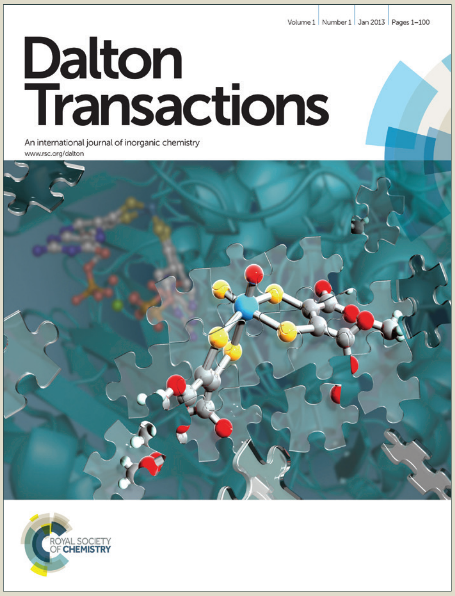
Dalton Transactions

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Journal Name

COMMUNICATION

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Homochiral 3D Coordination Polymer with Unprecedented Three-Directional Helical Topology from Achiral Precursor: Synthesis, Crystal Structure, and Luminescence Properties of Uranyl Succinate Metal-Organic Framework

Juan Wang,*[a] Zhen Wei,[a] Fengwan Guo,[b] Chenyang Li,[a] Pengfei Zhu[a] and Wenhua Zhu[a]

A luminescent homochiral uranyl succinate coordination polymer with unprecedented three-directional helices was synthesized hydrothermally via spontaneous symmetry breaking, and fully characterized. Its homochirality has been confirmed by single crystal x-ray diffraction and solid state circular dichroism (CD) spectra. The polymer exhibited a Stokes shift greater than 180 nm.

The exploration of coordination topologies and architecturesin coordination polymers and metal-organic frameworks have been exponentially increased in the past decades, not only because they are naturally beautiful but also because they are crucial in understanding the fasinating peroperties and functions of the cooresponding coordination complexes. Up to now, many topologies in coordination polymers have been reported, and several reviews on this topichave been published.[1] Among the various coordination topologies, helical structures[2] are arguably the most interesting architectures, due to their paramount existence and important roles in biologically systems. They also often lead to chiral coordination polymers, which have gained a lot of attention recently because of their potential applications in such as enantioselective catalysis and chiral molecular recognitions.[3] Currently, many helical structures containing single and double directional helices have been reported. However, no literature about three-directionalhelices was published thus far.

There are basically two approaches to the synthesis of chiral coordination polymers. One is to use chiral ligands or chiral reagents/solvents; the other is relied on spontaneous resolution and symmetry breaking during crystallization without any optically active ligands or reagents.[4] Clearly, the second approach is more attractive since it does not need chiral compounds, which generally are expensive and often require laborious synthesis. In spite of recent progress, chiral, especially homochiral coordination polymers synthesized from achiral precursors are still uncommon.

In the past decade, uranyl-containing polymers[5,6] have gained much momentum. Besides their potential applications shared by other common coordination polymers, these polymers possess remarkable optical properties such as long luminescence lifetime, large Stokes' shift, line-like emission band and negligible concentration quenching.[7] They also play an important part in nuclear waste treatment and extraction/separation of uranium from natural uraninium resources.[8] Additonally, uranyl has a unique spatial arrangement, in which the terminal oxygens are usually in axial positions and other ligating atoms in equatorial positions, thus frequently forming square, pentagonal and hexagonal pyramidals.[9] This gives chemists some degree of control on the topologies.Several research groups have exploited this structural feature and disclosed quite a few U-frameworks with diversity topologies, including helical architectures.[10]

Inspired by these promising results, we recently initiated a program on the synthesis of uranyl-containing polymers possibly withunique topologiesor even chirality from achiral ligands. Our strategy is to pair UO_2^{2+} with similarly semi-rigid organic ligands together. This combination may increase the chance of symmetry breaking. Similar principle has been convincingly demonstrated recently.[11] Gratifying, we have successfully synthesized a novel helical uranyl succinate coordination polymer, $\{[(UO_2)_4(Suc)_2(HSuc)_4]\cdot 2H_2O\}_n$(**I**, H_2Suc = succinic acid) from UO_2 and achiral butanedioic acid under hydrothermal condition. The complex is not only homochiral, but also features three-directional helices, which has never been reported before, to our best knowledge. In this contribution, we report the synthesis, its crystal structure and luminescence properties.

Results and discussion

Synthesis and Crystal Structure

Coordination polymer I was synthesized by reaction of succinic acid with uranyl nitrate, which was generated in situ by oxidation of uranium dioxide with nitric acid at pH~2.5 under hydrothermal condition at 170°C(see ESI). The pH was adjusted by ammonia aqueous solution. This reaction condition was carefully chosen to

---

[a] *Hubei Callaborative Innovation Center for Advanced Organic Chemical Materials, College of Chemistry and Chemical Engineering, Hubei University, Wuhan, 430062, China. Fax: +86-27-88663043; Tel: +86-27-88662747; E-mail: wangjuan_hd@163.com.*
[b] *College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, China. E-mail: fwg@pku.edu.cn*

† Electronic Supplementary Information (ESI) available. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

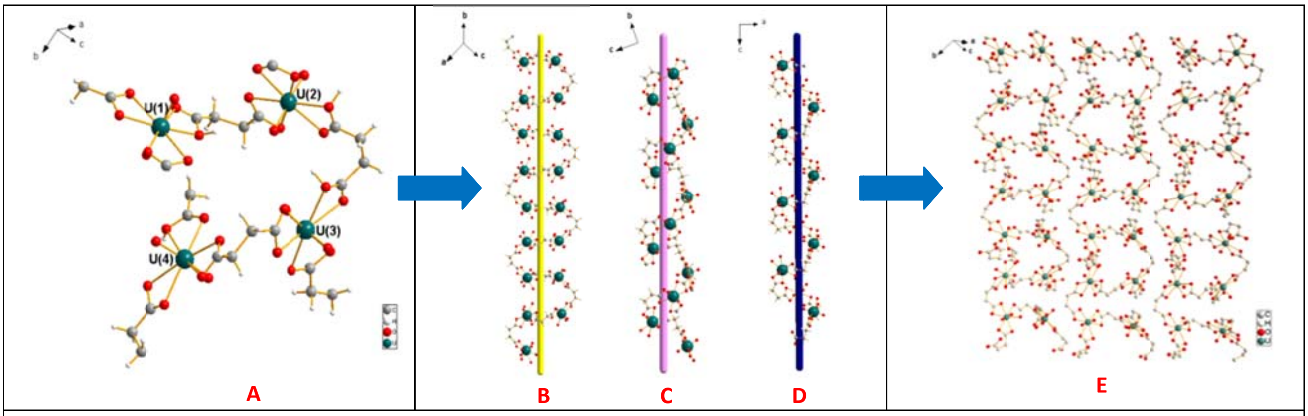


Fig.1 The molecular structure, R- helical chains and self-assembly of coordination polymer(water molecules are omitted)

increase the coordination chance between UO_2^{2+} and succinates based on the following considerations:[12] (1) uranyl may exist in multiple forms resulted from polymerization and hydrolysis. The isolated UO_2^{2+} form is the major one only in strong acidic medium (pH<3);[13] (2) hydrothermal condition decreases the chance of H_2O to coordinate with UO_2^{2+}; (3) Unnecessary solvents such as DMF and DMSO may compete for coordination with UO_2^{2+}; and (4) Other metal ions such as Na^+ and K^+ may compete for coordination with succinate ligands. The use of ammonia as pH adjuster served the purpose well since NH_3 becomes NH_4^+ in acid solution, which has low coordination capability. The elemental analysis of I clearly showed I is consisted of only UO_2^{2+} and succinates. It should be noted that this composition is different from those of U-frameworks obtained from uranyl with longer aliphatic diacids, which have formula $UO_2[^-OOC(CH_2)_nCOO^-]$ (n = 3-8).[5f-h]

The structure of complex I was confirmed by single crystal x-ray diffraction. The structure analysis revealed that complex I crystallized in a trigonal system, chiral space group P32 (145) with a Flack parameter of 0.086, which is close to zero. This clearly indicates that this complex is homochiral.[14] It is noteworthy that there are no chiral materials involved in the whole synthesis. This self-assembly process leading to homochiral crystals from achiral precursors via spontaneous symmetry breaking is a fascinating approach as stated above. However, very few chiral uranium coordination polymers constructed solely from achiral compounds have been reported thus far.[6]

As shown in Fig. 1A, there are four crystallographycally unique uranium centers, four mono-deprotonated succinic acids (HSuc), two doubly deprotonated succinic acids (Suc), and two free H_2O in the asymmetric unit. Each uranium center is coordinated with two terminal oxygens and six carboxyl oxygens from three different succinate ligands, and each acid ligand links two uranium atoms through its carboxyl groups in a chelate fashion. All uranium centers have slightly distorted hexagonal bipyramidal coordination geometries as expected. The two terminal oxygens locate in the axial position as usual, and the carboxyl oxygens form three chelate rings and locate in the equatorial position. All of the three quaternion rings, consisting of a carboxyl group and uranium, are not coplanar, with dihedral angle values of 0.329°-23.716°. The large radius of U reduces the tension of the quaternion rings to some extent, and thus increases the stability of the quaternion rings. The U=O bond lengths are in the range of 1.686(11)to 1.824(10) Å with an average value of 1.777Å, which is good accordance with literature values of 1.758-1.777 Å.[15] The O=U=O angles (178.3(4), 177.5(4), 176.2(4), 172.2(5)°) are slightly deviated from the theoretical value of 180°, possibly due to the hydrogen bonds between the terminaloxygens and water molecules. The bond lengths of U-$O_{carboxyl}$ are 2.326(9)-2.543(9)Å, which is within the range of reported values.[16] The carbon chains in succinates are close to adopt gauche conformation along the two middle carbons with varying dihedral angle values of 46-74 degree as measured in Mercury.

The most remarkable structural feature of complex I is that the complex is composed of three directional right-handedness helical chains: From the direction approximately parallel to b axis, unit U(1)⋯U(2)⋯U(3)⋯U(1)⋯U(2)⋯U(3) (Fig.1B) forms a helical channel. There is another helical chain in the direction of Fig.1C. In the above two helices, the helix unit length is not equal to the unit cell parameters, so the helix axis is not parallel with either a axis or b axis. Along the c axis, because helical unit (U(1)⋯U(3)⋯U(1)) length is equal to the unit cell parameters of c (11.7929Å), the helix axis parallel to the c axis (Fig.1D). Three helical chains self-assemble into stable three-dimensional molecular structure, as shown in Fig.1E. The hydrogen bondings between free H_2O and terminal oxygens should also play a role in stabilizing the 3D structure. Especially, it is easily seen from the direction of c axis, each helical channel containing U(1), U(2) and U(3) is surrounded by three axes that are made up of U(4) through U(1), U(2) and U(3), respectively. And similarly, each U(4) axis is encompassed by three U(1)⋯U(2)⋯U(3) helical channels. The gauche conformations of the carbon chains in succinate ligands as discussed above are beneficial to the formation of the helices. The above data demonstrates that the combination of semi-rigid metal center with semi-rigid ligand serve two purposes well: it allows coordination to occur, but the self-assembly process is not totally free. This constraint is believed to be the main reason for the unique architecture and homochirality of complex I.

CD/UV spectrum

The homochirality of complex I was further confirmed by solid-state circular dichroism (CD) spectra, which was obtained from KCl pellets using a single crystal(Fig. 2). The splitting peak is observed in the single crystal. The first Cotton effect is positive, and the second is negative, proving that coordination polymer **I** is R-chiral.[17]

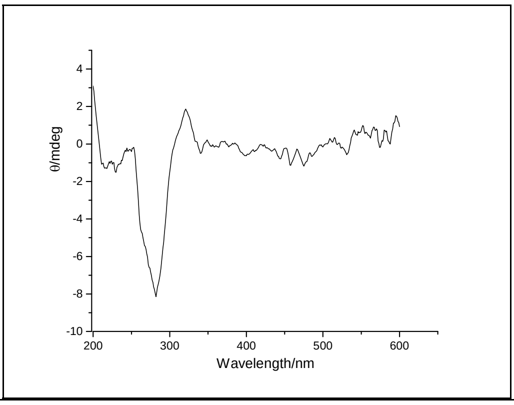


Fig.2 The solid-state circular dichroism (CD) spectra of coordination polymer

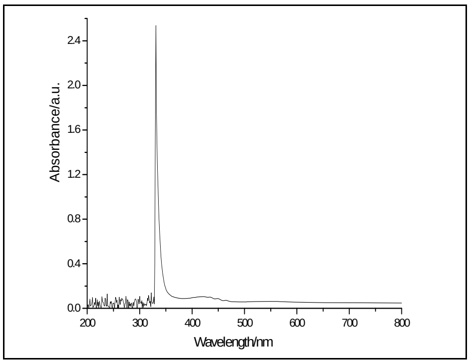


Fig.3 UV spectra of coordination polymer (nitric acid as the reference solution)

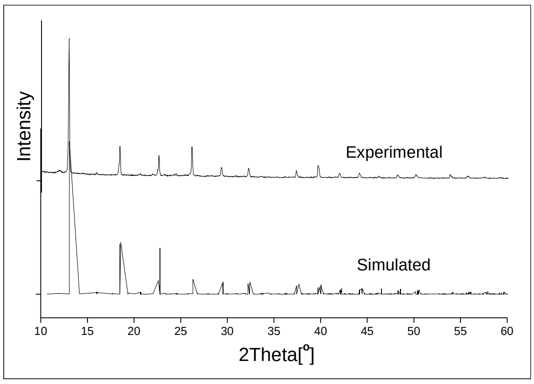


Fig.4 The measured and simulated X-ray powder diffraction patterns of coordination polymer

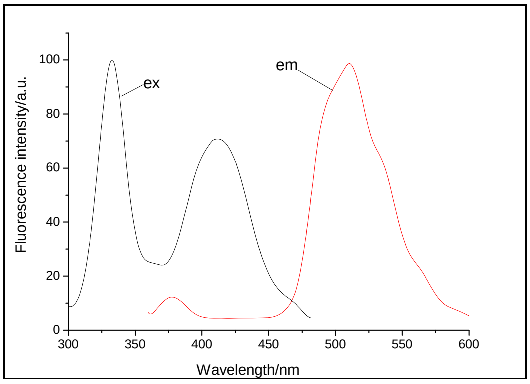


Fig.5 Fluorescence spectra of coordination polymer

The UV spectrum(Fig.3) of the compound exhibits two absorption peaks at 331 and 400-450 nm in HNO_3 solution with HNO_3 as reference. The former peak is strong and sharp, which can be ascribed to the charge transfer adsorption of O→U.[18]

The latter is weak and broad, which may arise from the symmetric stretching vibration of O=U=O. This is in accordance with the formation of coordination bonds between uranyl and succinates.

Powder x-ray diffraction

As shown in Fig. 4, the powder xrd pattern of I is in good agreement with the calculated one derived from the single crystal structure, except for small differences in the intensity of diffraction peaks, which may be caused by the spatial orientation of the crystal. This immediately implies that product I is in a pure phase.

Fluorescence spectrum

Under excitation of 325nm UV light at ambient temperature, fluorescent emission was observed at 510.5 nm (Fig. 5). It is caused by the electron transition of uranyl ion from the first excited state to the symmetric and antisymmetric stretching vibrational energy levels. Due to the spin orbit coupling effect remarkable, the metal to ligand charge transfer(MLCT) was detected in fluorescence spectrum.[19] A Stokes shift greater than 180 nm was observed, which may be causedby vibrational relaxation and solvent effect.

Conclusions

In summary, a novel three dimensional uranyl succinate coordination polymer was synthesized from achiral materials and fully characterized. Its homochirality has been confirmed by single crystal x-ray diffraction and solid state circular dichroism (CD) spectra. It also possesses unique three-directional helices. The approach described here, leading to the unique architecture and chirality by using semi-rigid metal center and semi-rigid ligand as precursors, has been successfully demonstrated. We believe this approach increases the chance of spontaneous symmetry breaking and should be very useful in preparing chiral coordination polymers from achiral ligands.

Notes and references

‡ Crystal data for **I**: $C_{24}H_{28}O_{32}U_4{\cdot}2H_2O$, M_r=1816.62, trigonal, *P32* (145), *a*=19.0913(3)Å, *b*=19.0913(3) Å, *c*=11.7929(5)Å, *α*=90.00°, *β*=90°, *γ*=120°, *V*=3722.4(2)$Å^3$, ρ_{calcd}=2.431 g·cm^{-3}, *Z*=3, F(000)=2448, Flack=0.086(11), *T*=291(2)K, R_{int}= 0.036, R_1=0.0440(I>2σ(I)), wR_2 = 0.1154, GOF=1.056, CCDC 899501.

1 (a)Lei Han, Maochun Hong, *Inorg. Chem. Comm.*, 2005, 8(4), 406; (b) X-D Zheng and T-B Lu, *CrystEngComm*, 2010, 12, 324; (c) M. Albrecht, *Chem. Rev.*, 2001, 101, 3457; (d) X-J Ke, D-S Li and Miao Du, *Inorg. Chem. Commun.*, 2011, 814, 788; (e) Girijesh Kumar and Rajeev Gupta, *Chem. Soc. Rev.*, 2013, 42, 9403; (f) Vladislav A. Blatov, Alexander P. Shevchenko, and Davide M. Proserpio, *Cryst. Growth Des.*, 2014, 14 (7), 3576.

2 (a) Sumi Ganguly and Raju Mondal, *Cryst. Growth Des.*, 2015, 15 (5), 2211; (b) F. Wang, H-R Fu and J. Zhang, *Cryst. Growth Des.,* 2015, 15, 1568; (c) M. Crespo Alonso, M. Arca, F. Isaia, R. Lai, V. Lippolis, S. K. Callear, M. Caricato, D. Pasini, S. J. Coles and M. C. Aragoni, *CrystEngComm*, 2014, 16, 8582; (d) Liyan Zhang, Lulu Rong, Guoli Hu, Suo Jin, W-G Jia, Ji Liu and Guozan Yuan, *Dalton Trans.,* 2015, 44, 6731; (e) Yue Wang, Yan Qi, Vladislav A. Blatov, Jimin Zheng, Qun Li and Chao Zhang, *Dalton Trans.*, 2014, 43, 15151; (f) H. Dong, H. Hu, Y. Liu, J. Zhong, G. Zhang, F. Zhao, X. Sun, Y. Li, and Z. Kang, *Inorg. Chem.*, 2014, 53 (7), 3434;

3 (a) Jung Soo Seo, Dongmok Whang, Hyoyoung Lee, Sung Im Jun, Jinho Oh, Young Jin Jeon & Kimoon Kim, *Nature*, 2000, 404, 982; (b) L. Ma, C. Abney & W. Lin, *Chem. Soc. Rev*. 2009, 38, 1248; (c) S-M. Xie, Z-J. Zhang, Z-Y. Wang & L-M. Yuan, *J. Am. Chem. Soc.*, 2011, 133, 11892; (d) D. Dang, P. Wu, C. He, Z. Xie & C. Duan, *J. Am. Chem. Soc.*, 2010, 132, 14321; (e) M. Yoon, R. Srirambalaji & K. Kim, *Chem. Rev*., 2012, 112, 1196; (f) J. Sun, Charlotte Bonneau, ÁngelCantín, AvelinoCorma, María J. Díaz-Cabañas, Manuel Moliner, Daliang Zhang, Mingrun Li and Xiaodong Zou, *Nature*, 2009, 458, 1154; (g) Horike Satoshi, Shimomura Satoru and Kitagawa Susumu, *Nature Chemistry,* 2009, 1, 695;

4 (a) Russell E. Morris and Xianhui Bu, *Nature Chemistry*, 2010, 2, 353; (b) Kendrick J., Gourlay M. D., Neumann M. A.& Leusen F. J. J., *Crystengcomm*, 2009, 11, 2391; (c) Ionut Mihalcea, Nicolas Zill, Valeriu Mereacre, Christopher E. Anson, and Annie K. Powell, *Cryst. Growth Des.*, 2014, 14 (9), 4729; (d) Somnath Choubey, Kishalay Bhar, Soumi Chattopadhyay, Arpan Hazra, Tapas Kumar Maji, Joan Ribasc and Barindra Kumar Ghosh, *Dalton Trans*., 2012, 41, 11551; (e) S. Yuan, Y-K Deng, W-M Xuan, X-P Wang, S-N Wang, J-M Dou and Di Sun, *CrystEngComm*, 2014, 16, 3829.

5 (a) Michael B. Andrews and Christopher L. Cahill, *Chemical Reviews*, 2013, 113 (2), 1121; (b) Pierre Thuéry, *Crystal Growth & Design,* 2011, 11 (6), 2606; (c) W. Yang, W. Tian, X. Liu, L. Wang, and Z. Sun, *Crystal Growth & Design,* 2014, 14 (11), 5904; (d) Jong-Young Kim, Alexander J. Norquist and Dermot O'Hare, *Dalton Trans.,* 2003, 2813; (e) S. An, L. Mei, C. Wang, C. Xia, Z. Chai and W. Shi; *Chem. Commun.*, 2015, 51, 8978; (f) L. A. Borkowski, C. L. Cahill, *ActaCryst*. 2005, E61, m816; (g) L. A. Borkowski, C. L. Cahill, *Cryst. Growth Des,* 2006, 2241; (h) Andrew T. Kerr and Christopher L. Cahill, *Crystal Growth & Design*, 2011, 11 (12), 5634;

6 (a) J. Diwu and Thomas E. Albrecht-Schmitt, *Chem. Commun.*, 2012, 48, 3827; (b) H. Wang, Z. Chang, Y. Li, R-M Wen and X-H Bu, *Chem. Commun.*, 2013, 49, 6659.

7 (a) Oleg I. Siidra, Evgeny V. Nazarchuk, Anna N. Suknotova, Roman A. Kayukov, and Sergey V. Krivovichev, *Inorg. Chem.*, 2013, 52, 4729; (b) Clare E. Rowland, Mercouri G. Kanatzidis, and L. Soderholm, *Inorg. Chem*., 2012, 51, 11798; (c) Pius O. Adelani and Thomas E. Albrecht-Schmitt, *Cryst. Growth Des.*, 2012, 12, 5800; (d) Ionut Mihalcea, Natacha Henry, Till Bousquet, Christophe Volkringer, and Thierry Loiseau, *Cryst. Growth Des.*, 2012, 12, 4641; (e) Pierre Thuéry, Claude Villiers, Joël Jaud, Michel Ephritikhine, and Bernardo Masci, *J. Am. Chem. Soc.*, 2004, 126, 6838.

8 (a) Y-L Wang, Z-Y Liu, Y-X Li, Z-L Bai, Wei Liu, Y-X Wang, X-M Xu, C-L Xiao, D-P Sheng, J-D Wu, Jing Su, Z-F Chai, Thomas E. Albrecht-Schmitt and Shuao Wang, *J. Am. Chem. Soc.*, 2015, 137 (19), 6144; (b) Aaron C. Sather, Orion B. Berryman, and Julius Rebek, J., *J. Am. Chem. Soc.*, 2010, 132 (39), 13572; (c) M. Carboni, C. W. Abney, S. Liu & W. Lin, *Chem. Sci*., 2013, 4, 2396.

9 (a) P. C. Burns, *Can. Mineral*, 2005, 43, 1839; (b) Pierre Thuéry, *Cryst. Growth Des.*, 2010, 10, 2061; (c) Pierre Thuéry, Zouhair Asfari, Martine Nierlich, Jacques Vicens, Bernardo Masci, *Polyhedron*, 2002, 21, 1949; (d) K. E. Knope, C. L. Cahill, *Inorg. Chem.,* 2008, 47, 7660.

10 (a) R. Łyszczek, L. Mazur, *Central Europ. J. Chem.*, 2012, 10,1165; (b) H. Wang, Z. Chang, Y. Li, R. M. Wen, X. H. Bu, *Chem. Commun*., 2013, 49, 6659; (c) P. Thuéry, B. Masci, *CrystEngComm*., 2012, 14, 131.

11 Jin-Tao Yu, Yan-Yan Shi, Junliang Sun, Jianhua Lin, Zhi-Tang Huang and Qi-Yu Zheng, *Nature*, 2013, 2947(3) , 1.

12 During the preparation of this manuscript, Xing and co-workers reported the synthesis of three uranyl coordination polymers, $[(UO_2)_4(\mu\text{-}OH)_7(OH)_6]$, $\{UO_2(\mu\text{-}OH)(OH)_3\}$, and $[(DMF)_2(\mu\text{-}OH)_4(UO_2)]$, in the presence of succinic acid. It is noteworthy that succinate did not incorporate into none of the polymers. Si Yue Wei, Feng Ying ai, Ya Nan Hou, Xiao Xi Zhang, Xue Ting Xu, Ji Xiao Wang, Huan Zhi Zhang, and Yong Heng Xing, *J. Coord. Chem.* 2015, 68(3), 507.

13 Karah E. Knope and L. Soderholm, *Chemical Reviews*, 2013, 113 (2), 944, and references cited therein.

14 H. D. Flack & G. Bernardinelli, The use of X-ray crystallography to determine absolute configuration. Chirality 20, 2008, 681.

15 (a) B. Masci, Pierre Thuéry, *Polyhedron*, 2005, 24. 229; (b) A. J.Stemmler, J. W. Kampf, V. L. Pecoraro, *Angew. Chem. Int. Ed. Engl.*, 1996, 35(23-24), 2841; (c) M. S. Bharara, K. Strawbridge, J. Z. Vilsek, T. H. Bray, and A. E. V. Gorden, *Inorg. Chem.*, 2007, 46, 8309; (d) M. Frisch, C. L.Cahill, *Dalton Trans.*, 2005, 1518.

16 R. S. A. Wai, *Phys. Chem. Chem. Phys.*, 1999, 1, 783.

17 (a) J. B. Chang, R. F. Chen, Q. Wang, P. Liu, *Acta Chimica Sinica*, 2000, 58, 554; (b) H. Wang, Z. Chang, Y. Li, R. M. Wen, X. H. Bu, *Chem. Comm.*, 2013, 49, 6659; (c)Prasad L. Polavarapu, *The Chemical Record*, 2007, 7, 125.

18 Eric J. Schelter, Ping Yang, Brian L. Scott, J. D. Thompson, Richard L. Martin, P. Jeffrey Hay, David E. Morris, and Jaqueline L. Kiplinger, *Inorg. Chem.*, 2007, 46, 7477.

19 (a) M. Schindler, F. C. Hawthorne, M. S. Freund, P. C. Burns, *Geochimicaet Cosmochimica Acta*, 2009, 73, 2471; (b) M. Frisch, C. L. Cahill, *Dalton Trans*., 2005, 1518; (c) R. C. Severance, S. A. Vaughn, M. D. Smith, Hans-Conrad zur Loye, *Solid State Sci.*, 2011, 13, 1344.