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MS35 From 0- to 3-dimensional porous systems

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MS35-O1

Metalorganic frameworks as platforms for biosignaling molecules

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Since pioneering work of Nobel laureates Furchogtt, Ignarro and Murad concerning nitric oxide (NO) as an important biosignaling molecule in the cardiovascular system, significant attention has been paid on the physiological and potential therapeutic role of NO and other endogenously produced small gas molecules, such as carbon monoxide (CO). The easiest administration route for these gas molecules into the body is the inhalation of their air mixtures. However, this strategy lacks of specificity and, in the case of CO, the higher affinity of this gas to haemoglobin/myoglobin compared to oxygen, as well as its poor solubility in water, means that high doses of inhaled CO are required to obtain a beneficial effect with the concomitant associated safety risk. In order to overcome these drawbacks, CO/NO-releasing materials (CORMAs and NORMAs) appear as solid CO/NO storage materials able to deliver the corresponding gas in a triggered manner. In this context, one of the most versatile strategies to design new CORMAs/NORMAs consists in the use of MOFs as biocompatible vehicles of these therapeutic gases.[1]

Taking into account this background, firstly, we have combined an existing CO-releasing molecule with the biocompatible MOF $[Al(OH)(SDC)]_n$ (H_2SDC: 4,4'-stilbenedicarboxylic acid) (CYCU-3) to obtain a new CORMA. In this work, we have shown the feasibility to control particle size and morphology in CYCU-3 by means of the coordination modulation method. With this aim, we have screened different reagent concentrations and modulator/ligand ratios. As a result, CYCU-3 materials with different particle features have been isolated including a new crystalline phase, for which a structural model based on a squeezed and defective structure of pristine CYCU-3 has been proposed. Besides, the air-stable and photoactive CO-releasing molecule ALF794 ($Mo(CNCMe_2CO_2H)_3(CO)_3$), which has demonstrated efficacy against acute liver injury in animal models, has been selected to be encapsulated in three selected CYCU-3 materials. Then, the influence of structure, crystal size and morphology over the resulting CORMAs properties including payload, CO-delivery and matrix stability have been evaluated.[2] Finally, we have also prepared novel NORMAs improving NO adsorption on the MOF $[Ni_8(OH)_4(H_2O)_2(BDP)_6]$ (H_2BDP=1,4-bis(pyrazol-4-yl) benzene-4) through the sequential introduction of missing-linker defects and extra-framework Fe^{2+} cations in this robust porous structure. In addition, a cation exchange strategy has been used with the same purpose on the cationic biocompatible MOF $(NH_2(CH_3)_2)_2[Zn_8(adeninate)_4(BPDC)_6]$ (BPDC = 4,4′-biphenyldicarboxylate). The NO releasing ability of these new NORMAs as well as their stability under physiological conditions have been compared.

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MS35-O2

Tuning properties and functionality in modulated crystallisation of high-valent metal-organic frameworks

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Metal-organic frameworks (MOFs) are network materials comprised of organic ligands connected by metal ion clusters into multidimensional structures that often have permanent porosity. Their chemically addressable structures, combined with their ability to store large quantities of small molecules within their pores, have led to applications in gas storage, heterogeneous catalysis, sensing, and drug delivery, amongst others. Coordination modulation, the addition of monomeric modulators to synthetic mixtures, can tune particle size from nanometres to centimetres, through capping of crystallites (decreasing) or coordinative competition with ligands (increasing).

The talk will cover the development of our own modulation techniques for high valent MOFs, and the use of modulation to control physical properties such as interpenetration, defectivity, and porosity. Our techniques provide access to high quality single crystals of many different MOFs, allowing the subsequent characterisation of their mechanical properties,[1] single-crystal to single-crystal postsynthetic modification,[2] development of fluorescent sensors,[3] and sequestration of toxic gases.

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