Friday Materials Science Colloquia #17

Friday, November 28th 2022, 12 p.m.
Seminar room, U5 Building – via Roberto Cozzi 55, Milano

Lecturer: **Daniele Perilli**

Title: **Designing functional graphene through doping and interfacing with metals and molecules**

Graphene (Gr) is the archetypal two-dimensional material, renowned for its exceptional physical properties but intrinsically limited chemical activity. To overcome this limitation, recent research has focused on chemical modification strategies such as doping or interfacing with other materials or molecules, which enhance the reactivity and versatility of Gr for applications in gas sensing and catalysis [1]. Computational modeling plays a key role in this context, providing atomistic insights that enable the rational design of functionalized Gr materials tailored for specific applications.
In this talk, I will present three examples of quantum mechanical calculations of graphene-based systems and their synergy with experiments. I will start by discussing doping strategies, in which i) metal (Co, Ni) or ii) non-metal (N) elements are incorporated into Gr supported on metal substrates [2,3], highlighting their potential for gas adsorption and permeation. As third example of Gr functionalization, I will show how interfacing Gr with molecules can be exploited for gas sensing applications [4].

References:
[1] D. Deng et al., Nat. Nanotechnol. 11, 218-230 (2016)
[2] D. Perilli et al., J. Phys. Chem. Lett. 11, 8887–8892 (2020)
[3] D. Perilli et al., Angew. Chem. Int. Ed. 64, e202421757 (2025)
[4] D. Perilli et al., Commun. Mater. 5, 254 (2024)

Lecturer: **Charl Xavier Bezuidenhout**

Title: **The Versatility of MOFs: From Molecular Design to Functional Materials**

Metal–organic frameworks (MOFs) represent one of the most versatile classes of materials in modern chemistry. Their structural diversity and tunability have enabled breakthroughs in carbon capture, gas separation, catalysis, and sensing, demonstrating how atomic-scale design can translate into materials that address global technological challenges.
My research integrates crystallography, adsorption calorimetry, molecular simulation, and solid-state NMR to uncover the relationships among structure, energetics, and dynamics, which, in turn, enable the rational design of next-generation functional porous materials. In particular, MOFs have been engineered by integrating molecular rotors into the crystal architecture, achieving ultrafast rotational motion in the solid state, even at temperatures as low as 1.5 K, in the GHz regime. This enables responsive, easily reorientable dipole arrays and exhibits cooperative net-dipole reorientation, a new generation of switchable ferroelectrics [1].
Gas capture and separation in porous materials relies on the challenging detection of associated adsorption heat, therefore, the development of a variable-pressure micro-calorimeter (DSC), allowing for high-sensitivity measurement of gas-solid interaction energy, was accomplished in collaboration with the L. Barbour group (Stellenbosch University, South Africa). This setup was implemented in our department by coupling a sorption analyser to a high-pressure micro-DSC for the simultaneous measurement of gas uptake and heat flow, providing direct adsorption enthalpies and positioning our laboratory among the few worldwide. The innovative instrumentation also enables cycling experiments to monitor the temporal evolution of pressure-driven crystal transformations of MOF frameworks. Furthermore, the direct quantification of gas

adsorption enthalpies, correlating energetic fingerprints with host–guest interactions and framework flexibility under dynamic pressure conditions, is crucial for real-world operation [2].
In situ X-ray diffraction and ss-NMR reveal structural transformations in response to external stimuli such as pressure, temperature, and gas uptake. High-quality structural resolution through Rietveld refinement is crucial for obtaining reliable crystallographic models, which enable quantitative structure–property correlations and insight into structural flexibility [3]. Additionally, periodic DFT calculations provide further molecular-level insights into these structural phenomena and identify preferred adsorption sites for gases such as CO_2, N2, H2O, Ar, Kr, Xe, and Rd, which are relevant to carbon-capture technologies and the capture of radioactive noble-gas nuclides. By utilizing isoreticular chemistry and structural tunability of MOFs, we developed high-Z MOF materials capable of concentrating low concentrations of radioactive noble-gas nuclides within their pores, thereby allowing for high-sensitivity detection of ^{85}Kr and ^{222}Rn gases. [4]
Integrating thermodynamic, structural, and spectroscopic insights, these works establish design strategies for MOFs where pore size, topology, and the physiochemical properties of the metal nodes and ligands govern function, enabling adaptive frameworks with tuneable performance across gas capture, sensing, and photonic technologies.

References:

[1] Perego, J.; Bezuidenhout, C. X.; Comotti, A. et al. Nat. Chem. 2020, 12, 845–851.
[2] Bezuidenhout, C. X.; Barbour, L. J. et al. J. Am. Chem. Soc. 2017, 139, 5923–5929.
[3] Perego, J.; Daolio A.; Bezuidenhout, C. X.; A. Comotti, et al. Angew. Chem. Int. Ed. 2024, 63, e202317094.
[4] Perego, J.; Bezuidenhout, C. X.; Monguzzi, A. et al. Nat. Commun. 2022, 13, 3504.