

具有强绿色荧光发射效应的 2,2'-二硝基 4,4'-联苯酸铀(VI)配聚合物

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Uranium(VI) Coordination Polymer Based on 2,2'-dinitro-biphenyl-4,4'-dicarboxylic Acid with Strong Green Fluorescent Emission

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Abstract: A very complex 3D Uranium(VI) metal-organic framework was obtained by the hydrothermal treatment of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with (*R,S*)-2,2'-dinitro-biphenyl-4,4'-dicarboxylic acid (BTNCA) (L) in water at 180 °C in Pyrex tubes. The crystal belongs to monoclinic system with space group $P2_1/c$, and $a=0.54590(3)$ nm, $b=3.67601(18)$ nm, $c=2.65981(13)$ nm, $\beta=91.4060(10)^\circ$, $V=5.3359(5)$ nm³, $Z=4$. CCDC: 659615.

Key words: uranium(VI) complex; hydrothermal reaction; crystal structure; fluorescence

In the last several years, many ligands such as bipyridine, dicarboxylate and even tricarboxylate organic compound were introduced into the coordination compounds for yielding a variety of metal-organic frameworks^[1-4]. Interestingly, through a highly versatile technique for the synthesis of polymer, hydrothermal treatment, lots of coordination compounds derived from main group metals and transition metals were afforded^[5-12]. Such materials exhibit catalytic, enantioseparation, optical, magnetic and any other physical properties. Herein, we would like to report the synthesis and crystal structure of a new kind of uranium coordination compound with atropisomeric ligand (*R,S*)-2,2'-dinitro-biphenyl-4,4'-dicarboxylic acid (BTNCA) (L). Uranium (VI) complex $\{[\text{UO}_2((R,S)-1,1'$ -biphenyl-2,2'-dinitro-4,4-

dicarboxylate)] $[\text{UO}_2((R,S)-1,1'$ -biphenyl-2,2'-dinitro-4,4-dicarboxylate)(H₂O)] $[\text{U}((R,S)-1,1'$ -biphenyl-2,2'-dinitro-4,4-dicarboxylate)(H₂O)₄]} (5H₂O) was obtained by the hydrothermal treatment of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with BTNCA, as shown in Scheme 1.

Compound $\{[\text{UO}_2((R,S)-1,1'$ -biphenyl-2,2'-dinitro-4,4-dicarboxylate)] $[\text{UO}_2((R,S)-1,1'$ -biphenyl-2,2'-dinitro-4,4-dicarboxylate)(H₂O)] $[\text{U}((R,S)-1,1'$ -biphenyl-2,2'-dinitro-4,4-dicarboxylate)(H₂O)₄]} bears a very complex and interesting 3D metal-organic framework with large voids which are full of water. At the meantime, this complex is a good green fluorescent material in solid state at room temperature.

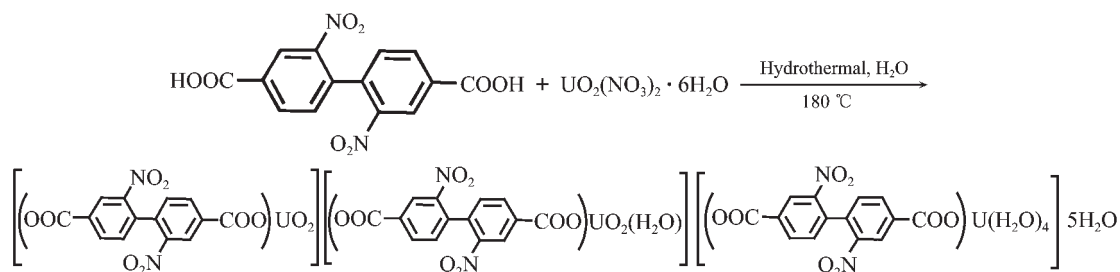
The crystal of the title complex belongs to monoclinic system with space group $P2_1/c$, and $a=$

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Scheme 1

0.545 90(3) nm, $b=3.676$ 01(18) nm, $c=2.659$ 81(13) nm, $\beta=91.4060(10)^\circ$, $V=5.335$ 9(5) nm³, $Z=4$. (CCDC: 659615). As Fig.1 shows, the complex with an interesting three-dimensions structure: nitro group fails to coordinate to uranium center, but there are three different uranium centers in the complex (Fig.1): U1 is surrounded by four equatorial oxides of carboxylic group from four different BTNCA and two axial oxygen which come into being a uranyl group together with the U1 center (O22-U1-O23 angle: 179.2°, U1-O23, 0.177 8(6); U1-O22, 0.178 2(7) nm) to form a slight distorted octahedron. U2 as a sept-coordinated centers coordinates to three organic atropisomeric ligand (*R,S*)-1,1'-biphenyl-2,2'-dinitro-4,4'-dicarboxylate (BTNCA), water and two oxygen to form a pentagonal bipyramid in which the axial sits belong to two oxides forming uranyl group (O17-U2-O21) angle: 178.5(3)°, U2-O21, 0.175 5(7) nm; U2-O17, 0.175 6(8) nm), while five equatorial sits are occupied by one oxygen atom from water and four oxygen atoms of three carboxylic groups of three organic ligand BTNCA, one of whose carboxylic group chelate to U2. The coordination environment of U3 can be best described as dodecahedron defined four oxygen from water and the other four oxygen atoms from

carboxylic group of two ligands which chelate to U3 center through oxygen atoms of the same carboxylic group, interestingly, four coordinated water lies in the same plane as the coordinated oxygen atoms of ligand do. However, although all of BTNCA as quadridentate connect three uranium centers through their four oxides of carboxylic groups (one of carboxylic group bridges two uranium centers, the other chelate to one uranium center), there are three different coordinate modes for BTNCA too. Ligand 1 (L1) whose dihedral of two phenyl rings is 63.9° connected three different coordinated environment uranium centers (U1, U2, U3) and chelate to U3; L2 whose dihedral of two phenyl rings is 77.5° differently coordinate to two same centers as U1 and chelate to one center as U3; while L3 links one uranium center as U1 and two uranium centers as U2, one of which coordinate to two oxide of the same carboxylic group. At the same time, some atoms of ligand, uranium center as U1 and uranium center as U2 come into being several eight-membered rings (such as U1A-O3A-C19-O1-U1-O3AA-C19A-O1A and U1-O2C17-O20-U2-O5-C33-O4), as a result, uranium subsequent in one chain is U2, U1, U1 and U2. Such chains connect to each other or connect with U3 (Fig.1) through ligand to form a novel three-dimensions framework.

However, such 3D framework bear large void (0.464 7 nm³), which are full of water. If removes the water through high temperature, a large solvent molecule such as toluene may be inserted in the void. In the end, as show in Fig.2, strong hydrogen bonds exist among uncoordinated water, coordinated water and carboxylic groups of ligands.

The fluorescent emission spectra for the complex wavelengths produced the characteristic vibronic structure of the UO²⁺ moiety which have five chara-

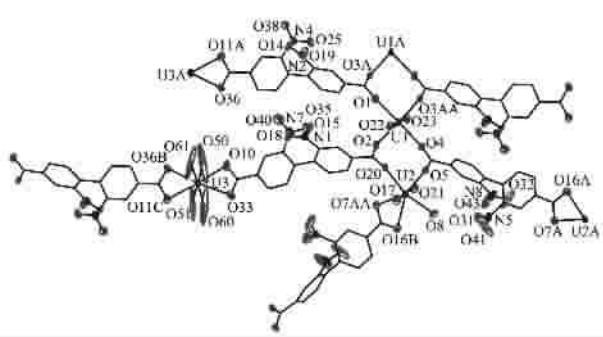


Fig.1 An asymmetric ORTEP of the complex, drawn at 30% ellipsoids probability, hydrogen atoms are omitted for clarity

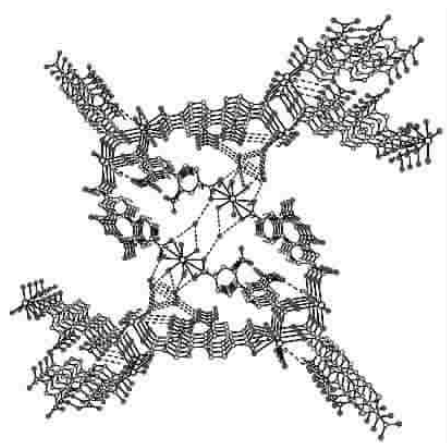


Fig.2 Hydrogen bonding interaction view of the complex (along *a* axis)

characteristic peaks of each spectrum ranged from about 425 ~500 nm and exhibit strong green fluorescent emission at room temperature in solid state (Fig.3).

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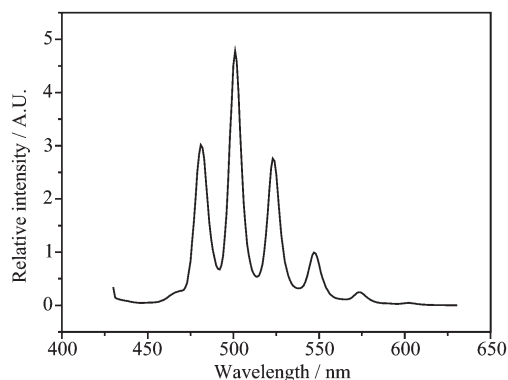


Fig.3 Fluorescence spectra of the complex in the solid state at room temperature