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Author(s)	Inokuma, Yasuhide; Matsumura, Kazuki; Yoshioka, Shota et al.
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Finding a New Crystalline Sponge from a Crystallographic Database

Yasuhide Inokuma,* Kazuki Matsumura, Shota Yoshioka, and Makoto Fujita*

Abstract: Empirical searching conditions were adopted to identify suitable candidates from the Cambridge Structural Database (CSD) for crystalline sponge hosts for X-ray crystallographic analysis of incoming guest compounds. After optimization of the solvent and soaking conditions, one of the candidates was used as a crystalline sponge for the structure determination of an aromatic guest.

Since the appearance of the crystalline sponge method,[1] porous single crystals, including metal–organic frameworks, porous coordination polymers, and porous organic crystals, have received considerable attention as potential crystalline sponge hosts for the single crystal X-ray analysis of non-crystalline and trace amounts of compounds.[2] However, only a limited number of porous crystals are known to serve as crystalline sponges, which can soak up and orient guest molecules inside their pores.[3] Moreover, there is not yet a well-established strategy for the design and synthesis of new crystalline sponge hosts. Considering the increasing number of porous crystals deposited in the Cambridge Structural Database (CSD),[4] it would not be surprising for a potential candidate for target-oriented crystalline sponges to be found in this database.[5] In this report, we demonstrate a semi-empirical database search to find new crystalline sponge candidates from the CSD. A new member of the crystalline sponge family was developed from these candidates by optimization of the solvent and guest uptake conditions.

For use as a crystalline sponge, the necessary features of a porous crystal are: (1) the pores are non-confined and large enough to accommodate target molecules from outside the crystal, and (2) guest exchange occurs in a single-crystal-to-single-crystal fashion. From a practical point of view, recent research[2] suggests that the following additional features are also preferred: (3) low-symmetry space groups to avoid trapping of guest molecules across symmetry planes or rotation axes, (4) relatively low porosity to ensure the stability of crystals on guest soaking, and (5) a flexible, interpenetrated host framework that can induce effective host–guest interactions as observed in the prototype crystalline sponge $[(ZnI_2)_3(tpt)_2]_n$ (**1**; tpt = tris(4-pyridyl)triazine).[3a] Among the five conditions listed above, (1), (3), (4), and (5) can be input into the searching conditions using ConQuest,[6] whereas condition (2) must be satisfied by experimental optimization.

In this work, our goal was to find a new crystalline sponge host with a larger pore diameter (>9.0 × 9.0 Å^2) than that of prototype sponge **1** (8 × 5 Å^2). To satisfy initial conditions (1)–(5), we adopted the following search criteria: (i) text search 'solvent' to find structures with solvent molecules or solvent-accessible voids (condition 1), (ii) monoclinic or triclinic crystal systems with Z ≤ 4 for low-symmetry structures (3), and (iii) text search 'catena' for interpenetrated structures (5). Because thousands of crystal structures met these conditions, we arbitrarily limited our search to (iv) porous Cu complexes composed of H, C, N, O, and Cu elements reported from 2010 to 2016 with R_1 ≤ 0.10 to give a reasonable number of candidates (189 hits) (Figure 1).

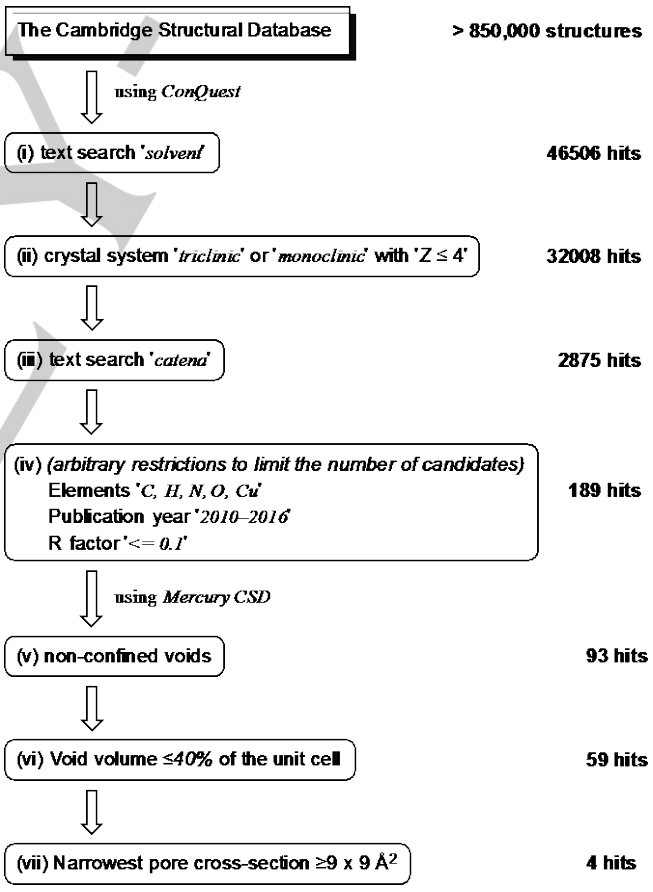

Figure 1. Flowchart for the search for crystalline sponge candidates.

The structures of the first candidates were visualized using Mercury CSD software[7] to determine whether the interstitial voids were confined or non-confined, and to calculate the proportion of void space in the unit cell. When the first candidates were refined with three further conditions: (v) non-confined voids, (vi) void volume ≤40% of the unit-cell volume calculated using a probe radius of 1.2 Å, and (vii) narrowest

[a] K. Matsumura, Dr. S. Yoshioka, Dr. Y. Inokuma. Prof. M. Fujita
Department of Applied Chemistry, School of Engineering
The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-8656 (Japan)
E-mail: mfujita@appchem.t.u-tokyo.ac.jp
inokuma@eng.hokudai.ac.jp
[b] Dr. Y. Inokuma
JST PRESTO, 4-8-1 Honcho, Kawaguchi, Saitama, 332-0012 (Japan)
[†] Current address: Division of Applied Chemistry, Faculty of Engineering
Hokkaido University
Kita 13, Nishi 8, Kita-ku, Sapporo, 060-8628 (Japan)

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cross-section of the pore ≥9 × 9 Å^2, four promising candidates[8] were obtained [see the Supporting Information (SI)].

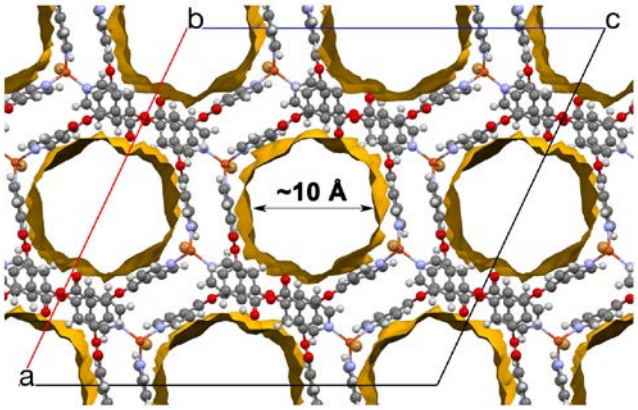

Figure 2. Network structure and pores of the crystalline sponge candidate $[CuBr(btt)]_n$ (**2**) viewed along the *b* axis.

Considering the synthetic accessibility and feasibility, we selected coordination network $[CuBr(btt)]_n$ (**2**; btt = benzene-1,3,5-triyl triisonicotinate), reported by Yang and co-workers,[9] as a crystalline sponge candidate to be studied for the optimization of the guest-soaking conditions (Figure 2). The interpenetrated framework of **2** contains one-dimensional cylindrical channels with a diameter of approximately 10 Å, which account for 40% of the unit cell volume (Figure 2).[10] We first conducted a solvent tolerance test using common organic solvents (cyclohexane, toluene, chloroform, CS_2, methanol, acetonitrile, and DMSO).

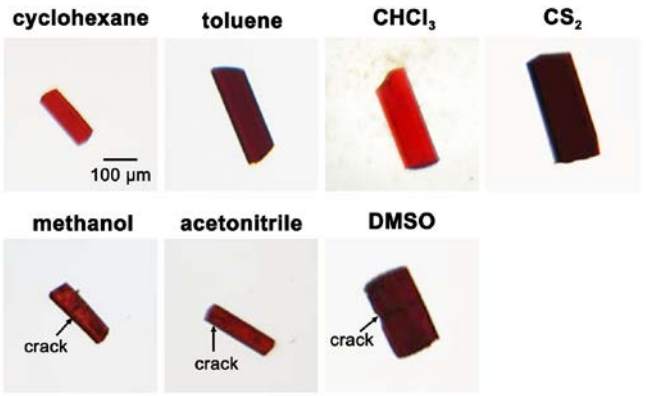

Figure 3. Microscope images of crystals of **2** soaked in test solvents at room temperature for 2 d. Crystals soaked in methanol, acetonitrile, and DMSO were damaged on soaking.

Coordination network **2** was synthesized from the btt ligand and CuBr in chloroform/acetonitrile according to the reported procedure[9] to give red rod-like crystals. As-synthesized crystals of **2** were soaked in each test solvent at room temperature for 2 d, and their crystallinity was checked using a microscope and X-ray diffraction. The crystallinity was preserved for crystals soaked in cyclohexane, toluene, chloroform, and CS_2, whereas those in methanol, acetonitrile, and DMSO were partially cracked after soaking and poorly diffracted X-rays (see the SI). For the former solvents, elemental analysis and extraction experiments using ^{1}H NMR spectroscopy indicated that the pore contents were almost completely replaced with the contacting solvent after soaking for 2 d. Thus, we next examined guest uptake using these solvents.

To demonstrate crystalline sponge analysis with host **2**, we selected 1-acetonaphthone (**3**), a liquid at room temperature, as a target guest because of its size and functional groups (aromatic π-plane, hydrogen-bond donor and acceptor). Because pore-embedded solvent molecules can sometimes block guest inclusion,[1b] we first conducted a contacting test to narrow down the most suitable solvent prior to the crystalline sponge analysis. Solvent-exchanged crystals **2** (*ca*. 1 mg) were directly contacted with guest **3** (50 μL) under neat conditions. The crystals were separated by filtration after 3 d, washed with the solvent originally contained in the crystals, and then digested by addition of ethylenediaminetetraacetic acid (EDTA). The ligand/guest ratios were then determined using ^{1}H NMR spectroscopy to be 1:0.92, 1:1.02, 1:1.80, and 1:0.94 for chloroform, cyclohexane, CS_2, and toluene, respectively. This result indicates that guest exchange from CS_2 to 1-acetonaphthone (**3**) is the most efficient among the four solvents that were compatible with the crystal.

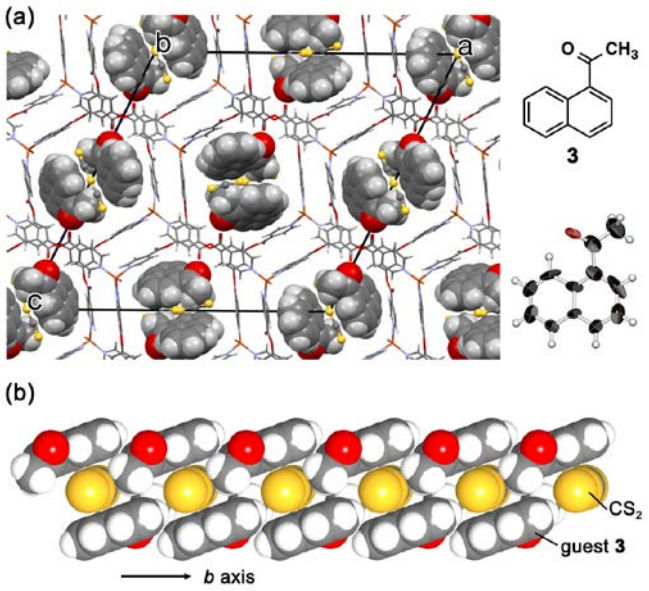

Figure 4. (a) Crystal structure of inclusion complex **3•2** (left: packing structure viewed along the *b* axis; guest **3**, solvent CS_2, and host **2** are drawn as CPK, ball-and-stick, and stick models, respectively; right: ORTEP drawing of guest **3** with 50% thermal ellipsoids). (b) Double-line arrangement of guests **3** with CS_2 molecules inside the 1D channel of host **2**.

After examination of several soaking conditions, a high-quality inclusion crystal of **2•3** was prepared by soaking a tiny CS_2-exchanged crystal of **2** (0.20 × 0.14 × 0.09 mm^3) in a 2.2 M solution of guest **3** in CS_2 (40 μL) over 3 d at room temperature. Single crystal X-ray analysis clearly showed that molecules of guest **3** were trapped in the 1D channel of host **2** (Figure 4), forming two columns along the *b*-axis.[11] Although the space group changed from *P*2/*n* (reported by Yang *et al.*)[9] to $P2_1/c$ upon guest inclusion, the network structure of host **2** was essentially the same as its as-synthesized form. The carbonyl group of guest **3** was doubly hydrogen-bonded by two C_{arom}–H

protons of host **2**, which resulted in a slightly non-planar conformation of **3** (the dihedral angles between the aromatic ring and the acetyl group were 30.7(4)º and 38.8(4)º for the two crystallographically inequivalent molecules of guest **3**).

Importantly, the solvent CS_2 molecules play a crucial role in filling the void space between the channel wall and the guest columns. Presumably, such tight packing in the channel is necessary to achieve high uptake and appropriate orientation of the guests. In fact, when we analyzed an inclusion crystal of **2•3** prepared from cyclohexane solution, structural determination was unsuccessful owing to the serious disorder of the guests and solvents.

In summary, our results strongly indicate that there are a large number of crystalline sponge candidates in the CSD that could be used to analyze the structures of compounds of interest. Although hundreds of candidates can be found quickly by adopting semi-empirical searching conditions based on the size of the target compound, the as-synthesized porous crystals do not always behave as good hosts without optimization of the soaking conditions. Therefore, pre-optimization of solvents and guest-soaking conditions are of great importance for successful structure analysis. We believe that our database search strategy will expand the repertoire of crystalline sponge hosts, and thus extend the scope of structural analysis available using the crystalline sponge method.

Experimental Section

Solvent exchange of host crystals of 2 with CS_2

Host crystals of **2** were synthesized in test tubes on a 20-mg scale in chloroform/acetonitrile according to the reported procedure.[9] After the mother liquor was removed by decantation, the crystals were washed by addition and decantation of CS_2 (5 × 5 mL). The crystals were then soaked in fresh CS_2 (10 mL) in a test tube for 2 d at room temperature. For X-ray diffraction analysis, crystals of **2** were kept in CS_2 solvent until they were mounted onto the X-ray diffractometer. For elemental and IR analyses, the crystals were filtered and air-dried on a funnel for 10 min before use.

Microscopic IR (single crystal, mineral oil): $\tilde{\nu}$ = 2924, 2853, 2361, 2158 (CS_2) 1736, 1601, 1489, 1458, 1248, 1204, 1169, 1138, 1055, 1012, 964, 874, 845, and 824 cm^{-1}. Elemental analysis: calcd (%) for $[CuBr(C_{24}H_{15}N_3O_6)•2.8(CS_2)]_n$: C 40.34, H 1.89, N 5.27; found: C 40.40, H 2.07, N 5.37.

Crystalline sponge analysis of 1-acetonaphthone 3

A CS_2-soaked crystal of **2** (0.20 × 0.14 × 0.09 mm^3) was placed in a microvial[1b] with 30 µL of CS_2 using a micropipette. After addition of 1-acetonaphthone (**3**) (10 µL), the vial was sealed with a screw cap. The cap was pierced with a needle (hole diameter: 0.80 mm), and the vial was allowed to stand at room temperature for 3 d. The resulting crystal was then taken from the vial using a cryoloop and cryoprotectant (paratone oil) and subjected to single crystal X-ray and microscopic IR analyses.

Microscopic IR of inclusion crystal **2•3** (single crystal, mineral oil): $\tilde{\nu}$ = 2925, 2864, 2359, 2164 (CS_2), 2104, 1748, 1671 (C=O in guest **3**), 1602, 1506, 1461, 1377, 1315, 1233, 1199, 1168, 1138, 1053, 1013, 966, 875, and 847 cm^{-1}.

Acknowledgements

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Keywords: Porous Materials • Host-Guest Chemistry • Crystallography • Database Search

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[10] The pores of **2** was visualized using Mercury CSD program with probe radius of 1.2 Å. In reference [9], the size of the effective channels and potential solvent-accessible voids (by PLATON) have been calculated to be 10 × 10 $Å^2$ and 40%, respectively.

[11] Crystallographic data for inclusion complex **2•3**: $[(C_{24}H_{15}N_3O_6)_2(CuBr)_2]•1.795(C_{12}H_{10}O)•1.147(CS_2)$, M = 1562.53,

crystal size: 0.20 × 0.14 × 0.09 mm^3, Monoclinic, space group $P2_1/c$, a = 32.249(6) Å, b = 7.770(2) Å, c = 30.641(6) Å, β = 116.03(3)°, V = 6899(3) $Å^3$, Z = 4, D_c = 1.504 g/cm^3, T = 93(2) K, 2.108° < θ < 27.291°, 13152 unique reflections out of 35147 with $I > 2\sigma(I)$, GoF = 1.066, final R factors R_1 = 0.0529, and wR_2= 0.1818 for all data. CCDC 1511768 contains the supplementary crystallographic data.

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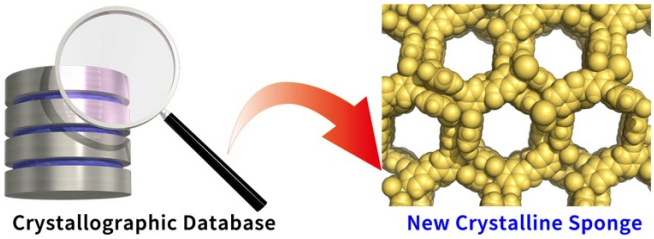

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Finding a New Crystalline Sponge from a Crystallographic Database

Promising candidates for new crystalline sponges for analysis of the structures of non-crystalline compounds by X-ray diffraction were selected from a crystallographic database using semi-empirical searching conditions. After optimization of the guest-soaking conditions, a new crystalline sponge with large one-dimensional channels was discovered.

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