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Construction of a microporous inorganic–organic hybrid compound with uranyl units†

Zhen-Tao Yu, Zuo-Lei Liao, Yu-Sheng Jiang, Guang-Hua Li, Guo-Dong Li and Jie-Sheng Chen*
State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China. E-mail: chemcj@mail.jlu.edu.cn

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A uranium–nickel–organic hybrid compound with micropores has been assembled from a hydrothermal system, and this compound exhibits photocatalytic activities for the degradation of methyl blue as a model pollutant.

The construction of inorganic–organic porous frameworks is gaining continuing interest owing to their fascinating structures associated with various metal–ligand coordinations, as well as properties tunable through the variation of building blocks and reaction conditions.[1] Among these hybrid compounds, some were acquired by self-assembly of organic ligands and polyoxoanions or metal–oxygen cluster components (MOCC) acting as inorganic subunits.[2] In these cases, the stability of the materials with respect to removal of the guest species can be enhanced.[3] However, most of the MOCC-containing hybrid compounds reported in the literature were formed by d-block transition metals such as Ni, Cu, Mo and V, Group 12 metals (Zn, Cd),[2,4] and La and other 4f-lanthanides.[3b,5] It is known that the 5f-element U in its high oxidation state has MOCC formation ability.[3c,6] Much study has been focused on the search for new uranium-bearing materials due to their interesting structural topologies and diverse physical–chemical properties for potential magnetic,[7] optical,[8] catalytic and ion-exchange applications,[9] as well as their ability for the binding and activation of N_2 for nitrogen fixation.[10] The use of uranyl units as nodes for the construction of porous frameworks is attractive because this may lead to unusual structures and interesting physical–chemical properties. Following the successful synthesis of a U-containing coordination polymer which is non-porous,[3c] we report in this communication the synthesis, structure and photocatalytic property of a novel 3D microporous uranium–nickel–organic compound built up from O-bridged uranium-cluster ribbons, namely, $[Ni_2(H_2O)_2(QA)_2(bipy)_2U_5O_{14}(H_2O)_2(OAc)_2]\cdot 2H_2O$ (**1**) (HOAc = acetic acid; bipy = 4,4′-bipyridine; H_2QA = quinolinic acid).

The pale-yellow crystals of **1** were obtained from the typical reaction of $Ni(OAc)_2\cdot 4H_2O$, $UO_2(OAc)_2\cdot 2H_2O$, bipy, H_2QA and water in a molar ratio of 1 : 0.75 : 1 : 1 : 500 at 160 °C for 7 days *via* the hydrothermal method (*ca.* 60% yield based on the amount of uranium). The product remained stable in water and air. An intense IR absorption band observed between 800 and 950 cm^{-1} is clearly assigned to the asymmetric O = U = O stretching mode of the uranyl moiety for **1**. Compound **1** was also characterized by single-crystal X-ray structural analysis,‡ and is supported by the microanalysis results.[11]

The structure of **1** (Fig. 1) can be described as a 3D-network constructed from the polyoxouranium ribbons and Ni metal–organic layers through sharing QA ligands, in which the polyoxouranium ribbons are composed of a UO_8 hexagonal bipyramid and two different UO_7 pentagonal bipyramids by joining these through μ_3-O bridges. The bridging QA ligands and the chelating OAc species are located on both sides of the polyoxouranium ribbons. In each ribbon, a pair of trinuclear U-cores are bridged by μ_3-O atoms to form a centrosymmetric pentanuclear U_5O core, which repeats itself along the *b* axis. The apical uranyl bonds and equatorial U–O bonds range from 1.796(6) to 1.806(7) Å and from 2.213(5) to 2.633(7) Å, respectively.[12] In the structure of **1**, there are two types of Ni octahedral coordination environments. The Ni(1) site is coordinated by two chelating QA ligands in the equatorial positions and by two nitrogen donors of two respective bipy ligands in the axial positions to furnish a NiO_2N_4 octahedral geometry. Ni(2) is coordinated by two axial nitrogen donors from two respective bipy ligands, and in the equatorial positions by two oxygen atoms of two QA ligands and two apical aqua oxygen atoms to complete its NiO_4N_2 octahedral coordination sphere. The two different Ni atoms are bridged by the QA ligands to form infinite 1D chains along the *a* axis, and adjacent chains are interlinked by the bipy spacers as pillars to generate an infinite 2D layer parallel to the *ab* plane. The 2D layers are further interconnected to the polyoxouranium ribbons by QA ligands, leading to the formation of a 3D bimetallic framework with channels, which are occupied by disordered water molecules, along the *a* and *b* directions.

1 has demonstrated a high thermal stability. From thermal gravimetric analysis, the dehydration weight loss of **1** is observed to be about 4.94 wt% in the range of room temperature to 200 °C, indicating that about six water molecules per formula unit can be released from the network (calculated value 4.50 wt%). It is worth noting that although no further weight loss is observed upon heating from 200 to 360 °C, the framework decomposes accompanied by a second weight loss of about 29.36 wt% in the range from 360 to 600 °C, corresponding to the removal of the organic component (calculated value 29.69 wt%). The powder XRD patterns for the product heated at 300 °C for 3 h remained unchanged relative to the as-synthesized sample of **1**, indicating stability of the framework after the dehydration process. After dehydration, **1** re-absorbs water molecules (2.60 Å in diameter) evidenced by measurement of its water sorption isotherms using an electrogravimetric balance. The water-sorption isotherm for **1** (Fig. 2) is suggestive of the existence of a microporous system with an estimated pore volume of 0.04 $cm^3\,g^{-1}$. The powder XRD patterns indicate that **1** maintains its structural integrity after dehydration–rehydration cycles. **1** has no N_2-adsorption capacity, probably because the pore size of **1** is not large enough to allow the penetration of N_2 molecules (3.64 Å in diameter).[1e]

So far, the search for photocatalytic materials is motivated largely by a demand for solving fuel and pollution problems in view

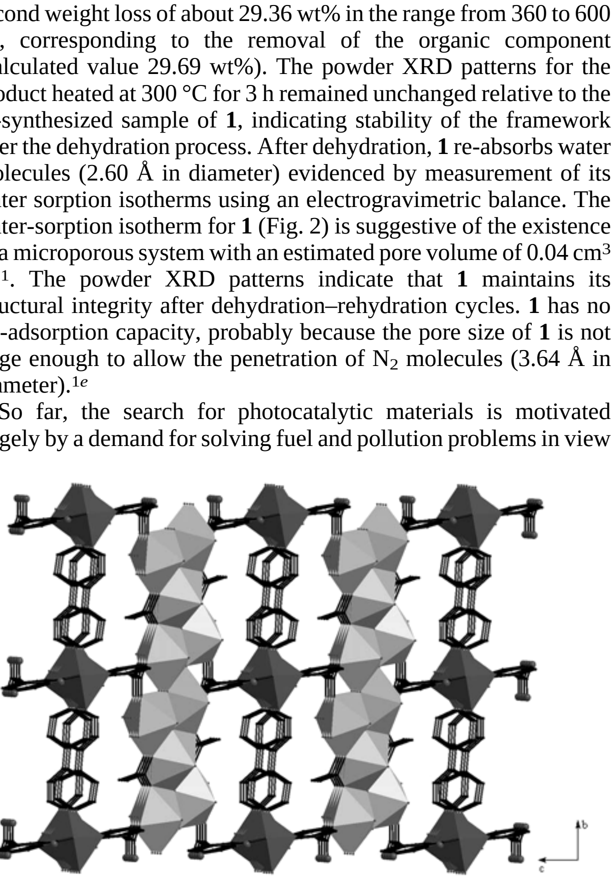

Fig. 1 View of the structure of **1** along the *a* axis. Water molecules occluded in the channels are omitted for clarity.

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† Electronic Supplementary Information (ESI) available: tables of crystal data, figures giving additional views and additional characterization data. See http://www.rsc.org/suppdata/cc/b4/b406019a/

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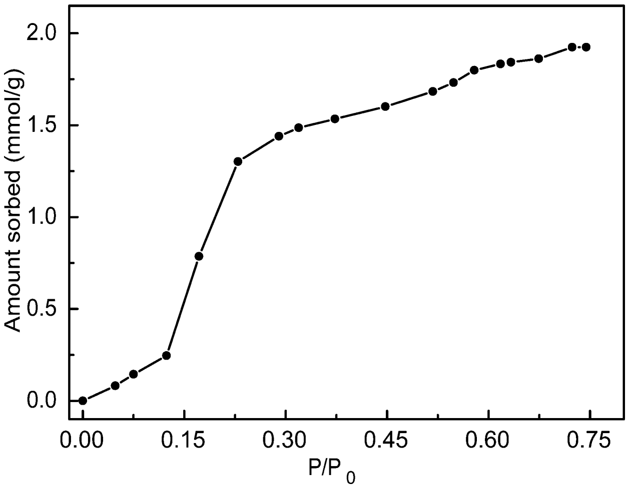

Fig. 2 Water sorption isotherm for **1** at 293 K. P_0 represents the saturated vapor pressure.

of their possible applications in the green degradation of organic pollutants and the splitting of water into H_2 and O_2 as a renewable energy source for the chemical utilization of solar energy.[13] In this regard, we have recently explored new water-insoluble and easily recycled materials with photocatalytic activities by combining the geometry and photochemistry of uranyl (UO_2^{2+}) units, because these uranyl units have the potential to photocatalytically oxidize organic substrates.[14] We have selected a N-containing dye, methyl blue (MB), as a model pollutant in aqueous media to demonstrate the photocatalytic effectiveness of **1**. The photocatalytic performance of **1** was estimated from the variation of the color in the reaction system by monitoring the absorbance (at λ = 600 nm) characteristic of the target MB, which directly relates to the structure change of its chromophore. As shown in Fig. 3, it is clearly indicated that **1** is effective in the degradation of the dye using UV light irradiation ([MB] = 0.10 mmol L^{-1}, 80 mL dispersion and 160 mg (0.067 mmol) of **1** loading). At the time of complete decolorization, about 45% of mineralization was achieved, as confirmed by the total organic carbon (TOC) analysis. It is important to note that **1** also exhibits photocatalytic activity for the degradation of MB with xenon-lamp light irradiation which is used to simulate solar light (the wavelength of the main output is longer than 400 nm). Although a more detailed mechanism is yet to be elucidated, it is believed that the uranyl units in **1** are responsible for the photocatalytical activity as UO_2^{2+} species in solution have already demonstrated photocatalytic properties.[14] We anticipate that the successful synthesis of **1** may assist in the design and exploitation of new interesting water-insoluble porous materials with uranyl sites that are able to find useful applications.

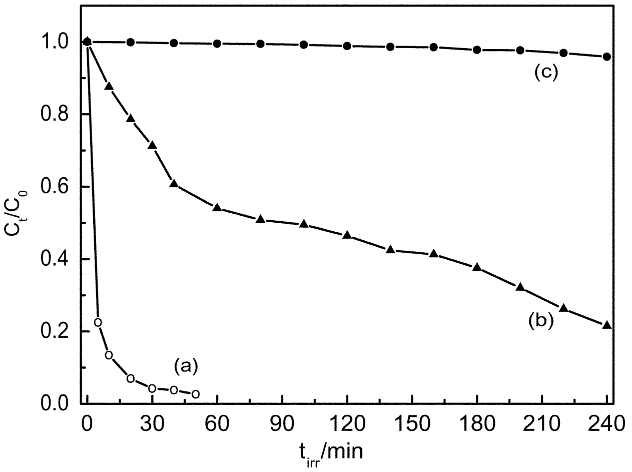

Fig. 3 Plots of concentration *versus* irradiation time for (a) MB irradiated with UV light in the presence of **1**, and (b) MB under xenon-lamp irradiation in the presence of **1** and (c) MB under xenon-lamp irradiation without photocatalyst. C_t and C_0 stand for the dye concentrations after and before irradiation, and t_{irr} for the irradiation time.

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Notes and references

‡ Crystal data for **1**: $C_{19}H_{20}N_3NiO_{16}U_{2.5}$, M_r = 1200.17, triclinic, space group $P\bar{1}$, a = 10.5466(2), b = 10.8779(2), c = 13.4741(3) Å, α = 89.1470(10), β = 74.0720(10), γ = 80.1120(10)°, V = 1463.54(5) $Å^3$, T = 293(2) K, Z = 2, μ(Mo–Kα) = 14.503 mm^{-1}, 7063 reflections measured of which 4979 were unique and 397 were observed (R_{int} = 0.0521). The final anisotropic values R_1 = 0.0346 and wR_2 (all data) = 0.0943, and the goodness-of-fit on F^2 is 1.046. CCDC 218126. See http://www.rsc.org/suppdata/cc/b4/b406019a/ for crystallographic data in .cif or other electronic format.

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