

2G03

共有結合性有機構造体の構造多様性の理論研究

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Theoretical analysis of structural diversity in covalent organic frameworks

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Covalent organic frameworks (COFs) are crystalline porous materials in which organic monomers are connected via covalent bonds. COFs have attracted many researchers because of their promising applications, such as gas storage and separation, catalysis, and optoelectronics, derived from their assembled framework structures and organic functional moieties. However, COFs often show low crystallinity, which prevents us from revealing the mechanisms

of their properties. On the other hand, theoretical analysis can provide their structures in atomic level relating to the functions. In this work, we theoretically investigated various structures of a double-stage 2-dimensional COF consisting of zinc 5, 10, 15, 20-tetrakis(4'-tetraphenylamino) porphyrin (ZnP), 2, 3, 9, 10, 16, 17, 23, 24-octahydroxyphthalocyaninato copper (II) (CuPc) and 4-formylphenylboronic acid (FPBA) and named CuPc-FPBA-ZnP, as shown in Fig. 1. The COF potentially shows a wide structural diversity caused by the connectivity and dynamics of the organic components resulting in the low crystallinity of COFs.

We used density functional tight binding (DFTB) method, which is an approximated fast method of density functional theory (DFT), to compare various monolayer and layered structures of the COF. First we focused on rotation of *p*-phenylene groups around ZnP in monolayer models. The energies of optimized rotational isomers distribute within a small range, which suggests that the local dynamics such as the rotation of the organic components has influence on the assembled framework structures and various isomers can be formed.

The variety of structures of the COF originates from not only the local conformations of linkers but also global structures such as layering manners. We optimized various layered structures, eclipsed (**E**), staggered (**SG**), serrated (**SR**), and inclined (**I**) for each rotational conformation. The most stable structure is **I** type (named **1**) with the largest stacking energy, 140.1 kcal/mol. However, the simulated powder X-ray diffraction (PXRD) pattern of **1** disagrees with the experimental one, as shown in Fig. 2. On the other hand, some simulated PXRD patterns of **E** and **SR** type structures agree with the experiment. We propose that the disagreement comes from the lack of thermal effects

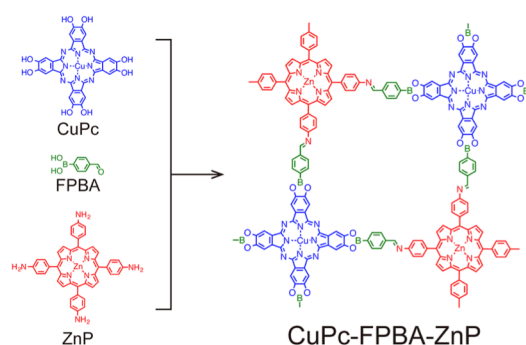


Figure 1. Schematic structures of monomers and CuPC-FPBA-ZnP.

in the geometry optimizations, and the thermal structural fluctuation can affect the layering manner. We focused on the effect of rotation of *p*-phenylene groups around ZnP on the assembled framework structures, comparing with monolayer structures.

To reveal the relationship between the rotational dynamics and the layering manners, we evaluated the rotational barrier of the *p*-phenylene group around ZnP depending on the rotational dihedral θ ($\theta = 0^\circ$ at the optimized **1**), as shown in Fig. 3a. The obtained rotational barriers were 12 kcal/mol in the monolayer model and 25 kcal/mol in the layered model, as shown in Fig. 3b. The larger energy barrier in the layered model makes the rotation of the *p*-phenylene group more difficult than in the monolayer model. In addition, the width of the dihedrals possessing lower energies, namely the dihedral range for vibrational rotation, is narrower in the layered model. The steric repulsion between the rotating groups and the adjacent layers causes the difference in the barriers, preventing the formation of the most stable crystal structure, furthermore the diversity of layered structures would arise.

In conclusion, we suppose that CuPc-FPBA-COF can have a wide structural variety based on the diversity of both local and global structures, and the thermal fluctuations such as rotation of *p*-phenylene groups may play some roles on the diversity of the framework. The structural diversity affected by the connectivity and the dynamics of the components is possibly one of the reasons of low crystallinity in COFs.

Reference

[1] X. Chen, M. Addicoat, E. Jin, H. Xu, T. Hayashi, F. Xu, N. Huang, S. Irle, D. Jiang, *Sci. Rep.* 5 (2015) 14650

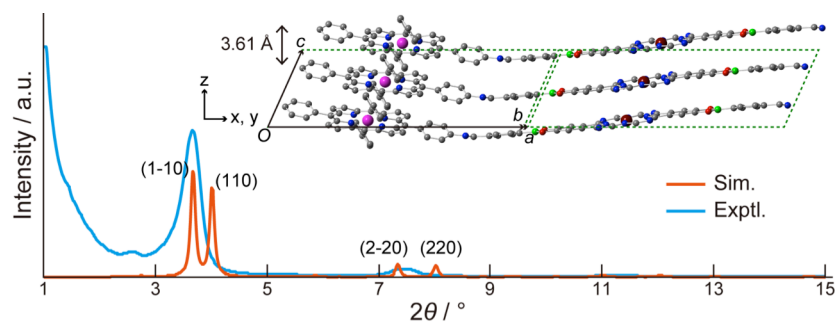


Figure 2. The experimental (light blue) and simulated (orange) XRD pattern and side view structure of **1**.

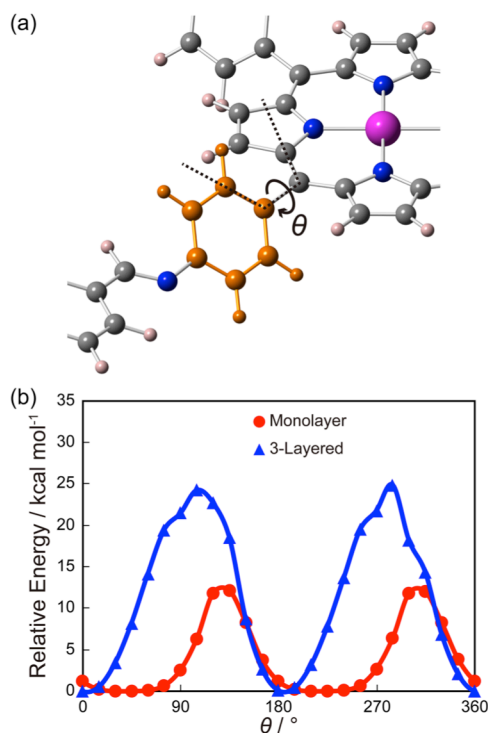


Figure 3. (a) Rotating *p*-phenylene group (orange) and rotational dihedral θ . (b) Potential energy curves of the *p*-phenylene group rotation in monolayer model (red) and 3-layered model (blue).