Ab initio study of a new class of covalent organic frameworks: RIO

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INTRODUCTION

Covalent organic frameworks (COFs) are an emerging class of porous crystalline polymers with a wide variety of applications, including gas storage, sensing, energy storage and carriers for drug. Usually, COFs are composed of light elements, such as: H, B, C, N, and O, which crystallize into periodic two-dimensional (2D) layers or threedimensional (3D) networks.

The interlayer interactions in 2D COFs can be attributed mainly to the weak van der Waals (vdW) forces. Consequently, 2D COFs can easily delaminate to single-layers, limiting their applications. Then, a chemically stable COF which combines permanent porosity and structural 3D ordering is highy desirable.

Here we report a new chemically stable COF, RIO-2, but due to its poor crystallinity, its srucuture is still unresolved.

In order to collaborate with this investigation, we perform *ab inito* calculations based on Density Functional Theory (DFT), for the structural and electronic properties of RIO-2. Geometrical analysis, including stacking sequence, interlayer distances, X-ray diffraction and Raman spectroscopy, were analyzed and presented.

METHODS

Calculations were performed with Quantum Espresso Code. To include weak vdW interactions, a semi-empirical dispersion terms (DFT-D) were included. The lattice dimensions were optimized simultaneously with the geometry.

RESULTS AND DISCUSSION

Based on experimental results, differents 2D structural configurations were modeled and analyzed. The optimal model system has 102 atoms and a lattice constant of a=b=19.57Å and c = 4.00Å.

Van der Waals interactions play a crucial role in determining the structure, stability and dictate the optimal stacking mode and the interlayer sliding corrugation of RIO-2.

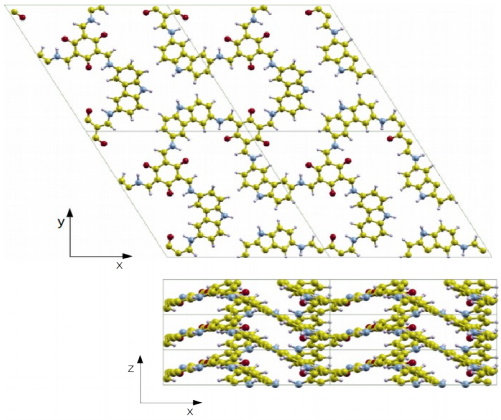

Figure 1.RIO-2 structure

Theoretical calculations indicate that RIO-2 behaves as a semiconductor, providing an additional advantage over its thiophene-based analogues, which are suggested to be insulators[1]. Due to its relatively small band gap (calculated as 1.56 eV), RIO-2 is a good candidate for optoelectronic devices.

CONCLUSIONS

Our calculations indicated that Rio-2 is a chemically stable material. Our results are in good agreement with experimental data.

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[1] Guillaume H. V. et. al.; Proceedings of the National Academy of Sciences, 13, 4923, (2013).