Tuning mechanical responses of crystalline cadmium(II) coordination polymers through cyano functionality and halide anions

M. Pisačić, M. Đaković

Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, 10 000 Zagreb, Croatia

mateja.pisacic@chem.pmf.hr

Controlling supramolecular synthetic output, with the aim to achieve targeted macroscopic properties, is the main goal of crystal engineering.[1] Mechanical flexibility, as one of the highly desired properties of functional materials, has recently become a feature of a growing number of crystalline compounds.[2-5] Plastic deformation, together with elastic response, is frequently observed among organic molecular crystals,[3] but quite rarely noticed among crystalline metal-organic compounds.[4,5] Since the introduction of metal cations to organic systems allow us to achieve specific properties such as magnetic and electric ones, and therefore opens a wide range of possible applications, it is clear that there is a need for determining structural requirements that need to be fulfilled to equip metal-organic crystals with mechanical flexibility.

Recently, it was shown that cadmium(II) coordination polymers equipped with halopyrazine ligands adaptably respond to applied external stimuli, displaying elastic flexibility.[5] It was observed that introducing a slight structural changes, simply by exchanging bridging halide anion or halogen atom on halopyrazine ligand, changes the extent of elastic response significantly, while the quantification of their mechanical behaviour clearly showed that they can be categorized into three main subgroups, highly, moderately and slightly elastic. To get an invaluable insight into the phenomenon, we decided to systematically examine similar classes of coordination polymers by introducing slight structural differences through the exchange of supramolecular functionalities only. Herein we opted for pyridine-based ligands decorated with cyano functionality to explore their impact on macroscopic mechanical output. It was determined that the position of cyano group on pyridine ring, as well as used bridging halide anion, dictate the nature and extent of mechanical response. For crystals that displayed elastic behaviour, the responses were quantified and correlated with structural features, primarily the strength and geometry of supramolecular interactions, and compared with the mechanical behaviour of similar metal-containing systems.

[1] Desiraju, G. R. (2007) *Angew. Chem. Int. Ed.* **46**, 8342.

[2] Commins, P., Tilahun Desta, I., Prasad Karothu, D., Panda, M. K., Naumov, P. (2016) *Chem. Commun.* **52**, 13941.

[3] Saha, S., Mishra, M. K., Reddy, C. M., Desiraju, G. R. (2017) *Acc. Chem. Res.* **51**, 2957.

[4] Worthy, A., Grosjean, A., Pfrunder, M. C., Xu, Y., Yan, C., Edwards, G., Clegg, J. K., McMurtrie, J. C. (2018) *Nat. Chem.* **10**, 65.

[5] Đaković, M., Borovina, M., Pisačić, M., Aakeröy, C. B., Soldin, Ž., Kukovec, B.-M., Kodrin, I. (2018) *Angew. Chem. Int. Ed.* **57**, 14801.

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