BENZOTHIAZOLIUM-FUNCTIONALIZED NU-1000 FOR CARBON DIOXIDE ADSORPTION

Giorgio Mercuri [a,b], Corrado Di Nicola [c], Riccardo Pettinari [a], Caludio Pettinari [a,b] and Andrea Rossin [b]

[a] School of Pharmacy, University of Camerino, Via S. Agostino 1, 62032 Camerino; [b] Institute of Chemistry of Organometallic Compounds, Via Madonna del Piano 10, 50019 Sesto Fiorentino; [c] School of Science and Technology, University of Camerino, Via S. Agostino 1, 62032 Camerino

A tailor-made benzothiazolium bromide salt functionality (**BzTz**) (*Figure 1*) is introduced via solvent-assisted ligand incorporation (SALI) into the mesoporous Zr-based metal–organic framework NU-1000 (*Figure 2*). The resulting **NU-1000-BzTz** composite has been thoroughly characterized in the solid state. The functional group loading has been determined through ^{1}H NMR analysis of the digested sample (5% HF-DMSO-d_6): a maximum value of 1.7 **BzTz** ligand per [Zr_6] node is achieved (*Figure 3*). The material preserves its pristine crystallinity after SALI, as witnessed by powder X-ray diffraction (*Figure 4*). The N_2 adsorption isotherm collected at 77 K disclosed that its BET specific surface area (1530 $m^2\ g^{-1}$) is lower than that of pristine NU-1000 (2140 $m^2\ g^{-1}$), because of the space taken and weight added by the dangling benzothiazolium groups inside the pores (*Figure 5a*). A total CO_2 uptake of 2.0 mmol g^{-1} (8.7 wt% CO_2) has been calculated from the CO_2 adsorption isotherm collected at T = 298 K and pCO_2 = 1 bar. Despite the lower BET area, **NU-1000-BzTz** shows an increased thermodynamic affinity for CO_2 (isosteric heat of adsorption Q_{st} = 25 kJ mol^{-1}) if compared with NU-1000 (Q_{st} = 17 kJ mol^{-1}), confirming that the presence of a polar functional group in the MOF pores improves the interaction with carbon dioxide (*Figure 5b*).

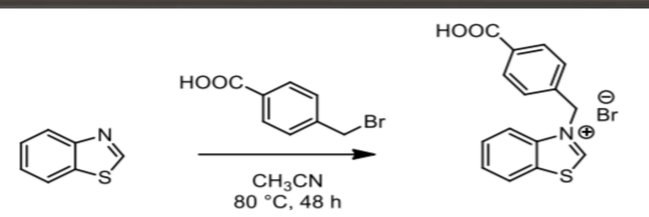

Figure 1: Synthesis of **BzTz**.

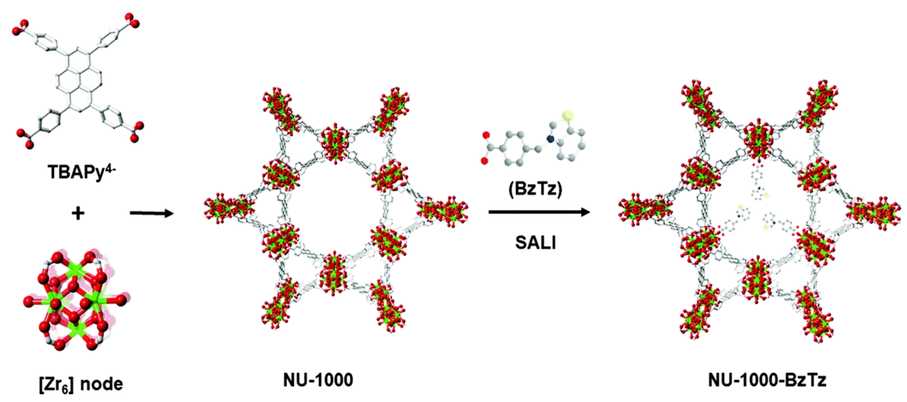

Figure 2: Molecular representations of NU-1000 and schematic representation of its SALI functionalization with a benzothiazolium salt.

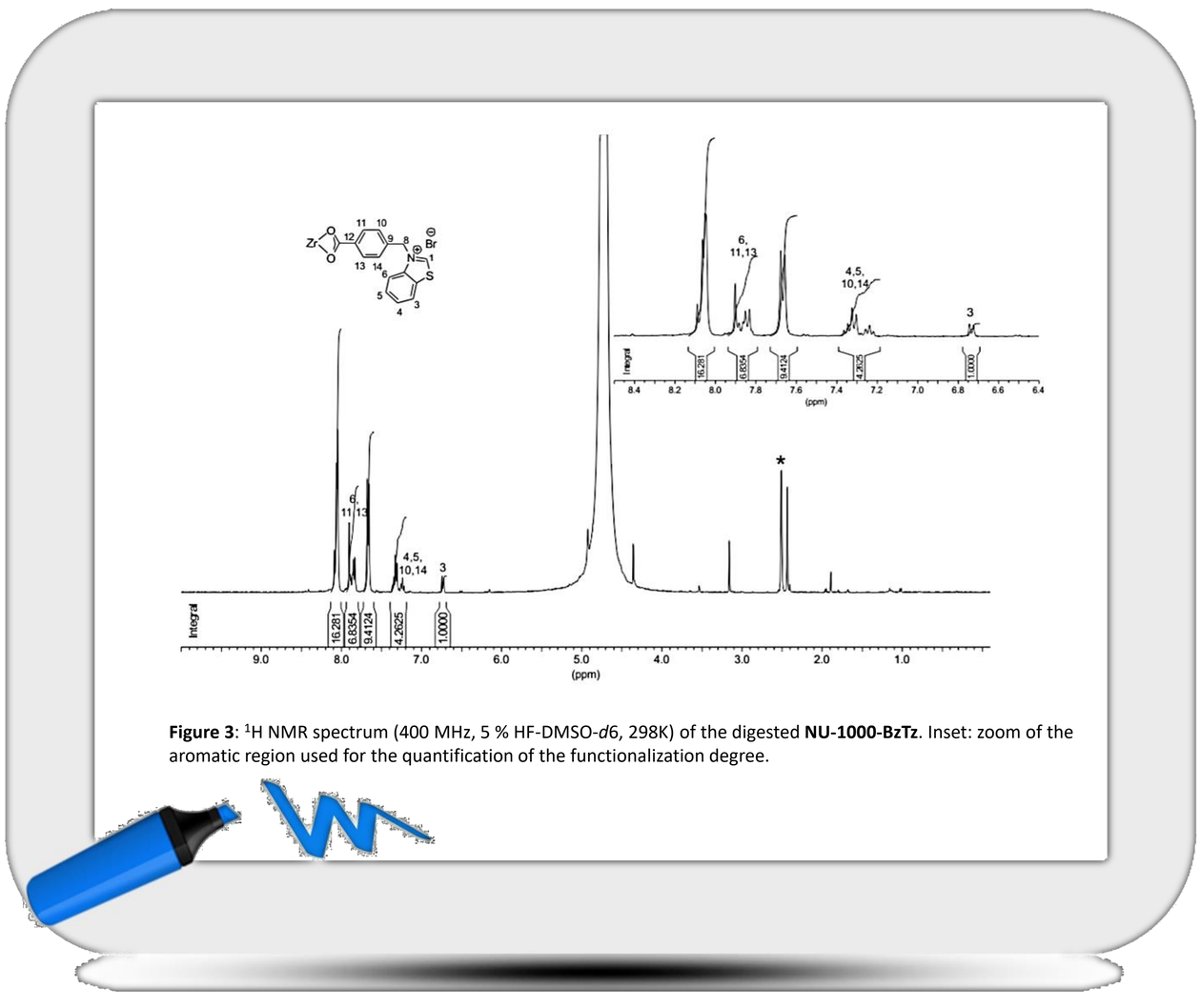

Figure 3: ^{1}H NMR spectrum (400 MHz, 5 % HF-DMSO-*d6*, 298K) of the digested **NU-1000-BzTz**. Inset: zoom of the aromatic region used for the quantification of the functionalization degree.

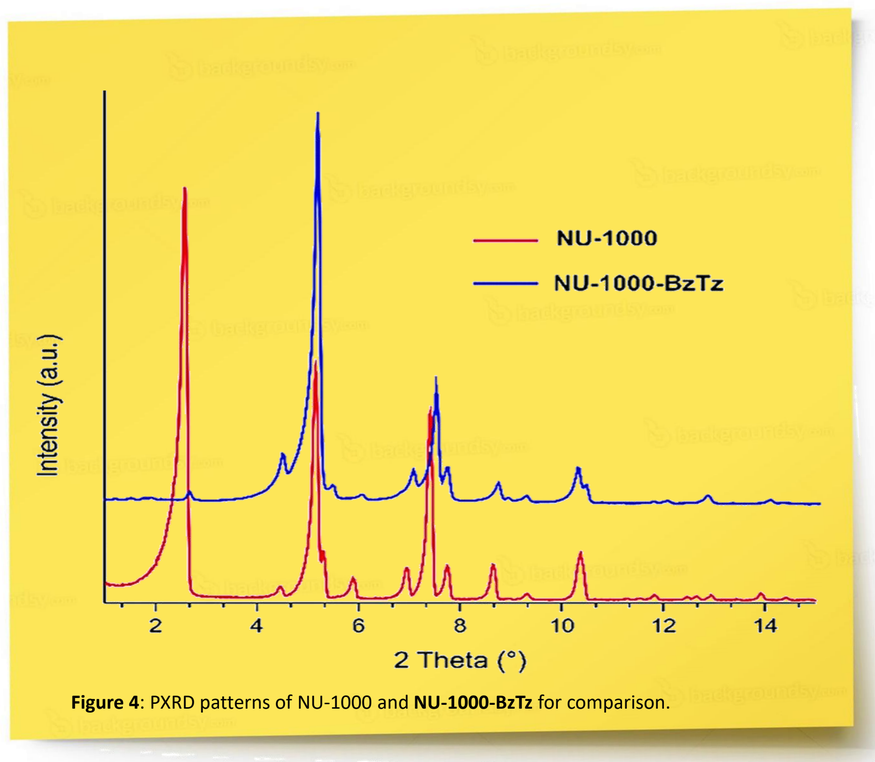

Figure 4: PXRD patterns of NU-1000 and **NU-1000-BzTz** for comparison.

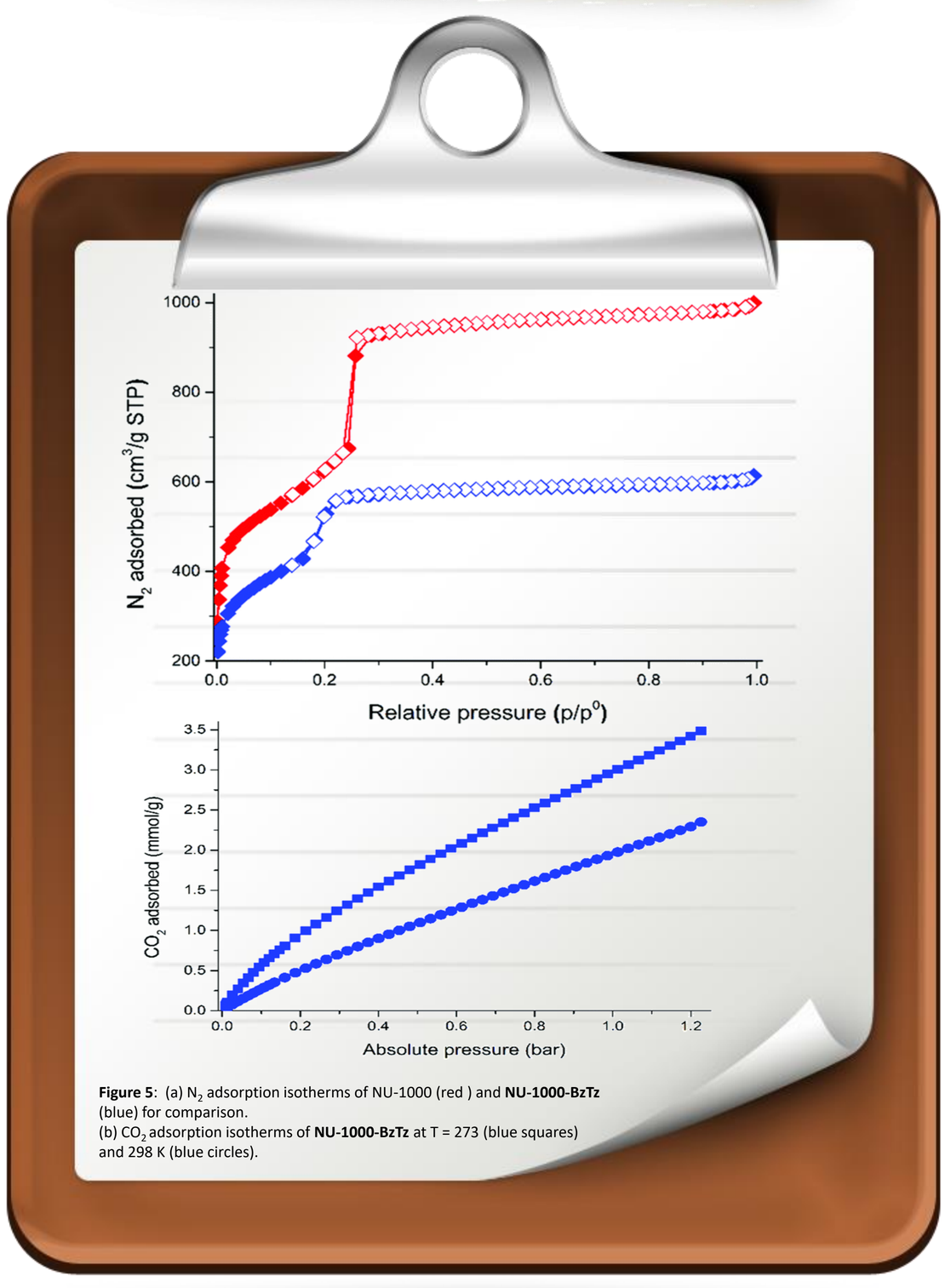

Figure 5: (a) N_2 adsorption isotherms of NU-1000 (red) and **NU-1000-BzTz** (blue) for comparison.
(b) CO_2 adsorption isotherms of **NU-1000-BzTz** at T = 273 (blue squares) and 298 K (blue circles).