

Engineered Design of New Self-Assembled Organic Frameworks Based on Situ Generated Squaric Acid with Pyrazine and 44'-Bipyridine

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1. Introduction

Hydrogen-bonded organic frameworks (HOFs) synthesized by the self-assembly process of different organic ligands started to be used as porous materials only at the beginning of the 2000s. Hydrogen bonding connection is the most important supramolecular interaction in molecular recognition, which intrinsic characteristics such as weakness, flexibility and directional properties allow to synthesize HOFs with variable functionalities absolutely different from zeolites and metal-organic frameworks [1]. By choosing appropriate hydrogen acceptors and donors for forming stable intermolecular bonds, high porous HOFs' structure with pore size depending on the organic ligands length can be constructed [2].

Squaric acid or 3,4-dihydroxy-3-cyclobutene-1,2-dione is stable molecule non-carboxylic, organic acid the flat square shape, with proton donor and acceptor ability. Pyrazine and 44'-bipyridine with aromatic six-membered heterocyclic organic compound and two nitrogen atoms, which has additionally sp² hybridized C atoms with C-H hydrogen bond. Therefore, in this work we selected squaric acid with pyrazine (PSQ) and bipyridine (BSQ) to produce HOFs with different geometry structure and properties.

2. Experimental methods

2.1 Synthesis

All chemical reagents were used as received. Squaric acid and pyrazine (PSQ)/44'-bipyridine (BSQ) were dissolved in water in the molar ratio 1:3 by ultrasonification and heated up to 50 °C. The reaction mixture was slowly cool down to room temperature. The formed yellow cubic shape PSQ and yellow rod-shape BSQ crystals were filtered and washed with deionized water and dried at room temperature in air.

2.2 Single X-ray and Powder X-Ray Crystallography

The crystal structure was determined using standard crystallographic methods. X-ray intensity data sets were collected at 173 K on a Bruker Venture X-ray diffractometer with a graphite monochromatic Mo K α

radiation source ($\lambda = 0.71073 \text{ \AA}$), using a microloop with immersion oil. Absorption corrections were performed using the SAINT and SADABS programs [3,4]. Initial structure solutions were obtained with and SHELXL 2018/3 using direct methods. All calculations were performed using WinGX - 14 crystallographic software package [5]. All of the structures were checked for missing symmetry with the Addsym program implemented into PLATON software, and no higher symmetry was found. Molecular drawings were obtained using DIAMOND 4.0 (demonstrated version).

Powder X-ray data was obtained using a Bruker D8-Advance diffractometer using Cu K α radiation at an operating voltage of 40 kV and a current of 40 mA. The powder samples were prepared by grinding the crystals, were mounted on the sample holder, and measured in the 2 θ range of 10-80° with a step size of 0.02° and a step time of 0.1 s.

3. Results and Discussion

Based on single crystal X-ray diffraction data, PSQ crystallizes in the triclinic P-1 space group with cell parameters: $a=5.2142(6) \text{ \AA}$, $b=5.2927(6) \text{ \AA}$, $c=14.8169(17) \text{ \AA}$, $\alpha=92.758(4)^\circ$, $\beta=92.029(4)^\circ$ and $\gamma=101.915(5)^\circ$. BSQ crystallizes in the monoclinic P 1 21/n 1 space group with cell parameters: $a=3.8006(8) \text{ \AA}$, $b=11.1997(21) \text{ \AA}$, $c=27.5014(54) \text{ \AA}$ and $\beta=92.029(4)^\circ$.

Each asymmetric unit of PSQ consists of H₂SQ and pyrazine, notated as R₂². Each squaric acid molecule donates one H atom to the pyrazine N atom (Figure 1).

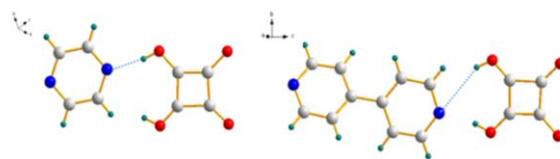


Figure 1. The asymmetric unit of PSQ (left) and BSQ (right).
Colour: N-blue, C-gray, O-red, H-green.

All bond lengths and angles in the PSQ showed no significant difference between the title compounds: pyrazine/44'-bipyridine and squaric acid. Crystallization in both structures occurs in a two-dimensional direction thus creating a space between the layers. Moreover, there are also weak van der Waals interactions between the planes, which are responsible for the presence of three-

dimensional structure. The layer distance between nearby O atoms from squaric acid in different layers equals 5.29 Å for PSQ and 3.80 Å for BSQ, which makes it very useful for trapping small molecules. The large size of the ligand and the nonlinear shape of the 44'-bipyridine leads to a decrease in the distance between the two layers in comparison with PSQ.

The experimental powder XRD patterns are in good agreement with the data collected using single - crystal patterns (Figure 2).

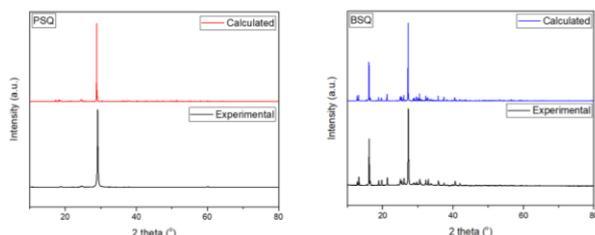


Figure 2. Experimental and calculated PXRD patterns of PSQ (left) and BSQ (right).

Conclusion

Two new HOFs were synthesized based on squaric acid with pyrazine and 44'-bipyridine and were measured by SC-XRD, PXRD, Raman and TGA. High quality PSQ and BSQ single crystals can be grown under simple conditions, not requiring high temperatures and pressures. The distances between the layers of HOFs are quite small and equal 5.29 Å and 3.80 Å for pyrazine and for 44'-bipyridine respectively. This feature can be used for small molecules trapping, such as gases. The applications of HOF have far-reaching implications and many advantages, including catalysis, fluorescence detection, gas storage and separation.

REFERENCES

- [1] Penghao Li, Matthew R. Ryder, and J. Fraser Stoddart. Hydrogen-Bonded Organic Frameworks: A Rising Class of Porous Molecular Materials. *Accounts of Materials Research* 2020 1 (1), 77-87. DOI: 10.1021/accountsmr.0c00019
- [2] Huang, Q., Li, W., Mao, Z. *et al.* An exceptionally flexible hydrogen-bonded organic framework with large-scale void regulation and adaptive guest accommodation abilities. *Nat Commun* **10**, 3074 (2019). <https://doi.org/10.1038/s41467-019-10575-5>
- [3] G.M. Sheldrick, SHELXS-97 - A Program for Automatic Solution of Crystal Structures, University of Goettingen, Goettingen, Germany, 1997.
- [4] Sheldrick, G. M. (2015). Crystal structure refinement with SHELXL. *Acta Crystallographica Section C Structural Chemistry*, 71(1), 3–8. <https://doi.org/10.1107/S2053229614024218>
- [5] Farrugia, L. J. (1999). WinGX suite for small-molecule single-crystal crystallography. *Journal of Applied Crystallography*, 32(4), 837–838. <https://doi.org/10.1107/S0021889899006020>