
CrystEngComm

Journal Name RSCPublishing

ARTICLE

Solvent-mediated crystal-to-crystal transformations from a cationic homometallic metal-organic framework to heterometallic frameworks

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Xinxiong Li, Yaqiong Gong, Huaixia Zhao, Ruihu Wang*

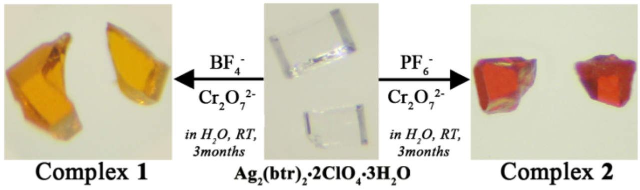
Two unprecedented heterometallic metal-organic frameworks (MOFs), $Ag_2(btr)_2Cr_2O_7{\cdot}0.5H_2O$ (**1**) and $Ag_9(btr)_6(Cr_2O_7)_4{\cdot}PF_6{\cdot}6H_2O$ (**2**) [btr = 4,4′-bis(1,2,4-triazole)], were synthesized through crystal-to-crystal transformation when a monometallic MOF $Ag_2(btr)_2{\cdot}2ClO_4{\cdot}3H_2O$ was immersed into the aqueous solution of KPF_6-$K_2Cr_2O_7$ and $NaBF_4$-$K_2Cr_2O_7$, respectively. The transformation follows a solvent-mediated anion-induced mechanism through the dissolving-reaction-crystallization process. Single-crystal X-ray diffraction analyses reveal that both **1** and **2** are three-dimensional structures based on Ag^+, $Cr_2O_7^{2-}$ and btr. In **1**, $Cr_2O_7^{2-}$ adopts a bidentate bridging mode, and Ag^+ ions are linked by $Cr_2O_7^{2-}$ and btr into a neutral framework. However, $Cr_2O_7^{2-}$ in **2** exhibits two types of unprecedented bridging modes through bridging four and five Ag^+ ions, respectively. Ag^+ ions in **2** are bridged by $Cr_2O_7^{2-}$ and btr to form a cationic framework. The non-coordination anions BF_4^-/PF_6^- show a structure-directing effect during the crystal-to-crystal transformations and can be considered as structure-directing agents. The second-harmonic-generation (SHG) measurement shows that **1** is a non-linear optical complex.

Introduction

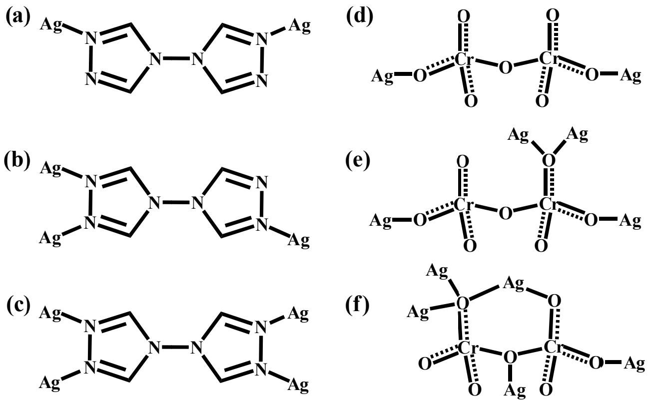
Recent decades have witnessed considerable progress in metal-organic frameworks (MOFs) due to their theoretical significance and potential applications in adsorption, ion exchange, sensor technology, drug delivery and catalysis.[1] Considering the existing MOFs, one notes that numerous monometallic structures have been reported, there has been relatively little progress concerning the synthesis of heterometallic MOFs.[2] Heterometallic MOFs have exhibited a great promise in molecular magnetism, optics and electrochemistry because of the charge-transfer properties between different metal centers.[3] One common methodology for the construction of heterometallic MOFs is to introduce two kinds of metal cations to react with organic ligands in one system. And a series of heterometallic MOFs based on 3d-4f, 4d-4f metal centers have been successfully constructed.[4] The other method is to introduce metal-oxo anions as secondary ligands to bind with metal cations. As well known, a few heavy metal-oxo anions, such as CrO_4^{2-}, $Cr_2O_7^{2-}$ and $Mo_2O_7^{2-}$, can form effective M-O-Cr or M-O-Mo bonds,[5] which provides us new opportunities to construct novel heterometallic MOFs by using these metal-oxo anions as secondary ligands. The dichromate ($Cr_2O_7^{2-}$) has long been known to bridge metal ions forming coordination polymers. Recently, a series of heterometallic MOFs based on late transition metal ions and $Cr_2O_7^{2-}$ have been reported.[6-11] However, the chemistry of heterometallic MOFs based on Ag^+ and $Cr_2O_7^{2-}$ is largely unexplored, although two 1-D hybrid chains based on Ag^+ and $Cr_2O_7^{2-}$ were presented.[12] One possible reason is that Ag^+ is a strong oxidizing agent and can be easily reduced into silver during the reaction process; the other reason may be ascribed to the rapid formation of insoluble silver dichromate when Ag^+ and $Cr_2O_7^{2-}$ are simultaneously present in one reaction system. Therefore, the exploration of new methods for the synthesis of heterometallic MOFs based on Ag^+ and $Cr_2O_7^{2-}$ still remains a great challenge.

Recently, there has been a growing interest in crystal-to-crystal transformation of MOFs because they can provide us new chances to obtain unique compounds that cannot be obtained by direct reaction.[13] What's more, the structural transformation may also bring new functions, such as adsorption and magnetic properties, into the resultant materials.[14] So far, the crystal transformation involving single-crystal to single-crystal process has been widely studied,[15] however, the transformations through solvent-mediated process was less studied.[16] Solvent-mediated structural transformation usually takes place under mild conditions as a result of external stimuli, such as heat, light, solvent molecules, anions, metal cations and redox reagents. It is noteworthy that in the reported solvent-mediated anion-induced crystal transformations, the external stimuli was just one kind of anion,[16,17] the transformation driven by two kinds of anions, especially by non-coordinated anions is rare . In this work, we report the syntheses of two heterometallic MOFs based on Ag^+ and $Cr_2O_7^{2-}$ through solvent-mediated crystal-to-crystal transformations from a cationic monometallic MOF. By immersing monometallic $Ag_2(btr)_2{\cdot}2ClO_4{\cdot}3H_2O$,[18] [btr = 4,4′-bis(1,2,4-triazole)] in aqueous KPF_6-$K_2Cr_2O_7$ and $NaBF_4$-$K_2Cr_2O_7$ solution, respectively, yellow crystals of $Ag_2(btr)_2Cr_2O_7{\cdot}0.5H_2O$ (**1**) and red crystals of $Ag_9(btr)_6(Cr_2O_7)_4{\cdot}PF_6{\cdot}6H_2O$ (**2**) were successfully obtained in three months, respectively (Scheme 1). It should be mentioned that the presence of KPF_6 and $NaBF_4$ in aqueous $K_2Cr_2O_7$ solution plays a key factor for the formation of **1** and **2**. The attempts to prepare **1** and **2** in the absence of KPF_6 or $NaBF_4$ were fruitless under the same conditions. To the best our knowledge, **1** and **2** is the first series of 3-D heterometallic MOFs based on Ag^+ and $Cr_2O_7^{2-}$.

Scheme 1 Synthetic route for **1** and **2**



Scheme 2 Coordination modes of btr and $Cr_2O_7^{2-}$ in **1** and **2**.



Results and discussion

Syntheses

Both **1** and **2** were prepared through crystal-to-crystal transformations, however, either direct one-step reaction or the absence of KPF_6 and $NaBF_4$ failed to give rise to **1** and **2**. Their formation was considered to follow a solvent-mediated mechanism.[16,17] It is well known that the reversible nature of metal coordination chemistry allows the crystals of a complex to dissolve slightly in certain solution, the dissolved complex may interact with the compositions in the solution, the subtle precipitation-dissolution equilibrium will be broken in the presence of extra inductive interaction, in turn unleashing the dissolving. When crystals of the homometallic precursor of **1** and **2** were immersed in an aqueous solution of KPF_6-$K_2Cr_2O_7$ or $NaBF_4$-$K_2Cr_2O_7$, $Cr_2O_7^{2-}$ will interact with trace amount of Ag^+ ions in the aqueous solution, but it is quite hard to be observed since the reaction rate is very slow and the newly formed compounds are too tiny to be seen with the naked eyes. As time goes on, the dissolving-reaction-crystallization process continues and the crystals of the newly formed products become large enough for X-ray diffractions, then **1** and **2** were formed. It is noteworthy that the uncoordinated anions PF_6^- and BF_4^- are important for the formation of **1** and **2**. When PF_6^- and BF_4^- were remove from the system, **1** and **2** cannot be isolated. Thus, the uncoordinated anions PF_6^- and BF_4^- may have a structure-inducing effect in the reassembly process. Interestingly, PF_6^- in **2** locates in the 1-D channels and acts as charge compensation anion to balance the cationic framework. Although BF_4^- does not appear in **1**, BF_4^- is indispensable for the formation of **1**.

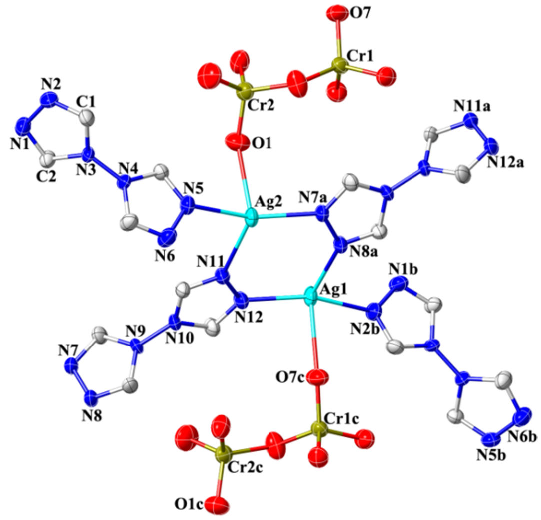


Figure 1 View of the coordination environment of Ag^+ in **1**.

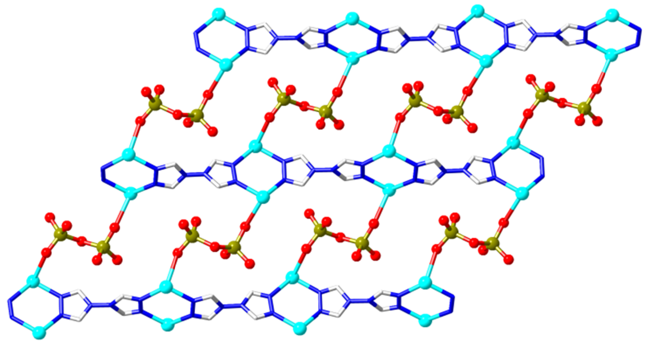


Figure 2 View of the 2-D layer based on Ag^+ and $Cr_2O_7^{2-}$ and tetradentate btr ligands.

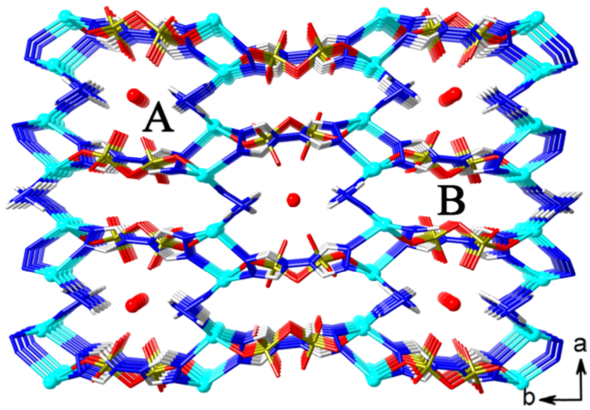


Figure 3 View of the 3-D framework of **1**.

Structural Descriptions

$Ag_2(brt)_2Cr_2O_7\cdot 0.5H_2O$ (1) Single-crystal X-ray diffraction analysis revealed **1** crystallizes in the orthorhombic non-symmetric space group *Fdd*2, and the asymmetric unit is made up of two Ag^+ ions, two btr ligands and one $Cr_2O_7^{2-}$ anion. As shown in Figure 1, Ag^+ is four-connected by three nitrogen atoms from three different btr ligands and one oxygen atom from $Cr_2O_7^{2-}$ in a distorted tetrahedral geometry.

The Ag-N and Ag-O bond distances are in the range of 2.187(3)~2.445(3) and 2.555(3)~2.682(2) Å, respectively (Table S1). Two crystallographically independent Ag^+ ions (Ag1 and Ag2) are connected by four nitrogen atoms (N11, N12, N7a and N8a) to form a binuclear six-membered Ag_2N_4 metallacycle (Figure 1). In the metallacycle, the Ag···Ag distance (Ag1-Ag2) is 4.139(9) Å, which is much longer than that of its precursor (3.719(6) Å). btr ligands adopt two types of coordination modes, one acts as a bidentate bridge connecting two Ag^+ ions (Scheme 2a), the other serves as a tetradentate linker binding to four Ag^+ ions (Scheme 2c). In addition, the inorganic $Cr_2O_7^{2-}$ anion joins two Ag^+ ions with Cr-O bond distances from 1.600(3) to 1.792(3) Å (Scheme 2d), which is consistent with those in the reported 1-D hybrid chain containing Ag^+ and $Cr_2O_7^{2-}$ [12b]. In **1**, the Ag_2N_4 metallacycles are connected by $Cr_2O_7^{2-}$ and tetradentate btr ligands to generate a 2-D layer (Figure 2), which is further extended by bidentate btr ligands into a 3-D neutral framework (Figure 3). In the 3-D framework, two types of channels (A and B) are formed along the crystallographic *c* axis, and the big one (A) hosts the lattice water molecules. To the best of our knowledge, **1** is the first example of 3-D neutral heterometallic MOF based on Ag^+ and $Cr_2O_7^{2-}$.

$Ag_9(btr)_6(Cr_2O_7)_4{\cdot}PF_6{\cdot}6H_2O$ (2) **2** crystallizes in the triclinic space group *P*-1, and its asymmetric unit consists of four and a half Ag^+ ions, three btr ligands, two $Cr_2O_7^{2-}$ anions, three isolated water molecules and one half of PF_6^- anion. One of interesting structural features in **2** is that Ag^+ ions exhibit three kinds of coordination geometry (Figure 4a). Both Ag1 and Ag3 are five-coordinated by three nitrogen atoms from different btr and two oxygen atoms from $Cr_2O_7^{2-}$ in a slightly distorted tetragonal pyramid configuration. Ag1 is coordinated by two oxygen atoms from one $Cr_2O_7^{2-}$ to forming a six-membered chelating ring (Figure 4b), while Ag3 is bond by two oxygen atoms from different $Cr_2O_7^{2-}$ (Figure 4d). Ag2 and Ag4 are four-connected in a slightly distorted square-planar environment. Ag2 is coordinated by two nitrogen atoms from different btr ligands and two oxygen atoms from two $Cr_2O_7^{2-}$ anions (Figure 4c), while Ag4 is coordinated by three nitrogen atoms from three btr and one oxygen atom from $Cr_2O_7^{2-}$ anion (Figure 4e). Different from Ag2 and Ag4, four-connected Ag5 ion adopts a distorted tetrahedral geometry and is surrounded by one nitrogen atom from btr, two terminal oxygen atoms and one bridging oxygen atoms from three independent $Cr_2O_7^{2-}$ anions (Figure 4f). The Ag-N and Ag-O bond distances in **2** are in the range of 2.178(3)~2.258(3) and 2.271(3)~2.667(3) Å, respectively (Table S2), which are within the normal range in reported Ag complexes.[19] Worthy of mention is the coordination modes of $Cr_2O_7^{2-}$ anions, the other interesting structural character in **2**. Two crystallographically independent $Cr_2O_7^{2-}$ anions exhibit two types of different coordination modes binding to Ag^+ ions, which are much different from simple bidentate bridging mode in **1**. The first mode is that $Cr_2O_7^{2-}$ bridges four Ag^+ ions through three terminal oxygen atoms (Scheme 2e), the other is that $Cr_2O_7^{2-}$ connects five Ag^+ ions through three terminal oxygen atoms and one bridging oxygen atom (Scheme 2f). To our knowledge, such two types of coordination modes have not been reported hitherto, though a lot of coordination modes of $Cr_2O_7^{2-}$ were presented in the literatures.[6-12] In addition, btr ligands in **2** also show two types of bridging modes. One links three Ag^+ ions in a tridentate mode (Scheme 2b) and the other bridges four Ag^+ in a tetradentate mode (Scheme 2c), which are different from that of the precursor and **1**. In **2**, Ag^+ ions were connected by $Cr_2O_7^{2-}$ anions to form a 2-D inorganic layer (Figure 5) which is further bridged by btr ligands, leading to the formation of a 3-D cationic framework (Figure 6). The framework possesses 1-D channel with diameter about 5.6 Å along the crystallographic *a* axis. The PF_6^- anions are located in the channel, playing the role of charge compensation and stabilizing the cationic framework. As far as we know, **2** not only represents the first example of 3-D cationic heterometallic MOF based on Ag^+ and $Cr_2O_7^{2-}$, but also is the first MOF that contains PF_6^- and $Cr_2O_7^{2-}$ in one structure.

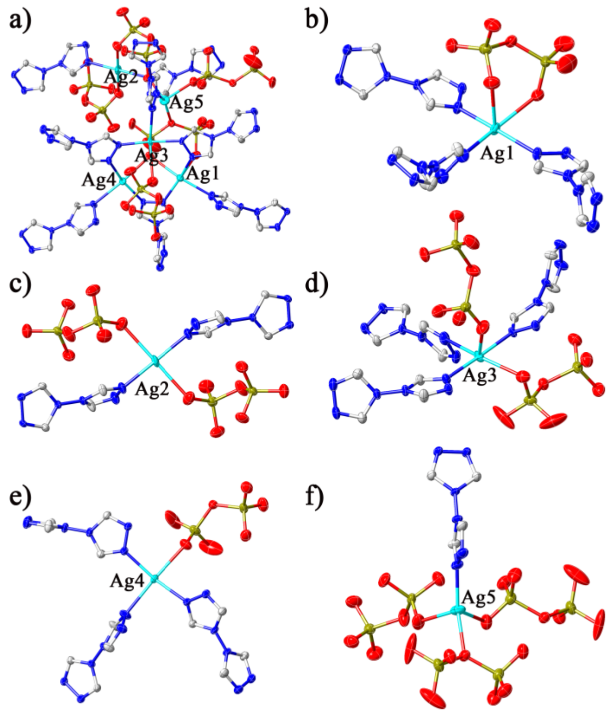


Figure 4 a) View of the coordination environment of Ag^+ ions in **2**; b-f) View of the coordination environment of Ag1-Ag5. All hydrogen atoms are omitted for clarity.

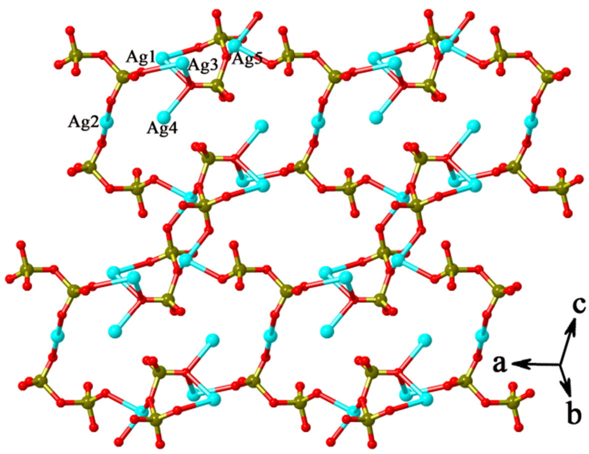


Figure 5 View of the 2-D inorganic layer structure based on Ag^+ and $Cr_2O_7^{2-}$ in **2**.

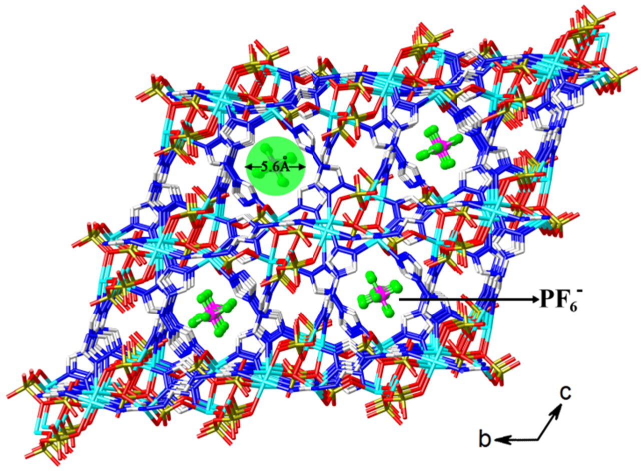


Figure 6 View of the 3-D framework of **2**.

PXRD, IR, TGA and Non-linear optical property

The phase purity of complexes **1** and **2** was checked by X-ray powder diffraction (XRPD) at room temperature using the as-synthesized samples. As shown in Figure S1 and S2, the peak positions of the experimental patterns are in good agreement with the simulated ones, which clearly indicates the good purity of the complexes. In infrared (IR) spectra of **1** and **2** (Figure 7 and 8), characteristic vibration bands of $Cr_2O_7^{2-}$ and PF_6^- are located at 771 cm^{-1} [18] and 843 cm^{-1} [21], respectively, which are consistent with their single-crystal structural analysis. Thermogravimetric analysis (TGA) curves (Figure 9) revealed that the weight loss of 1.45% from 30 to 150 °C in **1** is attributed to the loss of lattice water molecules (calcd 1.26%). For **2**, the removal of free water molecules occurs in the range of 30 to 150 °C (found 3.72%, calcd 3.57%). Drastic framework decompositions in **1** and **2** were observed after 215 and 200 °C, respectively, due to high nitrogen content and good oxygen balance, which is common in energetic MOFs.[22] In addition, **1** crystallizes in the nonsymmetric space group *Fdd2*, the non-linear optical property of **1** was studied. As shown in Figure S3, the second harmonic generation property of **1** is about 0.4 times that of KDP.

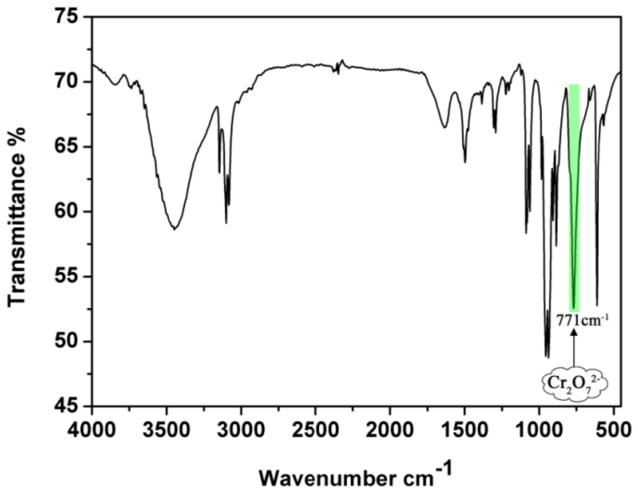


Figure 7 IR spectrum of **1**.

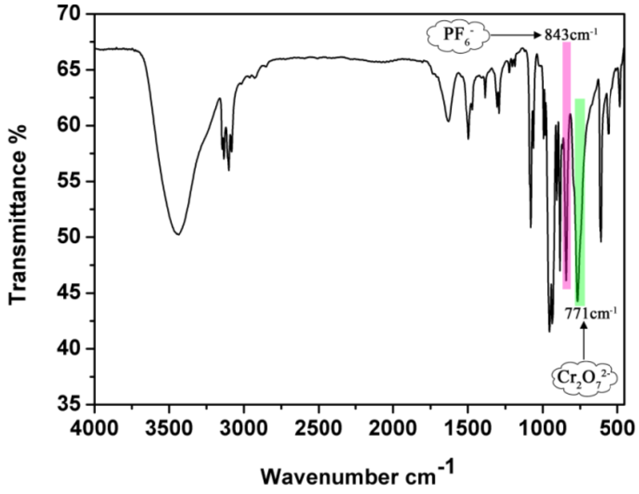


Figure 8 IR spectrum of **2**.

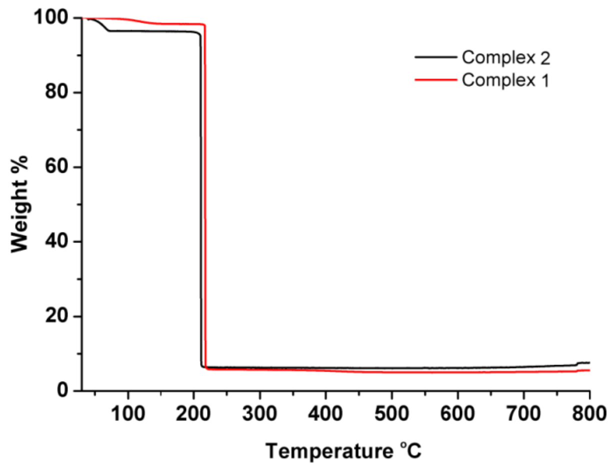


Figure 9 TGA curves of **1** and **2**.

Conclusions

Two unprecedented heterometallic MOFs have been prepared through solvent-mediated crystal-to-crystal structural transformations using a monometallic cationic MOF as a precursor. The structures represent the first series of 3-D heterometallic MOFs based on Ag^+ and $Cr_2O_7^{2-}$. The inorganic $Cr_2O_7^{2-}$ anion can act as an effective secondary ligand in the construction of heterometallic MOFs. Two new coordination modes of $Cr_2O_7^{2-}$ are presented for the first time. The non-coordination anions are firstly considered as structure-inducing agents during the solvent-mediate structural transformations. This work not only provides a new strategy in searching unique materials that cannot be obtained through conventional methods, but also enriches the structural diversity of heterometallic MOFs.

Experimental Section

Materials and General methods

The precursor $Ag_2(btr)_2{\cdot}2ClO_4{\cdot}3H_2O$ was prepared according to the literature method.[18] All other chemicals were obtained from commercial sources and were used without further purification. Elemental analyses of C, H and N were carried out with a Vario EL

III elemental analyzer. IR spectra were recorded on a PerkinElmer Spectrum One FT-IR infrared spectrophotometer. Thermal analyses were performed in a dynamic nitrogen atmosphere with a heating rate of 10 ºC/min, using a NETZSCH STA449C thermal analyzer. Powder XRD patterns were obtained using a Philips X'Pert-MPD diffractometer with CuKα radiation (λ = 1.54056 Å). The SHG measurements are carried out on the powder samples by the Kurtz-Perry method at room temperature. Fundamental 1064 nm light was generated with a nanosecond pulsed Q-switched Nd:YAG laser.

Synthesis of $Ag_2(btr)_2Cr_2O_7$·0.5H_2O (1)

As-synthesized $Ag_2(btr)_2$·2ClO_4·3H_2O (37 mg, 0.05 mmol) was immersed in an aqueous solution (20 mL) of $K_2Cr_2O_7$ (0.0025 mol L^{-1}), and then $NaBF_4$ (55 mg, 0.5 mmol) was added. The mixture was sealed in a 22 mL vial and shaken mildly at room temperature for 3 minutes, then left it undisturbed at ambient temperature. Orange block crystals suitable for X-ray diffraction were obtained after 3 months. Yield 11 mg (30% based on $Ag_2(btr)_2$·2ClO_4·3H_2O). IR (KBr, cm^{-1}): 3446(m), 3146(m), 3101(m), 3082(m), 1637(w), 1496(m), 1384(vw), 1305(w), 1292(w), 1223(vw), 1087(s), 1063(s), 983(m), 954(vs), 936(vs), 906(m), 844(s), 769(vs), 611(vs), 576(v). Elemental analysis (%) calcd for $C_8H_9N_{12}O_{7.5}Cr_2Ag_2$ (713.01): C 13.47, H 1.27, N 23.58; found: C 13.58, H 1.33, N 23.73.

Synthesis of $Ag_9(btr)_6(Cr_2O_7)_4$·PF_6·6H_2O (2)

Complex **2** was prepared according to a similar procedure to that of **1**, excepted for the replacement of $NaBF_4$ by equimolar KPF_6 (92 mg, 0.5 mmol). Yield 9 mg (25% based on $Ag_2(btr)_2$·2ClO_4·3H_2O). IR (KBr, cm^{-1}): 3436(s), 3145(w), 3133(m), 3101(m), 3082(w), 1629(m), 1496(m), 1384(w), 1305(m), 1291(m), 1223(vw), 1079(vs), 1063(m), 995(m), 983(m), 955(vs), 936(vs), 906(m), 885(s), 843(vs), 768(vs), 611(vs), 562(m), 482(m). Elemental analysis (%) calcd for $C_{24}H_{36}N_{36}O_{34}Cr_8Ag_9F_6P$ (2904.69): C 9.92, H 1.25, N 17.36; found: C 10.13, H 1.37, N 17.60.

Table 1 Crystallographic Data for **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_8H_9N_{12}O_{7.5}Cr_2Ag_2$	$C_{24}H_{36}N_{36}O_{34}F_6PCr_8Ag_9$
Formula weight (g/mol)	713.01	2904.69
Crystal system	Orthorhombic	Triclinic
Space group	*Fdd2*	*P-1*
a (Å)	22.870(5)	12.83740(10)
b (Å)	34.647(7)	13.000
c (Å)	9.535(2)	13.2175(5)
α (°)	90	118.924(8)
β (°)	90	102.910(15)
γ (°)	90	99.902(12)
V (Å^3)	7555(3)	1777.59(7)
Z	16	1
Dc (g/cm3)	2.507	2.713
μ(mm-^{1})	3.231	3.370
F(000)	5488	1388
Temperature (K)	298	298
θ range (°)	2.13~27.50	2.05~27.48
Reflections measured	6334	19371
Independent reflections	3910	8078
Observed reflections	3829	7376
Goodness-of-fit on F^2	1.005	1.068
R_{int}	0.0166	0.0154
R_1 (I >2σ(I))	0.0199	0.0351
wR_2 (I >2σ(I))	0.0474	0.0898

$^aR_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $^bwR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$, where x = 0.02950 , y =0 for **1**, x = 0.0444, y = 5.7316 for **2**.

X-Ray Crystallography

X-ray diffraction data for **1** and **2** were collected on a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo $K\alpha$ (λ = 0.71073 Å) at room temperature. The program SADABS was used for the absorption correction. The structures were solved by the direct method and refined on F^2 by full-matrix least-squares methods using the SHELX-97 program package.[20] All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of hydrogen atoms on the organic ligands were generated geometrically and refined using a riding model. CCDC 988556-988557 contain the supplementary crystallographic data for this paper. The summary of crystallographic data and structure refinements for **1** and **2** is listed in Table 1. The selected bond lengths and angles of complexes **1** and **2** are listed in Table S1 and S2 in the Supporting Information, respectively.

Acknowledgements

The authors acknowledge 973 Program (2010CB933501, 2011CBA00502), National Natural Science Foundation of China (21273239) and Natural Science Foundation of Fujian Province (2011J01064) for financial support.

Notes

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, China. E-mail: ruihu@fjirsm.ac.cn,
Fax: +86-591-83714946; Tel: +86-591-83711028

† Electronic supplementary information (ESI) available: Selected bond lengths and bond angles for **1** and **2**, PXRD patterns. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

References

1 (a) S. Chaemchuen, F. Verpoort, *Chem. Soc. Rev.*, 2013, **42**, 9304; (b) J. R. Li, J. Sculley, H. C. Zhou, *Chem. Rev*., 2012, **112**, 869; (c) L. J. Murray, M. Dinca, J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294.

2 (a) X. L. Hu, W. E. Li, Z. M. Su, *Chem. Commun.*, 2013, **49**, 3564; (b) E. Colacio, J. Ruiz-Sanchez, F. J. White, E. K. Brechin, *Inorg. Chem.*, 2011, **50**, 7268; (c) Y. Zhu, F. Luo, Y. M. Song, X. F. Feng, M. B. Luo, Z. W. Liao, G. M. Sun, X. Z. Tian, Z. J. Yuan, *Cryst. Growth Des.*, 2012, **12**, 2158.

3 (a) G. M. Li, T. Akitsu, O. Sato, Y. Einaga, *J. Am. Chem. Soc.*, 2003, **125**, 12396; (b) W. B. Sun, J. W. Zhang, H. Xu, *Inorg. Chim. Acta*, 2009, **362**, 1761.

4 (a) Y. Zhu, F. Luo, Y. M. Song, G. M. Sun, X. Z. Tian, Z. J. Yuan, *Cryst. Growth Des.*, 2012, **12**, 2158; (b) E. Colacio, J. Ruiz-Sanchez, F. J. White, E. K. Brechin, *Inorg. Chem.*, 2011, **50**, 7268.

5 (a) O. I. Siidra, E. V. Nazarchuk, S. V. Krivovichev, *Z. Anorg. Allg. Chem.*, 2012, **638**, 976; (b) P. J. Hagrman, D. Hagrman, J. Zubieta, *Angew. Chem. Int. Ed.*, 1999, **38**, 2638.

6 (a) L. Pan, N. Ching, X. Y. Huang, J. Li, *Chem. Commun.*, 2001, 1064; (b) G. D. Munno, T. Poerio, M. Julve, F. Lloret, J. Faus, A. Caneschi, *J. Chem. Soc., Dalton Trans.*, 1998, **10**, 1679.

7 B. C. Dave, R. S. Czernuszewicz, *Inorg. Chem.*, 1994, **33**, 847.

8 Y. Hayashi, T. Tagami, H. Mano, A. Uehara, *Chem. Lett.*, **2001**, 562.

9 X. Y. Chen, B. Zhao, P. Cheng, B. Ding, D. Z. Liao, S. P. Yan, Z. H. Jiang, *Eur. J. Inorg. Chem.*, 2004, 562.

10 R. Karmakar, S. Mitra, *Inorg. Chim. Acta*, 2004, **357**, 3785.

11 A. J. Norquist, K. R. Heier, P. S. Halasyamani, C. L. Stern, K. R. Poeppelmeier, *Inorg. Chem.*, 2001, **40**, 2015.

12 (a) G. Novitchi, V. Ciornea, J. P. Costes, A. Gulea, O. N. Kazheva, S. Shova, V. B. Arion, *Polyhedron*, 2010, **29**, 2258; (b) A. Beheshti, H. R. Zafarian, R. Khorramdin, M. Fattahi Monavvar, C. T. Abrahams, *Polyhedron*, 2012, **48**, 245.

13 (a) Q. Yao, J. Sun, M. V. Peskov, X. Zou, *Dalton Trans.*, 2012, **41**, 3953; (b) S. Das, H. Kim, K. Kim, *J. Am. Chem. Soc.*, 2009, **131**, 3814.

14 (a) Y. Kim, S. Das, S. Bhattacharya, S. Hong, M. G. Kim, M. Yoon, S. Natarajan, K. Kim, *Chem. Eur. J.*, 2012, **18**, 16642; (b) L. Wen, P. Cheng, W. B. Lin, *Chem. Commun.*, 2012, **48**, 2846.

15 (a) C. H. Zhan, Y. Kang, J. Zhang, *Inorg. Chem.*, 2012, **51**, 523; (b) J. Tian, L. V. Saraf, B. Schwenzer, S. M. Taylor, E. K. Brechin, J. Liu, S. J. Dalgarno, P. K. Thallapally, *J. Am. Chem. Soc.*, 2012, **134**, 9581; (c) G. D. Zou, G. G. Zhang, B. Hu, J. R. Li, M. L. Feng, X. Y. Huang, *Chem. Eur. J.*, 2013, **19**, 15396; (d) N. Li, F. L. Jiang, L. Chen, X. J. Li, Q. H. Chen, M. C. Hong, *Chem. Commun.*, 2011, **47**, 2327.

16 (a) X. Cui, D. H. Marsh, A. J. Blake, W. Lewis, N. R. Champness, C. J. Roberts, M. Schröder, *Chem. Eur. J.*, 2009, **15**, 8861; (b) H. Y. Yang, L. K. Li, J. Wu, H. W. Hou, B. Xiao, Y. T. Fan, *Chem. Eur. J.*, 2009, **15**, 4049; (c) A. N. Khlobystov, N. R. Champness, C. J. Roberts, M. Schröder, *CrystEngComm*, 2002, **4**, 426.

17 (a) F. F. Pan, J. Wu, H. W. Hou, Y. T. Fan, *Cryst. Growth Des.*, 2010, **10**, 3835; (b) H. J. Lu, H. W. Hou, Y. T. Fan, *Inorg. Chim. Acta*, 2012, **387**, 450.

18 X. X. Li, H. Y. Xu, F. Z. Kong, R. H. Wang, *Angew. Chem. Int. Ed.* 2013, **52**, 13769.

19 (a) J. C. Wu, L. Zhao, D. X. Wang, *Inorg. Chem.*, 2012, **51**, 3860; (b) W. J. Hu, L. Q. Liu, B. Jiang, K. Wen, *Inorg. Chem.*, 2013, **52**, 9309; (c) X. Jing, C. He, D. P. Dong, L. L. Yang, C. Y. Duan, *Angew. Chem. Int. Ed.*, 2012, **51**, 10127.

20 a) G. M. Sheldrick, SHELXS97, Program for Crystal Structure Solution; University of Göttingen: Göttingen, Germany, **1997**; b) G. M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, **1997**.

21 (a) L. Carlucci, G. Ciani, S. Maggini, D. M. Proserpio, M. Visconti, *Chem. Eur. J.*, 2010, **16**, 12328; (b) D. X. Wang, H. Y. He, S. Y. Feng, D. F. Sun, *CrystEngComm*, 2010, **12**, 1041; (c) W. Wei, H. T. Yu, F. L. Jiang, B. Liu, J. Ma, M. C. Hong, *CrystEngComm*, 2012, **14**, 1693.

22 (a) Q. Zhang, J. M. Shreeve, *Angew. Chem. Int. Ed.*, 2014, **53**, 2540; (b) A. S. Kumar, V. D. Ghuyle, A. K. Sahoo, *Chem. Eur. J.*, 2013, **19**, 509.

