MS33-P11 | ENHANCED SELECTIVITY FOR CO_2 IN MIXED-LIGAND BIS(PYRAZOLATE) ZN(II) MOFS THROUGH DILUTION OF FUNCTIONALIZATION: A STRUCTURAL AND TEXTURAL STUDY

Vismara, Rebecca (Università degli Studi dell'Insubria, Como, ITA); Tuci, Giulia (Istituto di Chimica dei Composti Organometallici, Sesto Fiorentino, ITA); Tombesi, Alessia (Università di Camerino, Camerino, ITA); Di Nicola, Corrado (Università di Camerino, Camerino, ITA); Giambastiani, Giuliano (Istituto di Chimica dei Composti Organometallici, Sesto Fiorentino, ITA); Chierotti, Michele Remo (Università di Torino, Torino, ITA); Bordignon, Simone (Università di Torino, Torino, ITA); Gobetto, Roberto (Università di Torino, Torino, ITA); Pettinari, Claudio (Università di Camerino, Camerino, ITA); Rossin, Andrea (Istituto di Chimica dei Composti Organometallici, Sesto Fiorentino, ITA); Galli, Simona (Università degli Studi dell'Insubria, Como, ITA)

In the past century, the global temperature rose by 0.7 K. CO2 concentration in the atmosphere, contributing by more than 60% to global warming, overcame 410 ppm in 2019. MOFs are a potential alternative to all-inorganic materials in applications requiring gas adsorption. Their performances can be optimized using one properly functionalized ligand or a mixture therefrom.

The four mixed-ligand MOFs Zn-H/NO2, Zn-H/NH2, Zn-NO2/NH2 and Zn-H/NO2/NH2, synthesized employing 4,4'-bipyrazole, 3-nitro-4,4'-bipyrazole and 3-amino-4,4'-bipyrazole, were characterized in the solid state. Their crystal structures were assessed by PXRD, they are isoreticular to the end-members Zn-H [1], Zn-NO2 [2] and Zn-NH2 [3], showing a 3-D open frameworks with 1-D square/rhombic channels. The ligand stoichiometric ratio was determined independently, with an excellent agreement, by 13C CPMAS solid-state NMR and PXRD. DSC and PXRD, upon application of the Vegard law, confirmed the formation of solid solutions. The four MOFs are thermally stable (Tdec = 708-726 K) and, as proved by variable-temperature PXRD, show permanent porosity. N2 adsorption at 77 K revealed BET surface areas in the range 400-600 m2/g. CO2 adsorption capacity, isosteric heat of adsorption (Qst) and CO2/N2 selectivity (at 1 bar and 298 K), were compared with those of their end-members. The amino-decorated compounds show higher Qst values and better selectivity vs. the nitro-tagged analogues; moreover, tag "dilution" is beneficial compared to the end-members.

[1] C.Pettinari et al. *Inorg.Chem.* 2012, *51*, 5235-5245.
[2] N.Mosca et al. *Chem.Eur.J.* 2018, *24*, 13170-13180.
[3] R.Vismara et al. *Inorg.Chem.Front.* 2019, *6*, 533-545.