Invited Lecture

Effects of polymorphism in network solids

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The phenomenon of polymorphism is well studied in molecular solids, thanks mainly to its relevance to pharmaceutical science, yet it remains understudied in covalent network solids such as coordination networks. In this contribution, we will highlight how subtle changes in crystal packing can profoundly influence certain bulk properties more than others:

(i) Aqueous solubility and melting point tend not to be strongly impacted by crystal packing in molecular solids as exemplified by drug substances (active pharmaceutical ingredients) [1]. We have found that this is also the case in families of polymorphic lithium-based coordination networks that are drug substance candidates [2].

(ii) Coordination networks are of topical interest thanks to their benchmark properties of relevance to gas and/or vapour sorption applications, in particular selectivity (for purification) and working capacity (for storage). We will highlight how polymorphism can profoundly impact C3 hydrocarbon gas sorption thanks to changes in pore size and chemistry [3]. We will also address how polymorphism impacts gas sorption in coordination networks that undergo phase transformations between closed (non-porous) and open (porous) forms of the coordination networks **X-sql-1-Cu** [4] and $Cd(PyImPr)_2$ [5]. As shown in Fig. 1, polymorphs A and B of **X-sql-1-Cu** exhibit very different CO_2 sorption profiles.

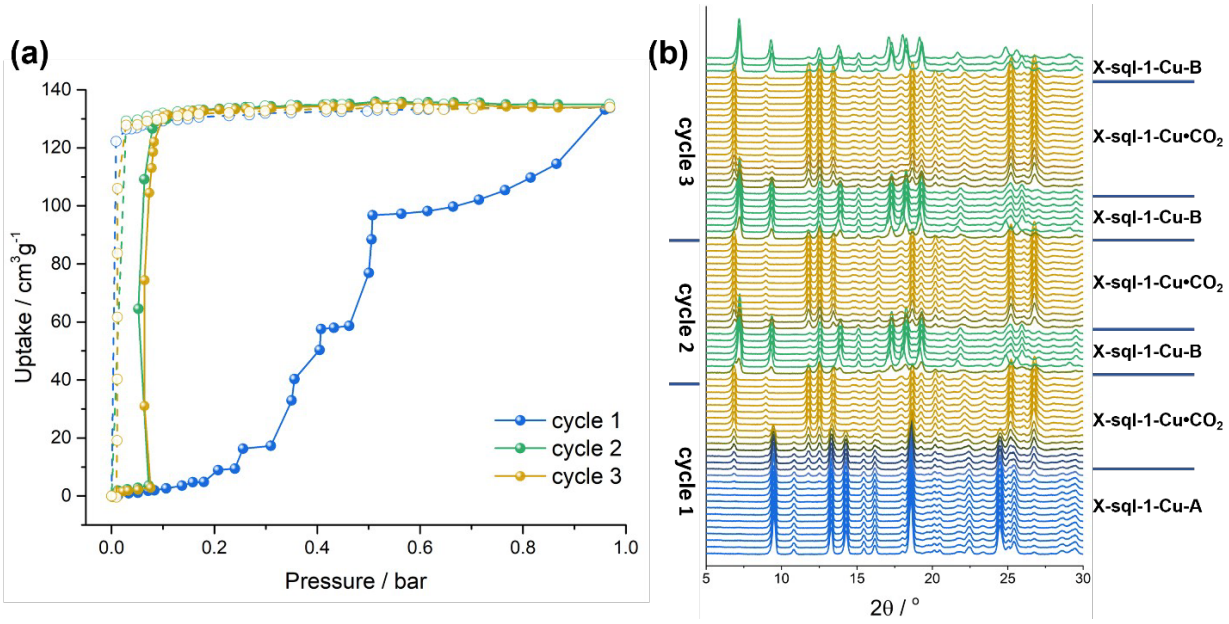

Figure 1. CO_2 sorption (a) and *in situ* PXRD (b) studies conducted upon the coordination network **X-sql-1-Cu**.

[1] Pudipeddi, M. & Serajuddin, A.T.M. (2005). *J. Pharm. Sci*., **94**, 929.

[2] Sanii, R., Andaloussi, Y.H., Patyk-Kazmierczak & Zaworotko, M.J. (2022). *Cryst. Growth Des*., **22**, 3786.

[3] Gao, M.Y.; Bezrukov, A.A.; B.Q.; He, M.; Nikkah, S.J.; Wang, S.Q.; Kumar, N.; Darwish, S.; Sensharma, D.; Deng, C.; Li, J.; Liu, L.; Krishna, R.; Vandichel, M.; Yang, S. & Zaworotko, M.J. (2023). *J. Amer. Chem. Soc.*, **145**, 11837.

[4] Subanbekova, A.; Bezrukov, A.A.; Bon, V.; Nikolayenko, V.; Koupepidou, K.; Sensharma, D.; Nikkah, S.J.; Wang, S.Q.; Kaskel, S.; Vandichel,
M. & Zaworotko, M.J. (2024). *ACS Applied Mater. Interfac*., accepted for publication.

[5] Andaloussi, Y.H.; Bezrukov, A.A.; Sensharma, D. & Zaworotko, M.J. (2023). CrystEngComm, **25**, 4175.