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## COMMUNICATION

## Anion induced structural transformation in silver-(3,6-dimethoxy-1,2,4,5-tetrazine) coordination polymers under mechanochemical conditions

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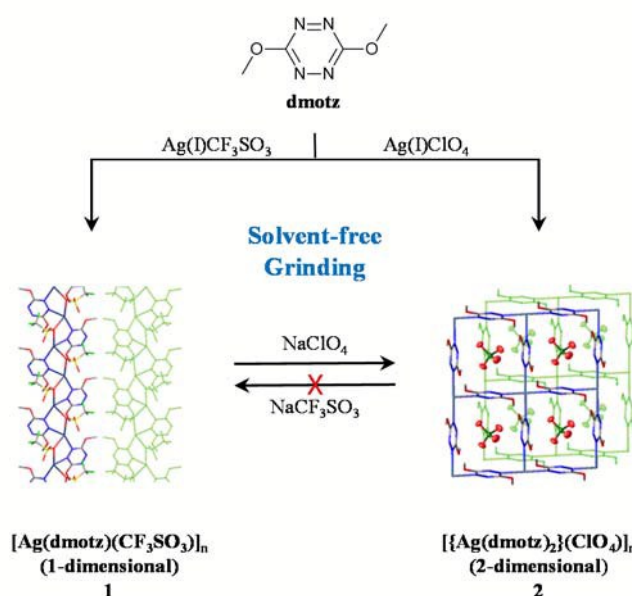
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Mechanochemical reactions of 3,6-dimethoxy-*s*-tetrazine (dmotz) with  $\text{AgCF}_3\text{SO}_3$  and  $\text{AgClO}_4$  afforded the 1D linear polymer  $[\text{Ag}(\text{dmotz})(\text{CF}_3\text{SO}_3)]_n$  (**1**) and the 2D grid polymer  $\{[\text{Ag}(\text{dmotz})_2](\text{ClO}_4)\}_n$  (**2**), respectively. Mechanochemical processes convert **1** to **2** in the presence of an equivalent of  $[\text{ClO}_4]^-$  and dmotz; even using excess  $[\text{CF}_3\text{SO}_3]^-$ , conversion from **2** to **1** was not observed.

Mechanochemistry, the chemistry of solid-phase reactions stimulated by mechanical energy, is one of the more active research areas at the forefront of medicinal and materials chemistry.<sup>1</sup> Mechanochemical methods offer not only an ideal solution to treat large amounts of reaction waste but also a great opportunity for higher yields and faster reaction rates than reactions in solution.<sup>1a, 2</sup> Mechanochemistry can offer alternative ways to synthesize diverse supramolecules like molecular cages, macrocycles, helicates, coordination polymers, etc.<sup>3</sup>

In the construction of supramolecular architectures, the use of a chemical template is a powerful tool to favor a desired structure in both solution<sup>4</sup> and solid-phase reactions.<sup>5</sup> Chemical templating is especially important in the solid-phase synthesis of porous materials, including coordination polymers and metal–organic frameworks, where the template plays an essential role in filling the pore spaces and stabilizing the porous topologies.<sup>6</sup> Recent progress obtained from the Frišćić group emphasizes the importance of ion templates in mechanochemical reactions,<sup>7</sup> where catalytic amounts of simple salts allow the formation of porous Zn-MOF( $[\text{Zn}_2(\text{ta})_2(\text{dabco})]$ ). Furthermore, selective synthesis of two  $[\text{Zn}_2(\text{ta})_2(\text{dabco})]$  isomers of tetragonal and hexagonal topology was achieved by varying the type of ion template used.

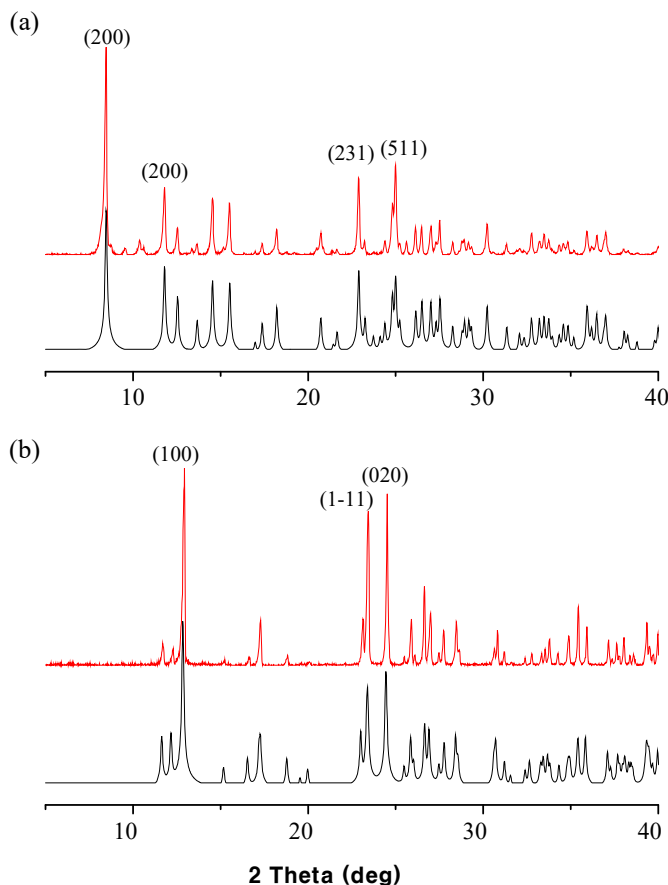


**Chart 1.** Mechanochemical synthesis of **1-2** and transformation from **1** to **2**.

As a part of our aim to understand the role of ion templates in structural formation under mechanochemical conditions, we noted the exceptional ability of *s*-tetrazine as an efficient receptor for various anions<sup>8</sup> and the structural diversity of *s*-tetrazine-silver(I) coordination polymers depending on the nature of anions. In the formation of the coordination polymers,<sup>9</sup> the anion- $\pi$  interactions

between selected anions and  $\pi$ -acidic *s*-tetrazine rings direct the resulting topologies of the coordination polymers. We focused on the solid-phase reactions, which can lead to the formation of a new series of *s*-tetrazine-silver(I) coordination polymers. We also studied how the anion- $\pi$  interactions influence the resulting topologies.

Chart 1 depicts a schematic overview of the synthesis and structural transformation of *s*-tetrazine-silver(I) coordination polymers under mechanochemical conditions.



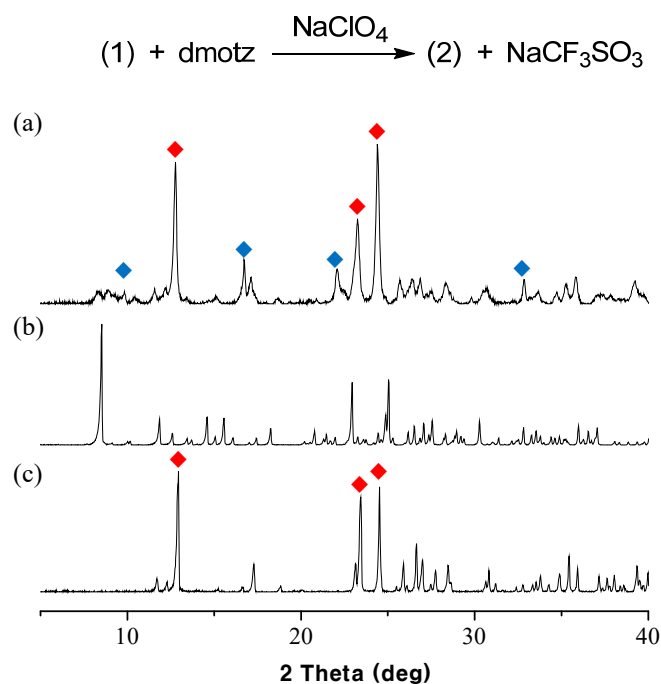
**Fig. 1** PXRD patterns of the complexes (a) **1**: experimental (red) and simulated (black) and (b) **2**: experimental (red) and simulated (black).

We describe here the mechanochemical synthesis of silver coordination polymers including 3,6-dimethoxy-*s*-tetrazine (dmotz) and the first example of anion-templation-induced structural transformation from 1D linear structure  $[\text{Ag}(\text{dmotz})(\text{CF}_3\text{SO}_3)]_n$  (**1**) to 2D grid structure  $[\{\text{Ag}(\text{dmotz})_2\}(\text{ClO}_4)]_n$  (**2**) under ball-milling conditions.

The ball milling reaction of dmotz with  $\text{AgCF}_3\text{SO}_3$  and  $\text{AgClO}_4$  yielded complexes **1** and **2**, respectively. The structural formation of the reaction products **1** and **2** were indicated by a color change, from pink to deep red. The powder X-ray diffraction (PXRD) patterns revealed that the reaction lead quantitative formation of highly crystalline complex **1** and **2** through no observation of starting materials of silver salts and dmotz.

The PXRD pattern of **1** (Fig. 1a, red) shows strong diffraction peaks at  $2\theta(^{\circ}) = 8.5, 11.8, 22.9$  and  $25$ , which exactly correspond to the diffraction pattern simulated from single-crystal XRD analysis (Fig. 1a,

black). Single crystals of **1** were grown through slow diffusion of ether into a dichloromethane solution of **1**. The crystal structure of **1** consists of 1D linear chains along the crystallographic *c* axis. The coordination geometry of the  $\text{Ag}^{\text{I}}$  ion is distorted tetrahedral, with four sites being occupied by the bridging of two different  $\text{CF}_3\text{SO}_3^-$  and two dmotz in *meta* orientation (Fig. 2a, Fig. S1). The Ag–N distances are in the range of 2.29–2.37 Å and the Ag–O distances are in the range of 2.49–2.52 Å. From the results of single-crystal and powder XRD, the comparison of the PXRD patterns shows that ball milling of  $\text{AgCF}_3\text{SO}_3$  with dmotz successfully led to the formation of the 1D linear coordination polymer  $[\text{Ag}(\text{dmotz})(\text{CF}_3\text{SO}_3)]_n$ .



**Fig. 2** PXRD patterns of (a)  $[\{\text{Ag}(\text{dmotz})_2\}(\text{ClO}_4)]_n$  and  $\text{Na}(\text{CF}_3\text{SO}_3)$  from the reaction of **1** with  $\text{NaClO}_4$ , (b) compound **1** and (c) compound **2**.  $\blacklozenge$  and  $\blacklozenge$  denote peaks of  $\text{Na}(\text{CF}_3\text{SO}_3)$  and **2**, respectively.

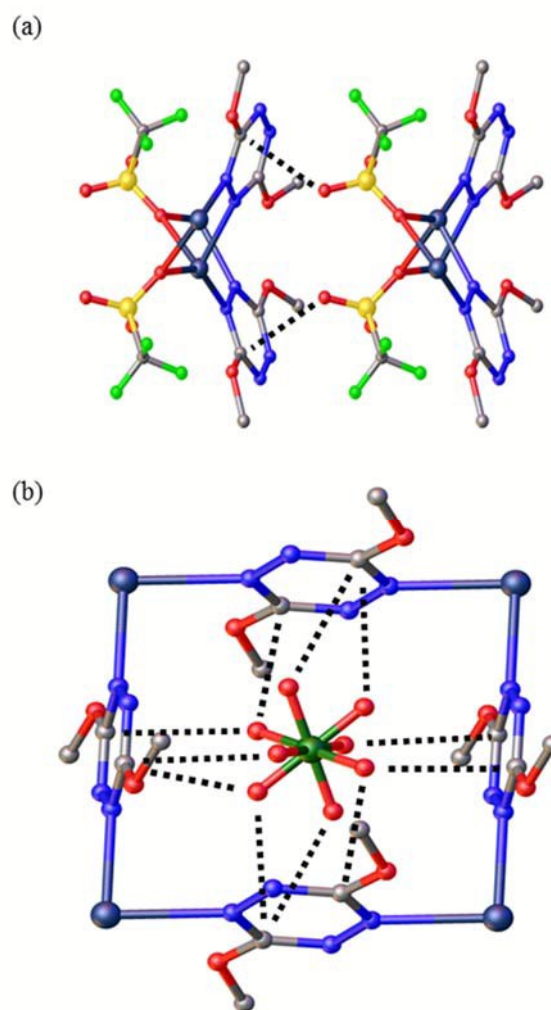
The comparison between the PXRD pattern of **2** (Fig. 2b, red) and the simulated PXRD pattern obtained from the single-crystal analysis (Fig. 2b, black) indicates that 2D grid structures of **2** were successfully synthesized by ball milling of  $\text{AgClO}_4$  with dmotz. The FTIR spectra of 1-2 exhibit a strong band of  $\text{CF}_3\text{SO}_3^-$  and  $\text{ClO}_4^-$  anions at 1269 and 1101  $\text{cm}^{-1}$  respectively (Fig. S6b, c) with all the characteristic bands of dmotz (Fig. S6a). The crystal structure of **2** consists of 2D grid sheets with  $\text{Ag}^{\text{I}}$  linked by four bridging dmotz moieties in a *para* orientation (Fig. 2b, Fig. S2). The coordination geometry of  $\text{Ag}^{\text{I}}$  is square planar, with the four sites occupied by dmotz ligands; here the Ag–N distances are in the range of 2.43–2.45 Å. Each pore is filled with a  $\text{ClO}_4^-$  ion, which are surrounded by four dmotz and four  $\text{Ag}^{\text{I}}$ , with the Ag...Ag cross-ligand distances of 7.67 Å and Ag...Ag...Ag vertex angles of 87.5° and 92.5°.

Interestingly, the 2D grids (**2**) could be obtained from the structural transformation of the 1D chains (**1**) in the presence of a equivalent  $\text{NaClO}_4$  and a equivalent of dmotz under ball milling conditions. The PXRD analysis shows that **1** was successfully transformed into **2**, with the emergence of the strong diffraction peaks of **2** and  $\text{NaCF}_3\text{SO}_3$ ,

which is the side product from the reaction. However, the reverse conversion was not observed from the ball milling of **2** in the presence of a large excess of  $\text{NaCF}_3\text{SO}_3$ . To the best of our knowledge, this result is the first example showing that the anion template effect leads to structural transformation under mechanochemical conditions.

The PXRD pattern of mechanochemically synthesized  $[\text{Ag}(\text{dmtz})(\text{CF}_3\text{SO}_3)]_n$  was recorded (Fig. 2b). After ball milling of **1** with  $\text{NaClO}_4$ , the strong peaks of (200, 020, 231, 511) at  $2\theta(^{\circ}) = 8.5, 11.8, 22.9, 25$  related to structure **1** disappeared and a set of strong diffraction peaks at  $2\theta(^{\circ}) = 13, 23.4, 24.5$  emerged, which correspond to the PXRD pattern of **2** (Fig. 2a,  $\blacklozenge$ ). Peaks at  $2\theta(^{\circ}) = 9.9, 16.8, 22.2, 32.9$  (Fig. 2a,  $\blacklozenge$ ) also emerged, indicating the formation of  $\text{NaCF}_3\text{SO}_3$ , which is further evidence of the structural transformation of  $[\text{Ag}(\text{dmtz})(\text{CF}_3\text{SO}_3)]_n$  into  $\{[\text{Ag}(\text{dmtz})_2](\text{ClO}_4)\}_n$ . The structural transformation is influenced by anion template effects through anion- $\pi$  interactions between  $\pi$ -electron-deficient tetrazine rings and  $\text{ClO}_4^-$  from the resulting solid structure. This result is supported by recent comprehensive studies for the role of anion- $\pi$  interactions as controlling elements in the formation and transformation of metallacyclophanes under solution reaction.<sup>10</sup>

The stabilization through anion- $\pi$  interactions in solid structures of compounds **1** and **2** is shown in Fig. 3. Intermolecular anion- $\pi$  interactions between the tetrazine ring and  $\text{CF}_3\text{SO}_3^-$  lead to the tightening of 1D linear chains in the solid structure of compound **1**. The interaction length from the O atoms of  $\text{CF}_3\text{SO}_3^-$  to the C atoms of the tetrazine rings is 3.07 Å, which is 0.15 Å shorter than the van der Waals radius of  $\Sigma R_{\text{vdW}} \text{O}\cdots\text{C} = 3.22\text{Å}$ . Fig. 3b shows templated  $\text{ClO}_4^-$  surrounded by four tetrazine rings; here the anion stabilizes the pores by strong anion- $\pi$  interactions in the solid structure of **2**. The O $\cdots$ C distances between the  $\text{ClO}_4^-$  and tetrazine rings are in the range of 2.93–3.20 Å, which shows that the  $\text{ClO}_4^-$  fills the pores and the structure becomes tightened due to the anion- $\pi$  interactions with the four tetrazine rings, compared with the van der Waals radius of  $\Sigma R_{\text{vdW}} \text{O}\cdots\text{C} = 3.22\text{Å}$ .



**Fig. 3** Molecular structures in  $[\text{Ag}(\text{dmtz})(\text{CF}_3\text{SO}_3)]_n$  (a) and  $\{[\text{Ag}(\text{dmtz})_2](\text{ClO}_4)\}_n$  (b), anion- $\pi$  interactions are depicted with dashed lines. Color code: Ag dark blue, C grey, N blue, O red, Cl green, F yellowish green, S yellow.

## Conclusions

In conclusion, the new tetrazine-silver coordination polymers,  $[\text{Ag}(\text{dmtz})(\text{CF}_3\text{SO}_3)]_n$  (**1**) and  $\{[\text{Ag}(\text{dmtz})_2](\text{ClO}_4)\}_n$  (**2**), were successfully prepared via a mechanochemical method. The ball milling of **1** with  $\text{NaClO}_4$  allowed the structural transformation from **1** to **2**. These results support the proposal that anion templates involving anion- $\pi$  interactions could well act as structure-controlling elements under mechanochemical conditions.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: Detailed synthetic procedure, crystallographic data, characterization details of the compounds here described. CCDC 1416102 and 1416104. see DOI: 10.1039/c000000x/

- (a) S. L. James, C. J. Adams, C. Bolm, D. Braga, P. Collier, T. Friščić, F. Grepioni, K. D. M. Harris, G. Hyett, W. Jones, A. Krebs, J. Mack, L. Maini, A. G. Orpen, I. P. Parkin, W. C. Shearouse, J. W. Steed, D. C. Waddell, *Chem. Soc. Rev.*, 2012, **41**, 413-447; (b) L. Takacs, *Chem. Soc. Rev.*, 2013, **42**, 7649-7659.
- A. Orita, L. Jiang, T. Nakno, N. Ma, J. Otera, *Chem. Commun.*, 2002, 1362-1363.
- (a) D. Braga, S. L. Giuffreda, F. Grepioni, A. Pettersen, L. Maini, M. Curzi, M. Polito, *Dalton Trans.*, 2006, **10**, 1249-1263; (b) A. L. Garay, A. Pichon, S. L. James, *Chem. Soc. Rev.*, 2007, **36**, 864-855.
- (a) R. Vilar, *Angew. Chem. Int. Ed.*, 2003, **42**, 1460-1477; (b) K. M. Mullen, P. D. Beer, *Chem. Soc. Rev.*, 2009, **38**, 1701-1713. (c) B. Hasenknopf, J. M. Lehn, O. Kneisel, G. Baum, D. Fenske, *Angew. Chem. Int. Ed.*, 1996, **35**, 1838-1840; (d) B. Hasenknopf, J. -M. Lehn, N. Boumediene, A. Dupont-Gervais, A. V. Dorsselaer, B. Kneisel, D. Fenske, *J. Am. Chem. Soc.*, 1997, **119**, 10956-10962; (e) R. L. E. Furlan, S. Otto, J. K. M. Sanders, *Proc. Natl. Acad. Sci. U.S.A.*, 2002, **99**, 4801-4804; (f) R. Vilar, *Coord. Chem. Rev.*, 2006, **250**, 3161-3189; (g) R. Vilar, *Struct. Bonding (Berlin)*, 2008, **129**, 175-206; (h) R. Vilar, *Eur. J. Inorg. Chem.*, 2008, **3**, 357-367; (i) R. L. Paul, Z, R, Bellm J, C, Jeffery, J. A. McCleverty, M. D. Ward, *Proc. Natl. Acad. Sci. U.S.A.*, 2002, **99**, 4883-4888; (j) S. Hiraoka, M. Fujita, *J. Am. Chem. Soc.*, 1999, **121**, 10239-10240; (k) H. Amouri, C. Desmarets, A. Bettoschi, M. N. Rager, K. Boubekeur, P. Rabu, M. Drillon, *Chem.-Eur. J.*, 2007, **13**, 5401-5407; (l) H. Amouri, L. Minassi, M. N. Rager, B. E. Mann, C. Guyarf-Duhayon, L. Raehm, *Angew. Chem., Int. Ed.*, 2005, **44**, 4543-4546.
- (a) T. Friščić, L. Fàbian, *CrystEngComm.*, 2009, **11**, 743-745; (b) A. Pichon, A. Lazuen-Garay, S. L. James, *CrystEngComm*, 2006, **8**, 211-214; (c) W. Yuan, T. Friščić, D. Apperley, S. L. James, *Angew. Chem. Int. Ed.*, 2010, **49**, 3916-3919.
- T. Friščić, *Chem. Soc. Rev.*, 2012, **41**, 3493-3510.
- T. Friščić, D. G. Reid, I. Halasz, R. S. Stein, R. E. Dinnebier, M. J. Duer, *Angew. Chem. Int. Ed.*, 2010, **49**, 712-715.
- (a) M. Mascal, A. Armstrong and M. D. Bartberger, *J. Am. Chem. Soc.*, 2002, **124**, 6274-6276; (b) I. Alkorta, I. Rozas and J. Elguero, *J. Am. Chem. Soc.*, 2002, **124**, 8593-8598; (c) D. Quiñonero, C. Garau, C. Rotger, A. Frontera, P. Ballester, A. Costa and P. M. Deyà, *Angew. Chem., Int. Ed.*, 2002, **41**, 3389-3392; (d) H. T. Chifotides, K. R. Dunbar, *Acc. Chem. Res.*, 2013, **46**, 894-906.
- (a) B. L. Schottel, H. T. Chifotides, M. Shatruk, A. Chouai, L. M. Pérez, J. Bacsá, K. R. Dunbar, *J. Am. Chem. Soc.*, 2006, **128**, 5895-5912; (b) D. A. Safin, A. Pialat, A. A. Leitch, N. A. Tumanov, I. Korobkov, Y. Filinchuk, J. L. Brusso, M. Murugesu, *Chem. Commun.*, 2015, **51**, 9547-9550; (c) K. Chainok, S. M. Neville, C. M. Forsyth, W. J. Gee, K. S. Murray, S. R. Batten, *CrystEngComm.*, 2012, **14**, 3717-3726; (d) I. A. Gural'skiy, D. Escudero, A. Frontera, P. V. Solntsev, E. B. Rusanov, A. N. Chernega, H. Krautscheid, K. V. Domasevitch, *Dalton Trans.*, 2009, **15**, 2856-2864.
- (a) C. S. Campos-Fernández, L. B. Schottel, H. T. Chifotides, J. K. Bera, J. Bacsá, J. M. Koomen, D. H. Russell, K. R. Dunbar, *J. Am. Chem. Soc.*, 2005, **127**, 12909-12923; (b) H. T. Chifotides, I. D. Giles, K. R. Dunbar, *J. Am. Chem. Soc.*, 2013, **135**, 3039-3055.

Mechanochemical processes allow that the 1D chain of  $[\text{Ag}(\text{dmtz})(\text{CF}_3\text{SO}_3)]_n$  easily converts to 2D grid network of  $\{[\text{Ag}(\text{dmtz})_2](\text{ClO}_4)\}_n$  in the presence of  $[\text{ClO}_4]^-$ .

