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Guest-containing supramolecular isomers of silver(I) 3,5-dialkyl-1,2,4-triazolates: syntheses, structures, and structural transformation behaviours†

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An in-depth synthetic study for potential new supramolecular isomers of silver(I) 3,5-dialkyl-1,2,4-triazolates was carried out through liquid diffusion and rapid solution mixing of $[Ag(NH_3)_2]OH$ and the related triazoles. Apart from the literature reported close-packing complexes of [Ag(dmtz)] (**1a**, Hdmtz = 3,5-dimethyl-1,2,4-triazole), [Ag(detz)] (**2a**, Hdetz = 3,5-diethyl-1,2,4-triazole), [Ag(dptz)] (**3a**, Hdptz = 3,5-dipropyl-1,2,4-triazole) and [Ag(diptz)] (**4a**, Hdiptz = 3,5-diisopropyl-1,2,4-triazole), four guest-containing isomers $[Ag_5(detz)_5]\cdot C_6H_6$ (**2b**), $[Ag_4(dptz)_4]\cdot 0.5C_6H_6$ (**3b**), $[Ag(diptz)]\cdot 0.5H_2O$ (**4b**) and $[Ag(diptz)]\cdot C_6H_6$ (**4c**) were discovered. Single-crystal X-ray diffraction studies revealed that **2b**, **3b** and **4b** are complicated coordination networks with small discrete cavities, while **4c** possesses an **nbo-a** framework topology with large discrete cavities embedding a unique supramolecular hexamer of benzene guest molecules with an orthogonal arrangement. Single-crystal and powder X-ray diffraction as well as thermogravimetry studies showed that, **2b** and **3b** can undergo reversible temperature- and guest-induced single-crystal-to-single-crystal structural transformations, respectively, in which the conformation changes of the flexible alkyl groups play important roles. On the other hand, single crystals of **4c** can transform into single crystals of another new isomer $[Ag_8(diptz)_8]\cdot C_6H_6\cdot CH_3OH$ (**4d**) with a completely different network connectivity, by immersing in methanol.

Introduction

Coordination polymers have attracted great interest for decades because they not only have unlimited possibilities of structures and properties but also intriguing structural dynamism due to the rich reversible coordination bonds and rotatable covalent/coordination connections.[1,2] Whether the crystal-to-crystal (CC) structural transformation under chemical stimulus occurs in a topochemical or recrystallization manner is usually questioned. In this context, solvent-free single-crystal-to-single-crystal (SCSC)[3,4] transformations are of particular importance because solvent-assisted recrystallization can be largely ruled out. Of course, some topochemical (CC or SCSC) transformations have to proceed in the presence of solvent, in which special care must be taken to elucidate the transformation mechanism. It should be noted that, solvent-assisted CC and/or recrystallization transformations can be also useful for obtaining special structures that are not available via direct synthesis.[5,6]

Among various kinds of coordination polymers, metal azolate frameworks (MAFs) based on deprotonated polyazaheterocycles are drawing more and more attention.[7] The framework compositions of MAFs can be readily controlled because the ligand coordination behavior is relatively predictable. This characteristic is useful for the design and synthesis of particular framework structures and/or supramolecular isomers, which can help better understanding the self-assembly mechanism and structure-property relationship of coordination polymers.[8,9] In addition, MAF isomers may undergo different types of CC or SCSC transformations. For example, the chicken-wire like interweaving isomer of silver(I) 2-isopropylimidazolate can irreversibly transform to a quintuple helix isomer in a CC manner by heating, while the sinusoidal isomer is stable under the same condition.[10] A porous silver(I) triazolate polymer can undergo revsersible SCSC transformations between a 5-fold and 6-fold interpenetration.[11]

As an important type of azolate ligands, 1,2,4-triazolates usually coordinate to three metal ions with a Y-shape coordination geometry but in a few cases with two or four metal ions and thus generate abundant types of frameworks. For instance, by varying the length of alkyl groups, we have synthesized several copper(I) dialkyl-1,2,4-triazolates with different 3-connected topologies including **sql-a**, **lvt-a**, and **nbo-a**.[12] On the other hand, by adjusting reaction time, temperature, reactant concentration and/or additives, [Cu(dmtz)] (Hdmtz = 3,5-dimethyl-1,2,4-triazole) can crystallize into three different supramolecular isomers with the 3-connected topologies of **lvt-a**, **lig-c** and **etf**,[13] while [Cu(2-pytz)] (2-Hpytz = 3,5-di-(2-pyridyl)-1,2,4-triazole) can crystallize into four isomers with chair, zipper, zigzag and helical chain structures.[14] Yang et al. showed that slow evaporation of the aqueous ammonia solution of $AgNO_3$ and dialkyltriazoles can construct four nonporous silver(I) 3,5-dialkyl-1,2,4-triazolates, including [Ag(dmtz)] (**1a**), $[Ag_3(detz)_3]$ (**2a**, Hdetz = 3,5-diethyl-1,2,4-triazolate), $[Ag_3(dptz)_3]$ (**3a**, Hdptz = 3,5-dipropyl-1,2,4-triazolate), and [Ag(diptz)] (**4a**, Hdiptz = 3,5-diisopropyl-1,2,4-triazolate) with **lig**, $(4^4.6^2)(4^7.6^8)$, **rtl**, and **qzd** topologies, respectively.[15] A nonporous isomer of [Ag(dmtz)] with **etf** topology (**1b**) has also been obtained by Wu et al. through liquid diffusion between $[Ag(NH_3)_2]OH$ and Hdmtz.[16]

Considering that silver(I) 3,5-dialkyl-1,2,4-triazolates are all nonporous structures without inclusion of any guest molecule, we carried out an in-depth synthetic study for their potential supramolecular isomerism, which led to the discovery of four new guest-containing isomers. Moreover, some of these new compounds display interesting temperature- and guest-induced SCSC, as well as solvent-assisted recrystallization structural transformation behaviours.

Experimental

Materials and methods

Commercially available reagents were used as received without further purification. Hdmtz, Hdetz, Hdptz, and Hdiptz were synthesized according to literature methods.[17] Elemental analyses (EA) were performed by an Elemental Vario EL analyzer (C, H, N). Thermogravimetry (TG) analyses were performed at a rate of 5 °C/min under N_2 using a TA Q50 system. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu Kα).

Synthesis of $[Ag_5(detz)_5]\cdot C_6H_6$ (2b)

Single crystals: An aqueous ammonia (25%, 2 mL) solution of Ag_2O (0.05 mmol, 0.012 g) was placed on the bottom of a 6-mL (I.D. = 6.3 mm) glass tube, and then benzene (1.0 mL) and a methanol (2.0 mL) solution of Hdetz (0.1 mmol, 0.013 g) were sequentially added to form three layers. The glass tube was then placed in dark, and colourless crystals were collected after 1 month (0.006 g, yield 24%). Powder: An aqueous ammonia (25%, 10 mL) solution of Ag_2O (0.25 mmol, 0.058 g) was added dropwise to a benzene/MeOH (10+10 mL) solution of Hdetz (0.5 mmol, 0.063 g) under stirring. The reaction mixture was kept in dark and further stirred for *ca.* 1 hour at room temperature. The resultant white precipitate was filtered, washed with 3×10 mL EtOH and dried in ambient air (0.102 g, yield 82%). EA calcd (%) for $[Ag_5(detz)_5]\cdot C_6H_6$ ($C_{35}H_{56}N_{15}Ag_5$): C 34.92, H 4.56, N 16.97; found: C 35.00, H 4.50, N 17.04.

Synthesis of $[Ag_4(dptz)_4]\cdot 0.5C_6H_6$ (3b)

Single crystals were prepared in a similar way as for **2b**, except that Hdetz was replaced by Hdptz (0.1 mmol, 0.017 g). The product was filtered, washed with 3×10 mL EtOH and dried in air at 150 °C for 30 min to obtain **3b'** (0.012g, yield 43%). EA calcd (%) for $[Ag_4(dptz)_4]$ ($C_{32}H_{56}N_{12}Ag_4$): C 36.94, H 5.43, N 16.16; found: C 36.85, H 5.31, N 16.13.

Synthesis of $[Ag_7(diptz)_7]\cdot 0.5H_2O$ (4b)

Single crystals were prepared (0.011 g, yield 42%) in a similar way as for **2b** except that Hdetz was replaced by Hdiptz (0.1 mmol, 0.017 g) and benzene was replaced by a mixture of aqueous ammonia and MeOH (1+1 mL). Microcrystals were prepared (0.104 g, yield 80%) in a similar way as for **2b** except that Hdetz was replaced by Hdiptz (0.5 mmol, 0.077 g). EA calcd (%) for $[Ag_7(diptz)_7]\cdot 0.5H_2O$ ($C_{32}H_{99}N_{21}O_{0.5}Ag_7$): C 36.76, H 5.45, N 16.08; found: C 36.81, H 5.42, N 16.03.

Synthesis of $[Ag(diptz)]\cdot C_6H_6$ (4c)

Single crystals were prepared (0.016 g, yield 46%) in a similar way as for **2b**, except that Hdetz was replaced by Hdiptz (0.1 mmol, 0.017 g). Powder: An acetone solution of Hdiptz (1.5 mmol, 0.215 g) was poured into a benzene (10 mL)/aqueous ammonia (25%, 10 mL) solution of Ag_2O (0.75 mmol, 0.174 g) under stirring. The resultant white precipitate was filtered, washed with 3×10 mL acetone and dried in ambient air (0.280 g, yield 55%). EA calcd (%) for $[Ag(diptz)]\cdot 0.83C_6H_6$ ($C_{14}H_{20}N_3Ag$): C 47.98, H 5.89, N 12.93; found: C 47.72, H 6.02, N 12.69.

X-ray crystallography

Diffraction data were collected on a Bruker Apex CCD area-detector diffractometer (Mo Kα). Absorption corrections were applied by using the multi-scan program SADABS. All the structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 with SHELXTL. All hydrogen atoms were generated geometrically (C-H = 0.96 Å), and anisotropic thermal parameter were applied to all nonhydrogen atoms except some atoms of the isopropyl groups of **4b** and the guest molecules in **3b**, **4b**, and **4d**. The crystal data and structure refinement results are listed in Table 1. CCDC 1031673-1031679 contain the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion

Syntheses

Silver(I) azolates can be usually prepared in the aqueous ammonia solution at room temperature. The four nonporous structures reported by Yang et al. were obtained through the solvent evaporation method.[15] Direct precipitation of insoluble MAFs (e.g. MAF-2, MAF-4 and MAF-7) by rapid solution mixing of aqueous ammonia solution of metal oxide/hydroxide and a solution of the azole ligand has been proved as a fast and effective synthetic method.[18] In order to obtain potentially porous or guest-containing silver(I) 3,5-dialkyl-1,2,4-triazolates, benzene was chosen as a template because the coordination framework should be hydrophobic.[10b, 19] As demonstrated by PXRD, in the rapid solution mixing reaction, [Ag(dmtz)] and [Ag(dptz)] always crystallize as the reported nonporous structures of **1a** and **3a**, respectively. On the other hand, new phases were found for Ag(I) 3,5-diethyl-1,2,4-triazolate (**2b**) and 3,5-diisopropyl-1,2,4-triazolate (**4b**). The new phase **2b** gradually changed to **2a** with the prolonging of the reaction time (Fig. 1), illustrating that **2a** is the thermodynamic product, whereas **2b** is the kinetic one. The structure transformation from **2b** to **2a** should be solvent-assisted recrystallization because the coordination of aqueous ammonia to Ag(I) ion can drastically increase the solubility of both **2a** and **2b**. However, **4b** did not transform to other product by prolonging the reaction time.

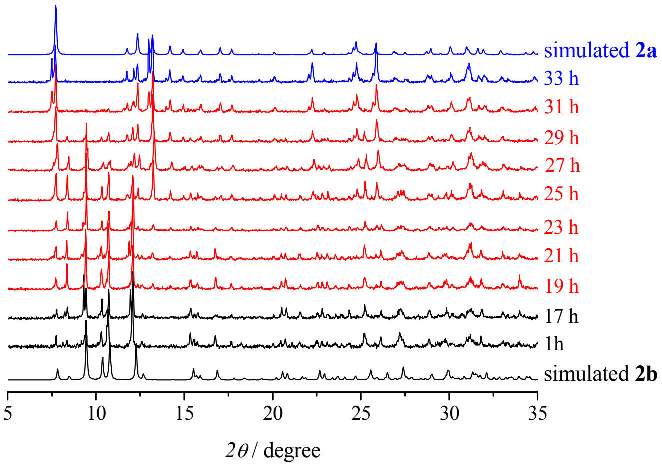

Fig. 1 PXRD patterns of the solid products obtained during the rapid solution mixing process for synthesizing **2b**.

Although liquid diffusion has drawbacks of long reaction time, low yield, low purity, and poor repeatability, it serves as an available method to produce high-quality single crystals. Through liquid diffusion, we not only obtained single crystals of $[Ag_5(detz)_5]\cdot C_6H_6$ (**2b**) and $[Ag(diptz)]\cdot 0.5H_2O$ (**4b**), but also discovered two new guest-containing isomers $[Ag_4(dptz)_4]\cdot 0.5C_6H_6$ (**3b**) and $[Ag(diptz)]\cdot C_6H_6$ (**4c**). Nevertheless, new isomer for 3,5-dimthyl-1,2,4-triazolate was still unavailable. However, crystals of the guest-containing structures **2b**, **3b**, and **4c** only grow at the buffering layer mainly containing benzene, while the guest-free isomers **2a**, **3a**, **4a**, and **4b** always appear at other places simultaneously. Therefore, pure **3b** and **4c** single crystals can be only obtained by careful manual selection. The yields for **2b**, **3b**, and **4c** through liquid diffusion are 24%, 43% and 46%, respectively, indicating that the larger propyl and isopropyl groups are more suitable to accommodate benzene as a template.

Crystal structures

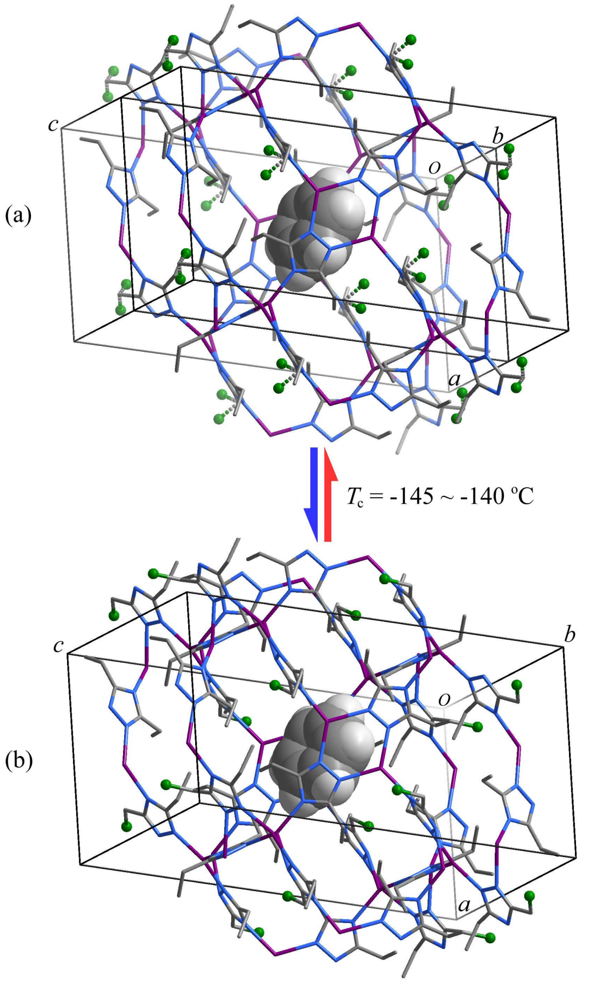

Fig. 2 Temperature-induced SCSC structural transformation between (a) **2b** and (b) **2b'**. Carbon, gray; nitrogen, blue; silver, purple. Hydrogen atoms of the host frameworks are omitted for clarity. The benzene guest molecules are highlighted in the space-filling mode, while the host frameworks are drawn in the stick mode. The terminal methyl carbon atoms of the ethyl groups involved in the order-disorder transition are highlighted as green spheres.

Compound **2b** crystallizes in the monoclinic space groups of $P2/c$, containing two and a half Ag(detz) units and half a benzene molecule in the asymmetric unit (Fig. S1). Each Ag ion is trigonally coordinated by three N atoms from three $detz^-$ ligands, and each $detz^-$ ligand coordinates to three Ag ions, giving a three-dimensional (3D) infinite coordination framework with discrete 0D cavities (void 13.1%) filled with guest benzene molecules. Regarding both Ag ions and detz⁻ ligands as 3-connected nodes, the framework represents a new trinodal 3-connected net with the point symbol of $\{4.8.10\}_2\{6.12^2\}\{6.8.12\}_2$,[20] which not been reported in the literature (Fig. S2). The most noteworthy structural feature of **2b** is that one of the five independent ethyl groups exhibits obvious two-fold disorder (Fig. 2a).

Table 1. Crystallographic data and structure refinement details

Compound	**2b**	**2b'**	**3b**	**3b'**	**4b**	**4c**	**4d**
Formula	$C_{36}H_{56}N_{15}Ag_5$	$C_{36}H_{56}N_{15}Ag_5$	$C_{35}H_{59}N_{12}Ag_4$	$C_{32}H_{56}N_{12}Ag_4$	$C_{56}H_{99}N_{21}O_{0.5}Ag_7$	$C_{14}H_{20}N_3Ag$	$C_{71}H_{122}N_{24}OAg_8$
F.W.	1238.31	1238.31	1079.42	1040.37	1829.65	338.20	2190.89
T (K)	153(2)	113(2)	113(2)	113(2)	113(2)	113(2)	113(2)
Space group	$P2/c$	$P2_1/c$	P-1	P-1	$P2_12_12$	Im-3	$P2_1/n$
a (Å)	11.365(5)	11.243(2)	9.8861(11)	10.3700(4)	25.5782(15)	16.332(2)	21.8059(6)
b (Å)	9.3329(4)	18.664(4)	14.3980(15)	14.3641(5)	25.6108(15)		20.5551(5)
c (Å)	20.985(10)	21.085(4)	15.8646(17)	15.3164(6)	11.5927(7)		22.2812(5)
α / (°)			91.9550(10)	89.5770(10)			
β / (°)	97.4147(15)	97.99(3)	73.9110(10)	74.1980(10)			115.8920(10)
γ / (°)			74.3040(10)	69.6300(10)			
V/(Å^3)	2206.4(17)	4381.4(15)	2074.2(4)	2048.28(13)	7594.1(8)	4356.3(6)	8984.4(4)
Z	2	4	2	2	4	12	4
D_c/g cm^{-3}	1.864	1.877	1.728	1.687	1.600	1.547	1.620
R_1 (all data) [a]	0.0392	0.0287	0.0317	0.0370	0.0408	0.0521	0.1281
wR_2 (all data) [b]	0.0906	0.0635	0.0664	0.0839	0.1010	0.1159	0.2426
GOF	1.087	1.008	1.028	1.009	1.083	1.095	1.073
Flack	/	/	/	/	0.22(4)	/	/

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$, [b] $wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

Compound **3b** crystallizes in a triclinic space group of P-1, containing four Ag ions, four dptz⁻ ligands and half a disordered benzene molecule in the asymmetric unit. Three Ag ions are trigonally coordinated by three dptz⁻ ligands while the fourth one is tetrahedrally coordinated by four dptz⁻ ligands (Fig. S3). Accordingly, one of the 12 independent N donors(N5) is coordinated by two Ag ions, which is uncommon and has been only observed in a few silver(I) triazolates, such as silver(I) 3,5-diphenyl-1,2,4-triazolate and silver(I) 3,5-bis(trifluoromethyl)-1,2,4-triazolate, and can be attributed to the coordination flexibility of Ag(I) resulting from its large ionic size.[21] Ag ions and dptz⁻ ligands coordinate to each other to generate a complexed 3D infinite coordination framework consisting of $Ag_2(dptz)_2$ and $Ag_4(dptz)_4$ polynuclear building blocks. Regarding the dinuclear and hexanuclear units as 4- and 6-connected nodes, **3b** can be simplified as an **fsc** topology (Fig. S4). The guest benzene molecules are embedded in the isolated 0D cavities (void 8.4%).

4b crystallizes in an orthorhombic space group of $P2_12_12$ with seven Ag ions and seven diptz⁻ ligands and half a water molecule in an asymmetric unit. For the seven independent Ag ions, two are trigonally coordinated, four are tetrahedrally coordinated, and the left one is linearly coordinated. Among the seven independent diptz⁻ ligands, four adopt the μ_3-N^1,N^2,N^4 coordination mode, two adopt μ_5-N^1,N^1,N^2,N^2,N^4 mode, and the last one coordinates in the imidazolate mode (Fig. S5). The various types of metal ions and ligands interconnect with each other to give a complexed 3D coordination framework containing very small and discrete cavities, which accommodate the guest water molecules (Fig. S6). The supramolecular isomerism of Ag(I) 3,5-diisopropyl-1,2,4-triazolate should arise from the different synthetic conditions for **4a** and **4b**, in which benzene, acting as a structural directing agent, is included in the synthetic process but excluded from the crystal structure of **4b**.

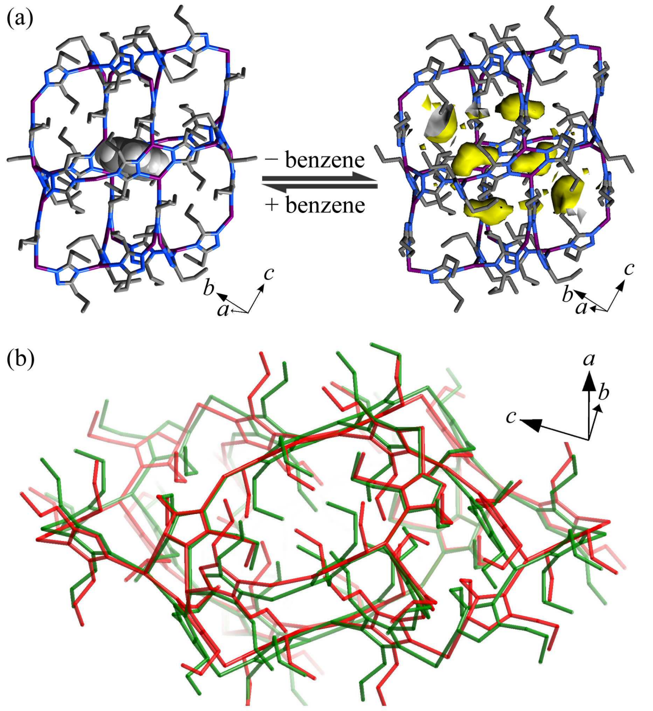

Fig. 3 (a) Guest-induced SCSC structural transformation of **3b** (atom colours follow Fig. 2; Connolly surface with probe radius 1.20 Å for the guest-free phase **3b'** is shown in yellow/gray) and (b) comparison of the host-framework structures of **3b** (red) and **3b'** (green).

4c crystallizes in a cubic space group of *Im*-3, containing half a Ag ion, half a diptz$^−$ ligand and half a benzene molecule in the asymmetric unit (Fig. S7). The Ag ion is trigonally coordinated by three diptz$^−$ ligands and the diptz$^−$ ligand is coordinated by three Ag ions, which interconnected to generate a 3D infinite framework with an **nbo-a** topology (Fig. 4a), being isostructual with [Cu(detz)] (MAF-2).[22] Although the isopropyl group is obviously larger than the ethyl group, the void of **4c** (41.4%) is slightly larger than that of the most expanded form of MAF-2 (39.7%), which can be explained by the larger radius of Ag(I). Similar to MAF-2, **4c** also possesses 0D cavities since the substituent groups block the channels between the cages (aperture size 2.8×2.8 Å^2). In comparison, the size of benzene molecule is 3.3×6.6×7.3 Å^3. Interestingly, in each cavity there are six benzene molecules, which locate at the six vertexes of an octahedron with their molecular planes paralleled to the *xy*, *xz* or *yz* planes of the corresponding Cartesian coordinate. This hexamer configuration is similar to a traditional Chinese toy, the *three rods Ming lock* (Fig. 4a), which is unprecedented for any other molecular aggregations. Structural analysis reveals that the benzene molecules are strictly confined in the cavities. The shortest intermolecular C···H and H···H contacts among benzene molecules are 2.71 and 2.13 Å, respectively, whereas the shortest distance of Ag···H is 2.74 Å (Fig. 4a), which are much shorter than the sum of their van der Waals radii (Ag: 1.72 Å; C: 1.70 Å; H: 1.20 Å), illustrating the strong host-guest interactions.

Structural transformation behaviours

The thermal stability and host-guest property of **2b**, **3b**, and **4c** were estimated by TG and PXRD measurements. TG curve of **2b** showed complete guest removal (found 6.2%, calc. 6.3%) between 250 and 270 °C, followed by a plateau to 300 °C. The guest removal temperature is much higher than the boiling point of benzene, because the guest molecules can hardly diffuse out the 0D cavities. On the other hand, **3b** and **4c** completely lost their guest benzene molecules at relatively low temperatures at 70-150 °C and were both stable to 250 °C, implying that they might retain their original framework structures after guest removal (Fig. 5). PXRD patterns were measured for the guest-free samples obtained by heating **2b**, **3b**, and **4c** at 260, 150, and 140 °C, respectively, as suggested by the TG curves. Only **3b** can retain its original framework structure, while **2b** and **4c** transformed to **2a** and an unknown structure, respectively (Fig. S9). These phenomena could be ascribed to the relatively flexible nature of the propyl group, as compared with ethyl and isopropyl groups. Judging from the crystal structures of **2b** and **4c**, the host frameworks should only be broken to release the benzene molecules, regardless of the guest removal temperatures. When guest-free **3b** (denoted as **3b'**) was further heated to 200 °C, it also transformed to its nonporous isomer **3a** (Fig. S9).

To remove guest molecules from **2b** and **4c** without destruction of their host structures, solvent exchange experiments have been performed. PXRD showed that (Fig. S9), **2b** remained unchanged after 7 days in both *n*-hexane and methanol, whereas **4c** transformed into microcrystalline **4a** in *n*-hexane or into single crystals of a new guest-containing structure $[Ag_8(diptz)_8]\cdot C_6H_6\cdot CH_3OH$ **(4d)** in methanol after 1 day.

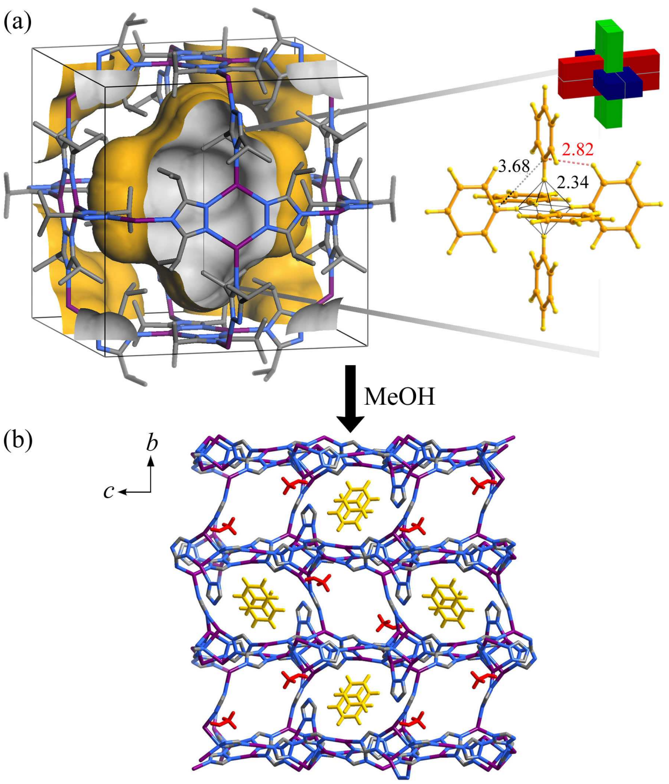

Fig. 4 Solvent-assisted irreversible recrystallization structural transformation from **4c** to **4d**. (a) The coordination framework and pore surface (Connolly surface with probe radius 1.9 Å shown in yellow/gray) structures of **4c** (hydrogen atoms of the coordination network are omitted for clarity; Inset: the *three rods Ming lock* like supramolecular hexamer of the guest benzene hexamer). (b) The host-guest structure of **4d**. Atom colours follow Fig. 2, except that the benzene and methanol molecules are highlighted in yellow and red, respectively.

4d crystallizes in a monoclinic space group $P2_1/n$ with eight Ag ions, eight diptz$^−$ ligands, one methanol and one benzene in the asymmetric unit. One Ag ion is linear coordinated, four Ag ions are trigonal coordinated, and three Ag ions are tetrahedral coordinated. Among eight independent ligands, one coordinate in the pyrazolate mode, five adopt the μ_3-N^1,N^2,N^4 coordination mode, and the rest two adopt the μ_4-N^1,N^1,N^2,N^4 coordination modes (Fig. S8). As a consequence, the 3D coordination framework of **4d** is very complicated and completely different with that of **4c** (Fig. 4b). Generally, topochemical transformations of coordination polymers involving breakage and formation of coordination bonds can be described by very few steps. Considering severe difference between **4c** and **4d**, the structural transformation should be solvent-assisted recrystallization instead of topochemical transformation.[23] However, it is very surprising to obtain single crystals suitable for X-ray diffraction analysis from short-time recrystallization of this compound with poor solubility.

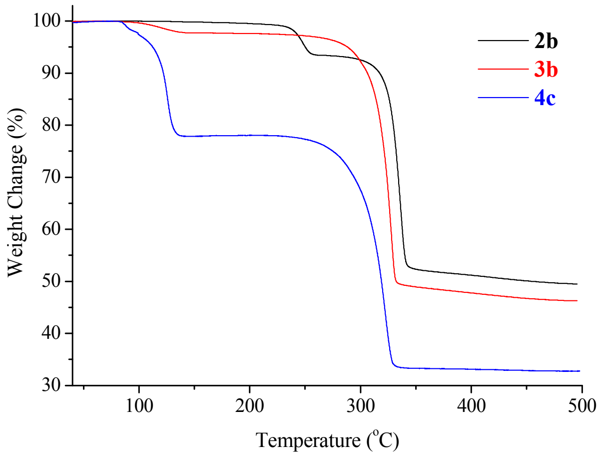

Fig. 5. TG curves of **2b**, **3b**, and **4c**.

The single-crystal structure of **3b'** was measured to confirm the retention of the host framework (Fig. S3). The unit-cell volume of **3b'** is about 1.5% smaller than that of **3b**, indicating that the benzene guest molecule is slightly larger than the cavity. Interestingly, the void ratio decreased significantly from 8.4% in **3b** to 2.0% in **3b'** (calculated by Platon using a probe radius of 1.20 Å), which can be hardly ascribed to the slight contraction of the host framework. Careful comparison of the host framework structures of **3b** and **3b'** showed that, besides small distortion of the silver(I) triazolate scaffold, large conformational changes can be found for the flexible propyl groups (Fig. 3). In the guest-free phase, the flexible chains spread into the space originally occupied by the guest, so that the cavity is divided into multiple portions which are too small for the conventional probe (radius 1.20 Å). It should be noted that, **3b** and **3b'** are not supramolecular isomers with each other because they possess the same framework connectivity. On the other hand, **3a** and **3b'** are genuine supramolecular isomers because they have identical chemical compositions.[8, 10b]

Although guest-induced structural transformation is not available for **2b**, we observed a crystal phase transition between -145 and -140 °C. The low-temperature phase of **2b** (denoted as **2b'**) crystallizes in a similar space group of $P2_1/c$, but the length of its *b*-axis is twice that of **2b**, meaning that the structure complexity is doubled. The coordination bonds lengths of **2b** and **2b'** are almost identical (Ag-N 2.161(3)-2.356(3) Å for **2b**; Ag-N 2.163(2)-2.380(2) Å for **2b'**), whereas their bond angles vary a lot [N-Ag-N 102.07(12)-138.64(16)^{o} for **2b**; N-Ag-N 95.78(9)-144.50(8)^{o} for **2b'**], which is similar with other flexible coordination polymers. More importantly, no obvious disorder can be observed for the ethyl groups in **2b'** (Fig. 2b), meaning that the crystal symmetry transition is mainly arise from the order-disorder conformational transformation of the ethyl groups.

Conclusions

In summary, by introducing benzene into the reaction system, four guest-containing isomers have been successfully synthesized for silver(I) 3,5-diethyl-1,2,4-triazolate, 3,5-dipropyl-1,2,4-triazolate, and 3,5-diisopropyl-1,2,4-triazolate, in which benzene serves either as the template or as the structure-directing agent. These guest-containing isomers are kinetic products, which transform to the thermodynamic isomers by prolonging reaction time, heating, and/or solvent exchange. On the other hand, no guest-containing isomer can be obtained for 3,5-dimethyl-1,2,4-triazolate yet, which illustrates the relatively weak interaction between the small methyl groups and benzene molecules. Besides several new coordination framework structures and an unprecedented supramolecular hexamer of benzene molecules, these compounds show very different structural transformation behaviors, including reversible temperature- and guest-induced conformational changes of the pendent alkyl groups and solvent-assisted supramolecular isomerization of the whole coordination framework. These results could serve as beneficial supplement for the research of supramolecular isomerism, host-guest interaction, and framework stability, flexibility, and reactivity.

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Notes and references

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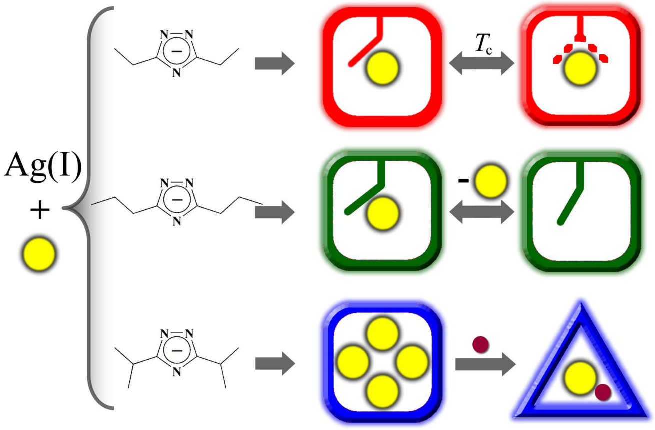
Graphic content (TOC)



Using benzene as a template, a series of guest-containing silver(I) 3,5-dialkyl-1,2,4-triazolate isomers showing different structural transformation behaviours have been synthesized.