ESRF

Experiment title:

Revealing the structure of covalent organic frameworks featuring donor and acceptor Lewis sites with PXRD and PDF methods

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3

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Report: The aim of this project was to investigation the structural properties of porous functional polymers, namely Covalent Organic Frameworks (COF), that are capable of storage or separation of technically and environmentally important gases such as H_2, CH_4, C_2H_4, N_2, CO_2. These are 2D COFs derived from tris((4-dihydroxyboron)phenyl)phosphine (**BP-COFs**). The specific features of these materials relies in the presence of both Lewis acidic (boron) and basic (phosphorous) centers embedded in the polymeric framework.

BP-COFs display lower crystallinity with respect to related boron COF materials. Synchrotron radiation experiments revealed some short-range structure ordering. Based on obtained synchrotron PXRD data and Pair Distribution Function we proposed several structural models and compared the generated PXRD patterns to the experimental one. The best fit was obtained with a 3D structure resembling the topology of COF-105 and COF-108 obtained from condensation of tetrahedral precursors M(4-B(OH)2Ph)4 (M = C, Si) and HHTP as a trigonal linker. However, in **BP-COF** ¼ of connections are replaced by the lone electron pair of the phosphorus atom. This partially resembles the situation observed in COF materials reported by Dichtel and Bunck by co-condensation of tetrahedral C(4-B(OH)2Ph)4 and truncated CR(4-B(OH)2Ph)3 (R = n-C12H26, allyl). In our case, the structure is even more labile and supposedly vulnerable for catenation. In our model we proposed a 2-fold interpenetration level, where two neighboring networks are related by the inversion center. We note, however, the proposed model should properly describe only the short-range order in this material. It seems the structure is not strictly defined due to variable orientation of phosphorus centers leading to significant disorder and lack of well-defined long-range order.

In addition, **BP-COFs** are considered to be labile. Theoretical calculations at M062X/cc-pVTZlevel of theory revealed that BP-COFs exhibit some tendency for additional interconnections through the dative B…P bonds. The interaction energy is however rather low, thus this effect seems to be too weak to organize the material into the well-defined crystal samples. On the other hand it can be expected that Lewis base and acid centers would appear in the appropriate distance to invoke the local electric field effect, which could then enhance the interactions with guest molecules. The electrostatic potential maps plotted on electron density isosurfaces show strong electronegative regions around the phosphorus atoms, while the slightly positive regions appear above the planes of boronate groups. Due to rather low Lewis acidity of the boron atom, the expected binding effect is weak and unsymmetrical with respect to classical frustrated Lewis pairs (FLPs). It would be mostly dominated by the interaction with P(III) donor, and only supported by the interaction with boron atom. Indeed, the performed calculations on the host-guest systems confirms that the presence of boron and phosphorus centers supports binding of H_2, CH_4 and CO_2 molecules by the framework, but this effect is insufficient to promote heterolytic bond splitting. On the other hand it enhances reversible binding of small molecules. Indeed, sorption experiments show that obtained materials exhibit significant sorption of dihydrogen (100 cm^3g^{-1} at 1 bar at 77 K), methane (20 cm^3g^{-1} at 1 bar at 273 K) and carbon dioxide (50 cm^3g^{-1} at 1 bar at 273 K).

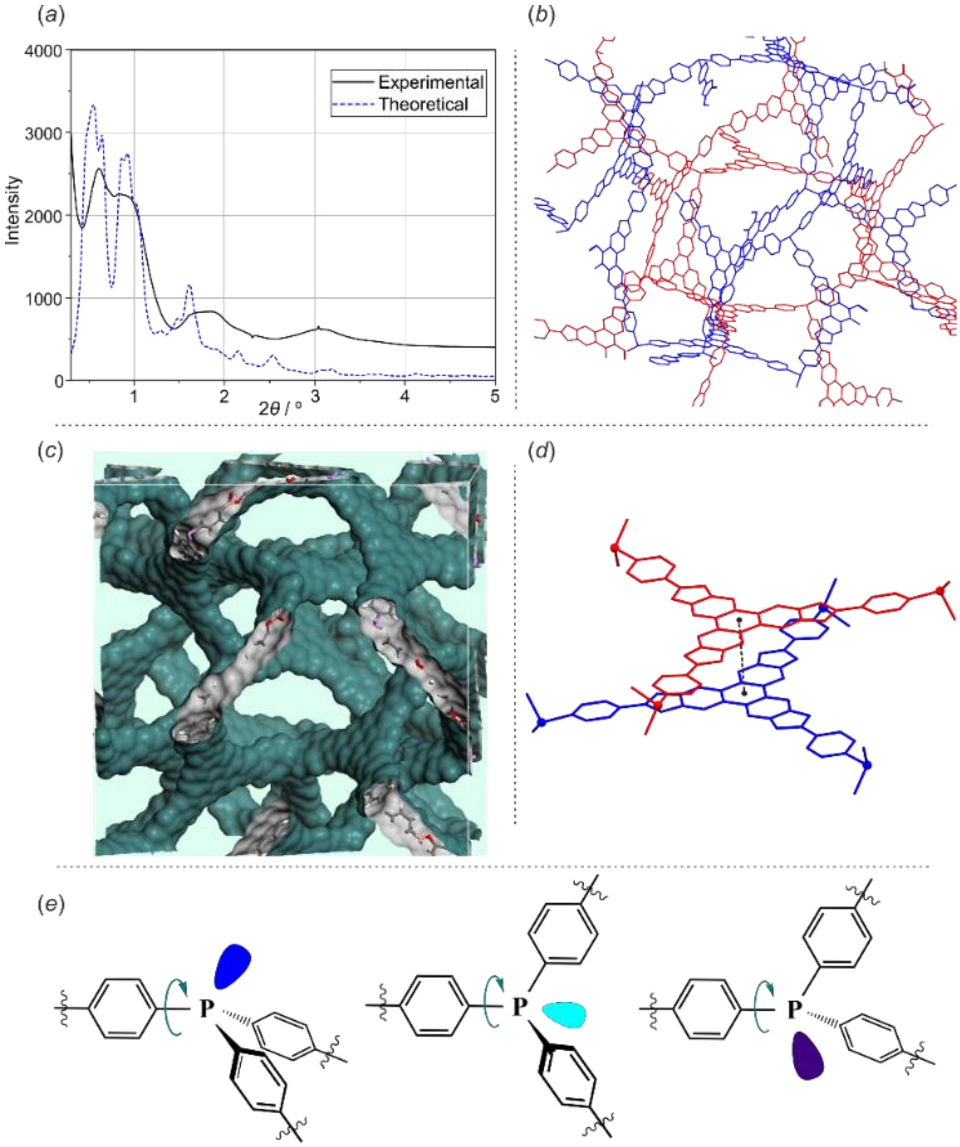

Figure 1. (*a*) Synchrotron-measured (black solid line) and simulated (blue dashed line) PXRD pattern of **BP-COF**. (*b*) Proposed structural model for the **BP-COF** material. (*c*) Connolly surface generated in the Mercury program; (*d*) two neighbored polymeric fragments are related by the symmetry center; (*e*) rotation around C-P bond as a source of structural disorder.

Obtained results were published:

P. Pacholak, K. Gontarczyk, R. Kamiński, K. Durka,* S. Luliński, "Boronate Covalent and Hybrid Organic Frameworks Featuring P(III) and P=O Lewis Base Sites", *Chemistry – A European Journal*, **2020**; 26, 12758-12768; DOI: doi.org/10.1002/chem.202001960; https://doi.org/10.1002/chem.202001960.