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A novel stable 3D luminescent uranyl complex for highly efficient and sensitive recognition of Ru^{3+} and biomolecules

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ABSTRACT

A novel highly stable 3D luminescent uranyl coordination polymer, namely $\{[UO_2(L)]\cdot DMA\}_n$ (**1**), was assembled with uranyl salt and a glycine-derivative ligand [6-(carboxymethyl-amino)-4-oxo-4,5-dihydro-[1,3,5]triazin-2-ylamino]-acetic acid (H_2L) under solvothermal reaction. Besides, It was found that complex **1** possesses excellent luminescent properties, particularly the efficient selectivity and sensitivity in the recognition of Ru^{3+}, biomacromolecule bovine serum albumin (BSA), biological small molecules dopamine (DA), ascorbic acid (AA) and uric acid (UA) in the water solution based on a "turn-off" mechanism. Accordingly, the luminescent explorations also demonstrated that complex 1 could be acted as an efficient luminescent probe with high quenching efficiency and low detection limit for selectively detecting Ru^{3+} and biomolecules (DA, AA, UA and BSA). It was noted that the framework structure of complex **1** still remains highly stable after quenching, which was verified by powder X-ray diffraction (PXRD).

1. Introduction

Over the decades, actinide-based coordination polymers have attracted ever-increasing attention not only because of their versatile appealing architectures and topologies in structural chemistry [1,2] but also their remarkable applications in photocatalysis [3,4], luminescence [5–8], separation [8,9], ion exchange [10,11] and biomaterial [12]. Uranium acting as the most representative element of actinide has a particular 5f orbit, which can be coordinated with the corresponding ligands. Among the uranium-bearing materials, the linear UO_2^{2+} cation is the major form of uranium (VI), the coordination environment of the uranyl in the equatorial plane is a flexible 4–6 atoms being coordinated, resulting in three uranyl primary building units (PBUs) including tetragonal, pentagonal and hexagonal bipyramids. It is precise because of the fixedness of two terminal oxygen atoms ($O^{=}U^{=}O$), one-dimensional and two-dimensional uranyl complexes are favored. There is thereby an urgent need but it is still a significant challenge to obtain three-dimensional uranium (VI)-organic frameworks (UOFs) with intriguing architectures and properties.

A succession of metal organic frameworks (MOFs) as highly selective luminescent sensors have been reported and their sensing scope includes gas molecules [13], solvent molecules [14], metal ions (Fe^{2+}, Fe^{3+}, Cu^{2+}, Hg^{2+}, Cr^{6+}, Al^{3+}, MnO_4^-) [15–19], small biomolecules thiamines (TPP, TCM, TCI, glycol) [20–23]. On this basis, we have broadened the scope of the detection of chemical substances, and the systematic study of these chemicals for efficient detection appears vital in particular. For example, Ruthenium, as the central atom of the synthesis of various catalysts with different catalytic performance, has been widely applied in pharmaceuticals [24,25], chemical materials [26,27], and industrial production [28]. Futhermore, dopamine (DA), ascorbic acid (AA) and uric acid (UA) are paramountly critical biochemical molecules in many physiological processes. Among them, dopamine (DA) is a derivative of catechins as a neurotransmitter used to help cells transmit pulsed chemicals [29,30]. Ascorbic acid (AA), a water-soluble vitamin, is an essential nutrient to the human body, which plays an important role in the growth and repair of human tissue, the function of the adrenal gland and the overall health as an antioxidant [31,32]. Uric acid (UA) is an end product from purine derivatives in human metabolism, slightly soluble in water, easy to crystallize [33]. These functional biomolecules (DA, AA and UA) coexist in body fluids. In addition, considerable research efforts have been devoted to studying the fluorescence quenching of biological

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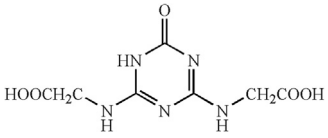

Scheme 1. Structure of ligand, [6-(carboxymethyl-amino)-4-oxo-4,5-dihydro-[1,3,5] triazin-2-ylamino] -acetic acid (H_2L).

Table 1
Crystallographic data and structure refinement for complex **1.**

Complex	**1**
chemical formula	$C_{11}H_{15}N_6O_8U$
M (g mol^{-1})	597.32
Crystal system	Tetragonal
Space group	*I* 41/*a*
a (Å)	13.879 (9)
b (Å)	13.879 (9)
c (Å)	39.672 (3)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
V ($Å^3$)	7642.1 (7)
Z	16
Temperature/K	293 (2)
D_{calcd} (g cm^{-3})	2.077
F (000)	4464.0
μ (M_O-Kα) (mm^{-1})	8.545
2θ (deg)	4.1–52.92
No. of reflns collected	21150
No. of independent reflns	3932
Patams	181
R_{int}	0.0578
Δ(ρ) (e $Å^{-3}$)	1.99 and – 0.81
GOF	1.591
R_1[a]	0.0511[b]
ωR_2[a]	0.1465[b]

[a] $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $\omega R_2 = [\Sigma\omega (F_o^2 - F_c^2)^2 / \Sigma\omega (F_o^2)^2]^{1/2}$; $|F_o| > 4\sigma(|F_o|)$.
[b] Based on all data.

macromolecules in MOFs. As is known to all, bovine serum albumin (BSA) is a globulin in bovine serum containing 583 amino acid residues, widely used in electrochemical research [34], genetic engineering [35] and drug research [36]. Despite these substances mentioned above appear to be infinitely important, unfortunately, to the best of our knowledge, MOFs that can act as luminescent sensors for these biological small molecules dopamine (DA), ascorbic acid (AA) and uric acid (UA) as well as biomacromolecule bovine serum albumin (BSA) have been less reported up to now [37,38].

In recent years, the construction of supramolecular coordination polymers via rigid or flexible carboxylic acid ligands [39] has become a hot research topic. The coordination conformations of the rigid ligands are predictable [40], however, flexible ligands can adopt different coordination conformations to overcome the steric hindrance effect, thus forming unpredictable intriguing topologies and properties. Therefore the flexible ligands containing triazine ring derivatives are widely used in the synthesis of MOFs because of their ease of synthesis and rich functional groups(- NH and - COOH), but there are not many literatures on the synthesis of uranyl complexes with triazine derivatives ligands and uranyl salts [41].

Herein, a new highly stable 3D luminescent uranyl-organic framework $[UO_2(L)\cdot DMA]_n$ (**1**) under solvothermal reaction was constructed for the first time by using a flexible glycine-derivative ligand 4,6-bis(carboxymethyl-amino)-2-oxo- 1,3,5-triazine (H_2L) featuring two carboxylate groups (Scheme 1). To the best of our knowledge, this is the first report on reaction of the actinide metal salts with the ligand H_2L up to now. Expectedly, complex **1** manifests satisfactory topologies and luminescent properties, and we systematically investigated and elaborated the detection of Ru^{3+} ion as well as biomacromolecule (BSA) and biological small molecules (DA, AA and UA).

2. Experimental section

2.1. Materials and methods

Caution! The standard procedures should be followed when handling radioactive materials, although uranyl nitrate hexahydrate ($UO_2(NO_3)_2\cdot 6H_2O$) in the laboratory contained depleted uranium. The chemicals were commercially available and used without further purification.

Powder X-ray Diffraction (PXRD) patterns were collected on a D8 Advance Bruker diffractometer with Cu Kα radiation (λ=0.71073 Å) with 2θ angles from 5° to 50°. An Elemental Vario EL III CHONS analyzer was used to collect the C, H, N elemental contents. The infrared spectrum (IR) was performed as KBr pellet using an Acatar (tm) 360 E.S.P. IR spectrophotometer in a range of 4000–400 cm^{-1}. Thermogravimetric analysis (TGA) was measured by using a STA449C integration thermal analyzer under a nitrogen atmosphere at a heating rate of 10 ℃/min. The UV spectra of complex **1** and H_2L were measured on a UV-3100 spectrophotometer (200–2500 nm). The fluorescent emission spectra of complex **1** and ligand H_2L were conducted on a Hitachi F-4500 spectrophotometer equipped with a 150 W xenon lamp as the excitation source at 298 K.

2.2. Synthetic procedures

2.2.1. Synthesis

H_2L was synthesized by improving the related literature [42].

2.2.2. {[$UO_2(L)$]·DMA}$_n$ (1)

A mixture of $UO_2(NO_3)_2\cdot 6H_2O$ (0.1 mmol, 0.0505 g) and H_2L (0.1 mmol, 0.0243 g) was added to the solution of DMA/H_2O

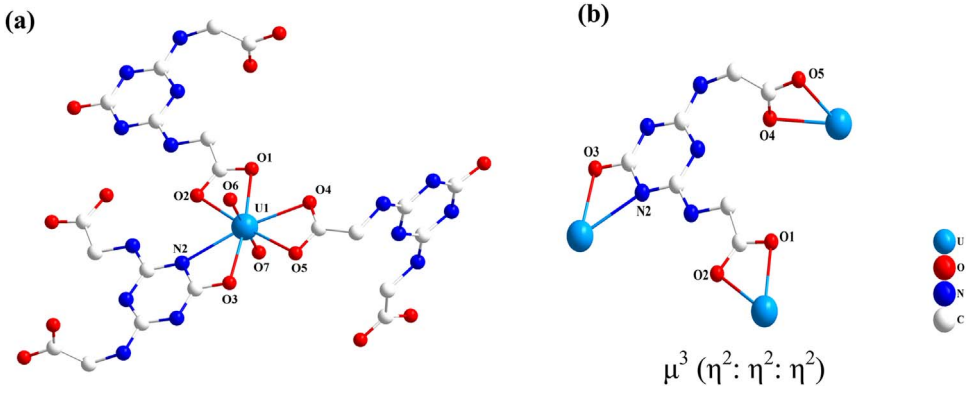

Fig. 1. Crystal structure of complex **1**: (a) UO_2^{2+} coordinated environment of complex **1**; (b) coordination mode of L^{2-}.