characterization and anticancer property of a Dy(III) compound with $[Dy_4(OH)_4]^{8+}$ secondary building units

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ABSTRACT

A novel $[Dy_4(pytza)_5(OH)_4(H_2O)_7Cl]Cl_2\cdot4H_2O$ compound based on 5-(4-pyridyl)tetrazole-2-acetic acid (Hpytza) has been designed and prepared. This compound is an unprecedented two dimensional network consisting of a tetranuclear cubic $[Dy_4(OH)_4]^{8+}$ secondary building unit (SBU) and tridentate pytza *via* the pyridine-N and the carboxylate group in a $\mu_{1,3}$-COO *syn-syn* bridging mode. PEG_{-5000} (poly(ethyleneglycol$_{-5000}$)) coated $[Dy_4(pytza)_5(OH)_4(H_2O)_7Cl]Cl_2\cdot4H_2O$ nanoparticles (NPs) have good dispersity in distilled water. *In vitro* study on Hela cells shows that such NPs show high toxicity while Hpytza is non-toxic in nature. Furthermore, such NPs can effectively inhibit the migration of Hela cells even at a low concentration, indicating their potential to inhibit the transfer of tumors *in vivo*.

Over the past decades, lanthanide coordination polymers have been given considerable attention due to not only their diversity of structures and topological networks, but also their potential applications as functional materials, such as luminescence, magnetism [1–5]. On the one hand, it is universally acknowledged lanthanide ions have much higher coordination numbers and flexible coordination environment, which can provide unique impetus for discovery of unusual network topologies, compared with other metal ions. It is, however, usually difficult to obtain desired structures because the molecular architectures of supramolecular isomers are determined by a variety of factors, pH value in particular [6–10]. On the other hand, tetrazole-carboxylate ligands have proven to be outstanding candidates for construction of coordination compounds because they tend to display various coordination modes, thus form fascinating coordination architectures [11–20].

The contemporary society bears the burden of healthy problems and cancer obviously poses a tremendous threat to the health of human beings. Therefore, great efforts have been made for ablation of cancer. Coordination compounds, as one type of drug with potential for cancer ablation, have been applied to cancer treatment [21]. However, these investigations usually focus on transition metal compounds, such as Ru(II), Ir(II) [22]. For example, D. Havrylyuk et al. reported two novel Ru(II) compounds and their photo-inactivation against cancer cells [23]. In contrast, anticancer property of lanthanide coordination compounds based on tetrazole-carboxylate ligands have been limited. In this paper, we are dedicated to investigating Dy(III)-tetrazole-carboxylate compounds derived from Hpytza (Hpytza = 5-(4-pyridyl)tetrazole-2-acetic acid). As a result, $[Dy_4(pytza)_5(OH)_4(H_2O)_7Cl]Cl_2\cdot4H_2O$ has been prepared and characterized by IR, elemental analysis and single crystal X-ray diffraction. The compound consists of a tetranuclear cubic $[Dy_4(OH)_4]^{8+}$ secondary building unit (SBU) and tridentate pytza *via* the pyridine-N and the carboxylate group in a $\mu_{1,3}$-COO *syn-syn* bridging mode, thus displays an unprecedented two dimensional network among Dy(III) compounds, to the best of our knowledge. PEG_{-5000} (poly(ethyleneglycol$_{-5000}$)) coated $[Dy_4(pytza)_5(OH)_4(H_2O)_7Cl]Cl_2\cdot4H_2O$ nanoparticles (NPs) have good dispersity in distilled water. *In vitro* study show that Hpytza is non-toxic itself while PEG_{-5000} (poly(ethyleneglycol$_{-5000}$)) coated $[Dy_4(pytza)_5(OH)_4(H_2O)_7Cl]Cl_2\cdot4H_2O$ NPs show a low IC_{50} (half-maximal inhibitory concentration) towards Hela cells. In addition, the two compounds can interfere with the migration of Hela cells, which may be able to inhibit the migration of tumors *in vivo*.

The X-ray diffraction reveals that $[Dy_4(pytza)_5(OH)_4(H_2O)_7Cl]Cl_2\cdot4H_2O$ crystallizes in monoclinic lattice with space group $P\bar{1}$. As illustrated in Fig.1, all the four Dy(III) ions are octa-coordinated and display distorted square antiprism coordination arrangements. Dy(1) is octa-coordinated by three oxygen atoms from three hydroxyl anions (O25, O27, O28), two atoms from two water molecules (O41, O42) and three oxygen atoms (O12, O16, O19) from three carboxylate groups of three independent 4-pytza ligands (Fig. 1a); Dy(3) by three hydroxyl oxygens (O26,

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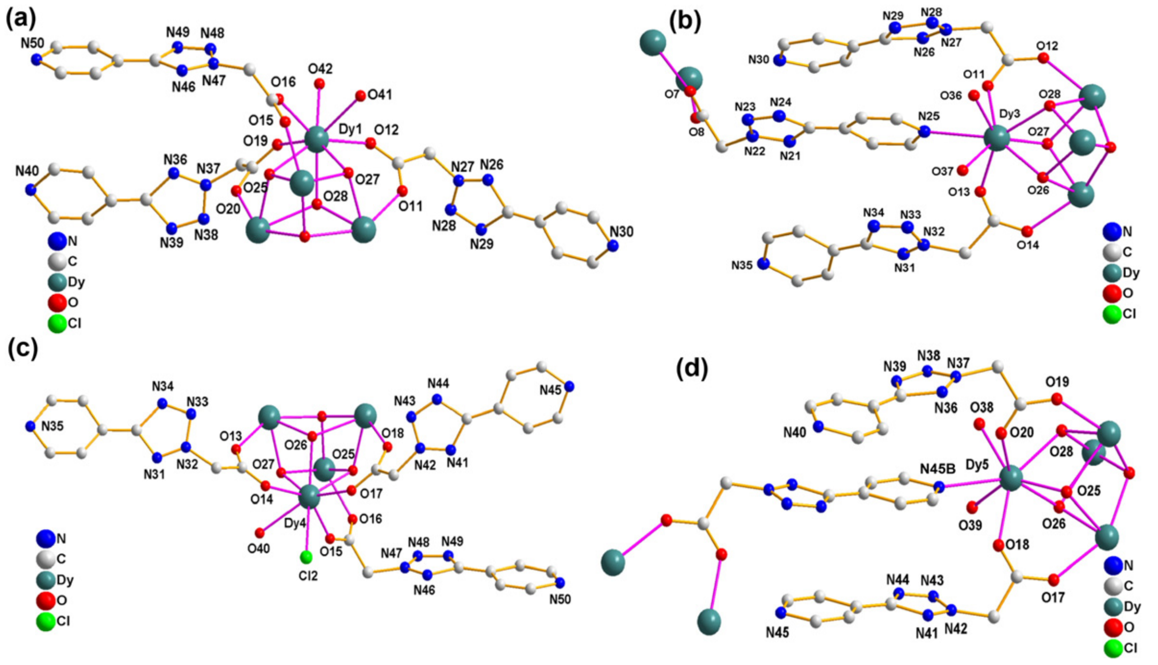

Fig. 1. The coordination environment of Dy(III) in $[Dy_4(pytza)_5(OH)_4(H_2O)_7Cl]Cl_2\cdot 4H_2O$, (a) for Dy(1); (b) for Dy(3); (c) for Dy(4) and (d) for Dy(5). Hydrogen atoms are omitted for clarity.

O27, O28), two water oxygens (O36, O37), two carboxylate oxygens (O11, O13) and one nitrogen atom (N25) (Fig. 1b); Dy(4) by three hydroxyl oxygens (O25, O26, O27), one water oxygen (O40), three carboxylate oxygens (O14, O15, O17) and one chloride anion (Cl2) (Fig. 1c); The coordination environment of Dy(5) is similar to that of Dy(4) (Fig. 1d). Each hydroxyl anion acts as a tridentate ligand to connect to three Dy(III) centers to form a distorted cubane-shaped $[Dy_4(OH)_4]^{8+}$ unit with four Dy(III) atoms at the corners of a slightly irregular tetrahedron (Fig. 2a–b), with four hydroxide oxygen atoms occupying positions outside the faces of the Dy(III) tetrahedron (Fig. 2c). Then neighboring Dy(III) centers are bridged by three bidentate 4-pytza ligand in a $\mu_{1,3}$-COO *syn-syn* mode, respectively (Fig. 2d). These tetranuclear $[Dy_4(OH)_4]^{8+}$ clusters, which behave as SBUs, are bridged by tridentate pytza *via* one pyridyl nitrogen and carboxylate group in a $\mu_{1,3}$-COO *syn-syn* bridging mode to form a two dimensional layer extending along the *bc* plane (Fig. 2e). The Dy—O distances ranging from 2.374 to 2.669 Å are in good agreement with those of the previously reported Dy(III) compounds [26]. The structure is unprecedented among Dy(III) compounds, to the best of our knowledge. Adjacent layers are further held together by various hydrogen bonds to form a three dimensional network (Fig. S1, Table S2).

The absorption spectra of Hpytza and $[Dy_4(pytza)_5(OH)_4(H_2O)_7Cl]Cl_2\cdot 4H_2O$ were shown in Fig. 3a, Hpytza and $[Dy_4(pytza)_5(OH)_4(H_2O)_7Cl]Cl_2\cdot 4H_2O$ show two peaks at 233, 273 nm, 224, 272 nm, respectively. The peak at 233 and 224 nm is attributed to π-π* transition of the ligand. The absorption detected within the region of 261–350 nm for Hpytza, 250–352 nm for $[Dy_4(pytza)_5(OH)_4(H_2O)_7Cl]Cl_2\cdot 4H_2O$ are associated with n-π* transitions of the ligands. For the emission, Hpytza and the compound show emission with maximum intensity at 431 and 474 nm, respectively. The red shift of the emission spectrum are associated with the coordination of Dy(III) to Hpytza. In the IR spectrum of the compound (Fig. 3c), peak at 2418 cm^{-1} is attributed to the vibration of the O—H bond from both coordinated and guest water molecules; the absorbance at 1617 cm^{-1} is ascribed to the asymmetric vibration of the carboxylate group while peaks ranging from 1529 to 1432 cm^{-1} are assigned to the characteristic peaks of the C═N of both tetrazole and pyridine rings. DLS (dynamic light scattering) indicates that $[Dy_4(pytza)_5(OH)_4(H_2O)_7Cl]Cl_2\cdot 4H_2O$ can self-assemble into nanoparticles with size distribution from 90 to 220 nm, respectively (Fig. 3d).

To further study the toxicity of these compounds, MTT assay was performed. Different concentrations of $[Dy_4(pytza)_5(OH)_4(H_2O)_7Cl]Cl_2\cdot$

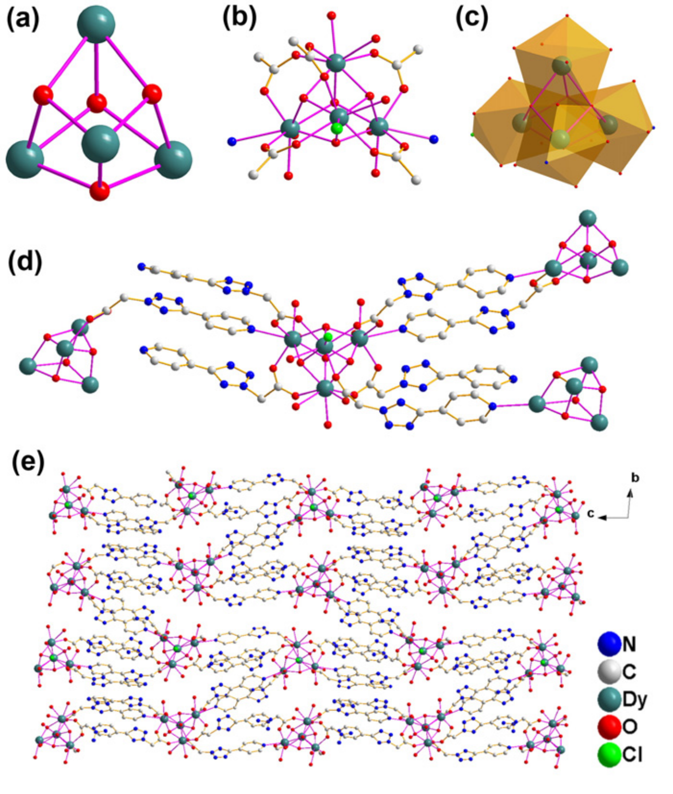

Fig. 2. (a) Illumination of cubic $[Dy_4(OH)_4]^{8+}$ SBU; (b) bridging mode of Dy(III) ions in $[Dy_4(OH)_4]^{8+}$; (c) polyhedrons around Dy(III) ions; (d) illumination of the tetra-bridge of adjacent $[Dy_4(OH)_4]^{8+}$; (e) Two dimensional layer structure of $[Dy_4(pytza)_5(OH)_4(H_2O)_7Cl]Cl_2\cdot 4H_2O$ extending along the *bc* plane.