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# Targeted Synthesis of a Zeolite with Pre-Established Framework Topology

Donghui Jo and Suk Bong Hong*

**Abstract:** Given their great potential as new industrial catalysts and adsorbents, the search for unprecedented zeolite structures is of major importance in nanoporous materials chemistry. However, although an innumerable number of theoretical frameworks have been proposed, none of them have been synthesized by a priori design yet. Here, we have generated a library of diazolium-based cations inspired from the organic structure-directing agents (OSDAs) recently reported to give two structurally related zeolites PST-21 and PST-22 under highly concentrated excess fluoride conditions and compared the stabilization energies of each OSDA cation in ten pre-established hypothetical structures. A combination of the ability of the OSDA selected in this way with the excess fluoride approach has allowed us to crystallize PST-30, the targeted aluminosilicate zeolite structure. We anticipate that our scheme, which aims to rationally couple the ability of computationally predicted OSDAs into an experimental setup, will take a step forward in the synthesis of hypothetical zeolites with desired properties.

Owing to their outstanding shape- and surface-selective properties, zeolites and molecular sieves are finding commercial applications in catalysis and separation.[1] While about 250 distinct framework types are now recognized,[2] a combination of theory and experiment suggests that the number of chemically feasible hypothetical structures is practically inexhaustible.[3] Although many innovative synthetic concepts, such as organic structure-directing agent (OSDA) design, charge density match/mismatch, Ge introduction in OSDA-mediated zeolite synthesis and assembly-disassembly-organization-reassembly, have been developed,[4] the discovery of new zeolite structures is mostly achieved by trial and error. The synthesis of materials with known framework topologies, e.g., DAF-5 (framework type CHA), HPM-1 (STW), SSZ-39 (AEI), SSZ-52 (SFW), etc., can be accomplished using computationally predicted OSDAs.[5] However, no attempt has yet been made to synthesize a hypothetical zeolite structure a priori.

Under the so-called excess fluoride conditions where the F$^-$ concentration in zeolite synthesis mixtures is higher than that of the OSDA, we have recently synthesized PST-21 (PWO) and PST-22 (PWW), two novel high-silica (Si/Al ~ 10) zeolites, using 1,2,3-trimethylimidazolium (123TMI$^+$) and 1,3,4-trimethylimidazolium (134TMI$^+$) or 1,2,3,4-tetramethylimidazolium (1234TMI$^+$) ions as OSDA, respectively.[6] As-made PST-21 and PST-22 were both characterized to possess one OSDA molecule on average per the 18-hedral cavity, being either the *t-pwo* ($[4^6.5^8.9^4]$) or *t-pww* ($[4^6.5^8.8^2.10^2]$) unit (Figure S1). Their structures can be constructed exclusively from *bre* ($[4^2.5^4]$) units by linking the corners of this small building unit by edges. Thus, by definition,[2] the *bre* unit is a secondary building unit (SBU) of PST-21 and PST-22. This stimulated us to generate ten chemically feasible hypothetical zeolite structures constructed from the same SBU (Figure S1).[6a,7]

Considering the SBU as a vertex, on the other hand, all derived theoretical frameworks have the same net topology (primitive cubic; **pcu**)[8] as that of PST-21 and PST-22 (Figure 1a,b and Table S1). Consequently, most of them have only one type of '18-hedral' natural building units[9] (NBUs) surrounded by eight *bre* units. We therefore thought that organic compounds with similar sizes and shapes compared to the experimentally validated OSDAs in the synthesis of PST-21 and PST-22 would direct the formation of cavities towards the predicted hypothetical frameworks. Here we report the synthesis of one of ten hypothetical zeolites proposed in our recent study.[6a] The successful design of this new zeolite, denoted PST-30, arose from our insights into structural relationships between the existing PST-21 and PST-22 and the hypothetical structures, combined with energy calculations of intrazeolitic OSDA stabilization. This led us to rationally identify a suitable organic cation for the targeted framework.

We first carried out stabilization energy calculations[10] for five methyl-substituted imidazolium derivatives in PST-21, PST-22, and ten hypothetical frameworks based on the *bre* unit as SBU (Figure S2 and Table S2). It was calculated that 123TMI$^+$ has a stabilization energy of -13.7 kJ (mol Si)$^{-1}$ in PST-21, whereas 134TMI$^+$ and 1234TMI$^+$ provide energies of -13.4 and -13.8 kJ (mol Si)$^{-1}$ in PST-22, respectively. Thus, we set -13.0 kJ (mol Si)$^{-1}$ as a threshold energy to assess whether a particular OSDA could play a structure-directing role in formation of a targeted structure. We also calculated the stabilization energies of a series of methylated pyrazolium cations with two adjacent nitrogen atoms in the aromatic ring, given the structural similarity between these diazolium species (Figure S2 and Table S2). Among them, the 1,2,3-trimethylpyrazolium (123TMP$^+$), 1,2,4-trimethylpyrazolium (124TMP$^+$), and 1,2,3,5-tetramethylpyrazolium (1235TMP$^+$) ions, with geometric shapes and sizes similar to those of 123TMI$^+$, 134TMI$^+$, and 1234TMI$^+$, respectively, gave stabilization energies less than -13.0 kJ (mol Si)$^{-1}$ not only in PST-21 and PST-22 but also in some hypothetical structures like C1_L1_1.

To minimize the effects of inorganic synthesis parameters, we performed zeolite synthesis using the above-mentioned three pyrazolium-based OSDAs under the same conditions as those of PST-21 and PST-22 syntheses (Table S3).[6a] While no hypothetical zeolites were found, PST-21, ferrierite (FER), and PST-22 were obtained using 123TMP$^+$, 124TMP$^+$, and 1235TMP$^+$ as OSDA, respectively. It is worth noting that 124TMP$^+$, despite its similarity to 134TMI$^+$, produced ferrierite instead of PST-22, demonstrating a non-negligible effect of differences in the charge distribution of OSDAs on the synthesis product.[11]

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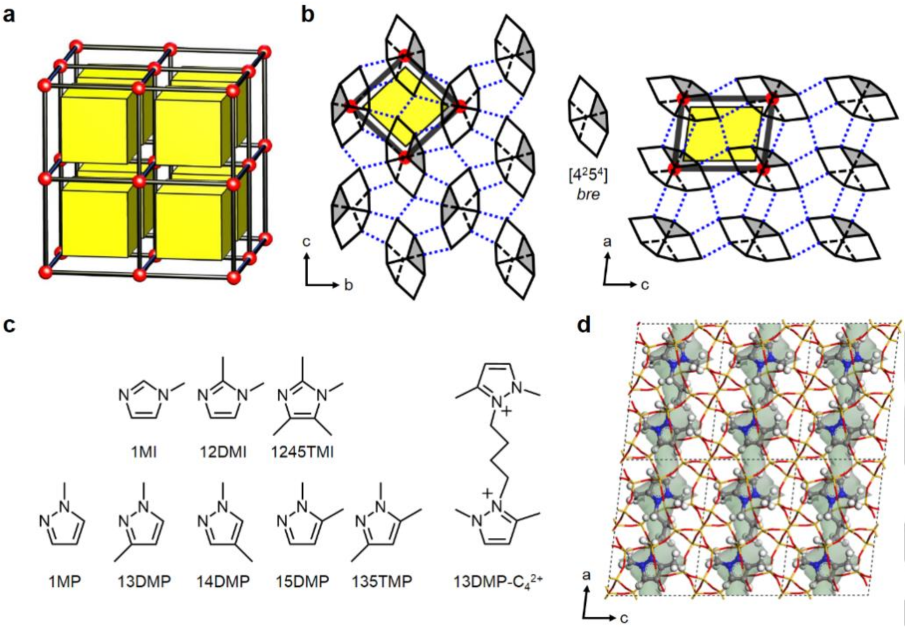

***Figure 1.*** Zeolite structures built from the *bre* unit as SBU and OSDAs used for their synthesis. a) **pcu** net topology. Vertices, red; edges, black; tiling, yellow. b) PST-21 (left) and BRE_L1_1 (right) structures with the **pcu** net of *bre* ([$4^2.5^4$]) units. The bridging O atoms have been omitted for clarity, and the bonds interconnecting *bre* units are represented by blue dotted lines. c) Eight quaternizable methyl-substituted diazole molecules (left) and 13DMP-$C_4^{2+}$ (right), one of the 32 candidate OSDAs obtained by combining two diazoles and one methylene chain. d) Energy minimized-conformation of 13DMP-$C_4^{2+}$ in the BRE_L1_1 structure. C, grey; N, blue; H, white; Si, yellow; O, red. The regions marked in translucent green indicate the accessible surfaces calculated using a solvent radius of 1.4 Å.

We then moved our attention to diquaternary OSDAs, built from methylated diazolium moieties connected by methylene chains with different lengths, in a manner similar to Camblor and other groups who extended the OSDAs for zeolite syntheses from monoquaternary imidazolium ions to diquaternary analogs.[5b,12] It was reasoned that their diazolium rings could still organize the **pcu** net of *bre* units, whereas the central methylene chain could arrange a 10-ring window connecting neighboring cavities. We established a library of a total of 32 diquaternary candidate OSDAs by combining eight representative methyl-substituted diazole molecules and methylene linkers and calculated their stabilization energies not only in PST-21 and PST-22 but also in ten hypothetical structures (Figures 1c,d and 2 and Table S4). Here, when combining the same two diazoles and a methylene chain, we designated the resulting diquaternary OSDA as 'diazole acronym-$C_n^{2+}$' (*n*: methylene chain length, 3-6; Figure 1c). Seven members of this library were calculated to have stabilization energies below -13.0 kJ (mol Si)$^{-1}$ in at least one hypothetical structure. For example, while 13DMP-$C_4^{2+}$ gives a stabilization energy of -13.6 kJ (mol Si)$^{-1}$ in BRE_L1_1, the other six OSDAs (i.e., 1MP-$C_4^{2+}$, 1MP-$C_5^{2+}$, 1MP-$C_6^{2+}$, 14DMP-$C_4^{2+}$, 15DMP-$C_4^{2+}$, and 12DMI-$C_4^{2+}$) are characterized by energies ranging from -13.0 to -14.3 kJ (mol Si)$^{-1}$ in PST-21_H1.

It is remarkable that among the latter six OSDAs described above, all of them, except 1MP-$C_6^{2+}$, experimentally produced PST-22 rather than PST-21_H1, in which all the OSDAs display more favorable stabilization energies (Figure 2 and Tables S4 and S5). This indicates that the framework energy[13] of targeted hypothetical structures can affect the phase selectivity of the crystallization (14.8 (PST-22) vs. 17.7 (PST-21_H1) kJ (mol Si)$^{-1}$; Table S6). More interestingly, we found that 13DMP-$C_4^{2+}$, i.e., 1,1'-(1,4-butanediyl)bis(2,5-dimethyl-1H-pyrazol-2-ium), with a molecular shape very difficult to mimic using an imidazolium-like nitrogen distribution, crystalizes the targeted structure BRE_L1_1 (PST-30), as computationally predicted (Table S5 and Figure S3), although the HF/OSDA$^{2+}$ and Si/Al ratios in the synthesis mixture leading to the successful formation of PST-30 are very narrow (ca. 4 and 10, respectively), similar to the case of PST-21 and PST-22 (Table S7).

The successful synthesis of the hypothetical BRE_L1_1 structure can be demonstrated by comparing its simulated powder X-ray diffraction (XRD) pattern with the powder XRD pattern of the proton form (H-PST-30) of PST-30 and was further confirmed by Rietveld analysis (Figure 3a,b and Tables S8-S10). The integrity and stability of PST-30 were verified by scanning electron microscopy (SEM), $N_2$ adsorption, and $^{27}$Al and $^{29}$Si MAS NMR (Figures 3a, S4, and S5). While $^{1}$H-$^{13}$C CP MAS NMR indicates that 13DMP-$C_4^{2+}$ in as-made PST-30 remains intact, its $^{19}$F MAS NMR spectrum is characterized by a prominent resonance at -128 ppm (Figure 3c,d). This resonance can be attributed to the free F$^-$ ions within the PST-30 channels and/or the anions in fluorosilicate species, where Si is hexacoordinated, but not to the F$^-$ ions occluded in a small cage.[12f] A combination of elemental, thermal, and $^{19}$F MAS NMR analyses on as-made PST-30 gave a unit cell composition of $|(\text{13DMP-C}_4^{2+})_{0.5}\text{F}^-_{0.2}(\text{H}_2\text{O})_{0.4}|[\text{Al}_{0.8}\text{Si}_{9.2}\text{O}_{20}]$ (Figures 3d and S3). This indicates that each 18-hedral cavity is occupied by one pyrazolium moiety of 13DMP-$C_4^{2+}$, as assumed in the computational screening analysis of the OSDA library (Figure 1d).

The PST-30 structure is built by stacking the *bre_L1* layer, a hypothetical layer proposed in our recent paper,[6a] along the *b* axis, without imposing any interlayer symmetry operation (Figure 1b). This layer is made up of a building chain nonjointly connecting *bre* units, denoted *bre* chain, which can be obtained by deconstructing the layer in the BRE structure. Consequently, PST-30 has a two-dimensional (2D) pore system consisting of 10-ring (4.7 × 6.7 Å) channels interconnected by 8-ring (4.2 × 4.4 Å) channels, which comprises unprecedented [$4^6.5^8.8^2.10^2$] cavities (Figures 3e and S1). The framework density (defined as the number of tetrahedral atoms per 1000 Å$^3$) of PST-30 was calculated to be 17.1, which is essentially the same as the values (17.1 and 17.2, respectively) of PST-21 and PST-22. The *n*-hexane/3-methylpentane cracking test reveals that H-PST-30 has a constraint index of 9.0, which is within the range for medium-pore zeolites (Figure S6).[14] It should be noted that H-PST-30 shows a comparable isobutene yield compared to H-ferrierite, one of the best 1-butene skeletal isomerization catalysts (Figure S7),[15] probably due to the similarity in their pore architecture.

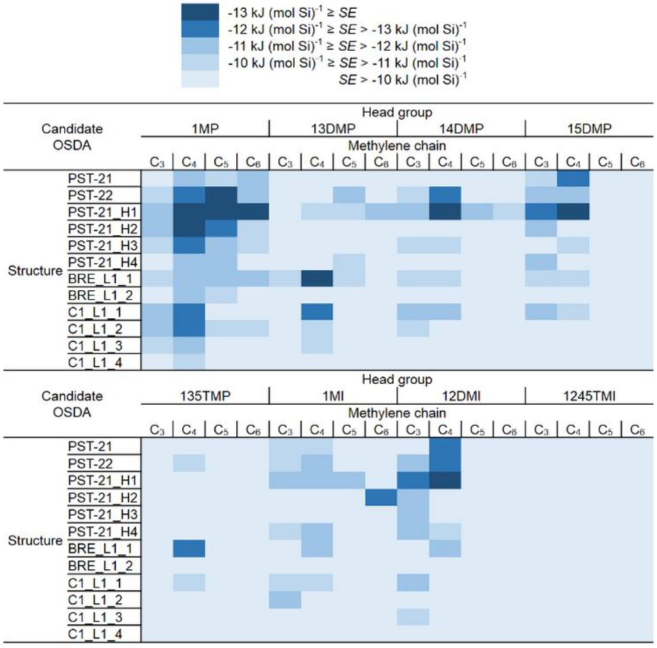

*Figure 2.* Stabilization energies (*SEs*) of a total of 32 candidate OSDAs in PST-21, PST-22, and ten hypothetical structures. Each OSDA consists of methyl-substituted diazole moieties connected by methylene chains with 3-6 carbon atoms.

We also carried out powder XRD and Rietveld analysis on as-made PST-30, as well as as-made PST-21 and PST-22 synthesized using 123TMI$^+$ and 1234TMI$^+$, respectively, to determine the OSDA locations in each zeolite. (Figure S8 and Tables S11-S14). All diazolium rings in OSDAs were found to be located around the center of 18-hedral cavities, which is in excellent agreement not only with the positive difference electron density maps after initial scaling [16] (Figure S9), but also with the theoretically calculated OSDA locations (Figures S10-S12). This again illustrates the usefulness of the computational method in the search for a suitable OSDA to direct the synthesis of a given pre-established zeolite framework.

Finally, we note that most of the zeolites including our PST-30, which have been synthesized using computationally predicted OSDAs, possess only one type of NBU cavities with occluded OSDA molecules (Table S15). In addition to these zeolite structures, there are at least another 16 framework types having such a type of large cages when the number of types of NBUs present is limited for simplicity to three or lower (Table S16). Thus, once there are hypothetical zeolites that are structurally related to the above zeolites, the scheme described here, which integrates the known synthesis information into the computer-aided design of synthesis experiments, may be a possible way to synthesize such theoretical frameworks.

In conclusion, the targeted synthesis of a specified hypothetical structure was found to be possible when the structure-directing ability of the organic additives computationally predicted to give this targeted structure is suitably combined with the experimental insights obtained from the synthesis of existing zeolites. BRE_L1_1 is a pre-established theoretical framework, which contains a 2D medium-pore system with intersecting 10- and 8-ring channels, and its synthesis has been achieved by the use of an OSDA with the largest calculated stabilization energy in the corresponding framework under excess fluoride conditions. We believe that our integrated approach can be extended to the synthesis of other hypothetical structures. To make it possible to routinely crystallize hypothetical zeolites with desired pore structures, however, it is necessary to better understand the effects of inorganic synthesis parameters, most notably the concentration of water and hydroxide or fluoride anions and the type of alkali metal cations and heteroatoms other than Si in zeolite synthesis mixtures, on the product selectivity.[6b]

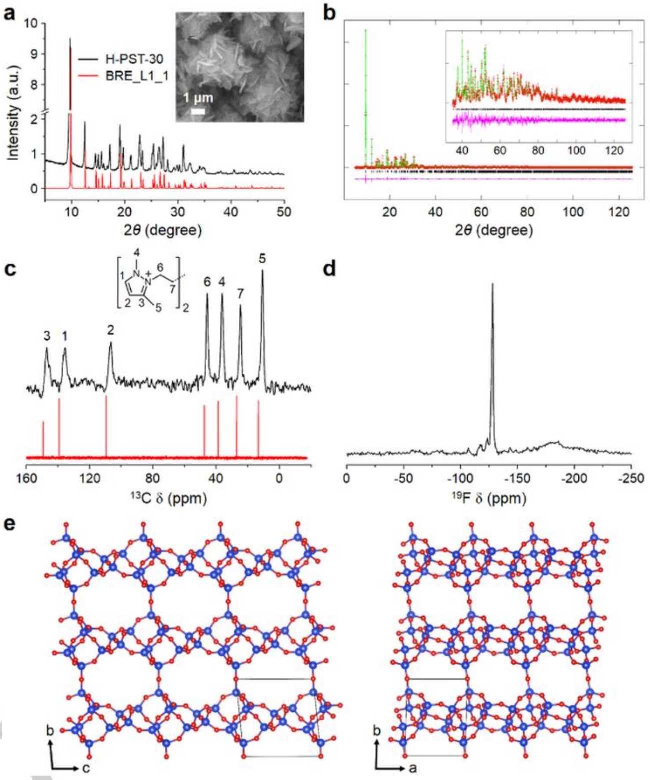

*Figure 3.* a) Experimental and simulated (λ = 1.541874 Å) XRD patterns of H-PST-30 and BRE_L1_1, respectively, and SEM image (inset) of as-made PST-30 synthesized using 13DMP-$C_4^{2+}$ as an OSDA. b) Rietveld plot of H-PST-30 (λ = 1.5167 Å): observed data (+), calculated fit (solid line), and difference plot (lower trace). The tick marks represent the positions of allowed reflections. c) $^1$H-$^{13}$C CP and d) $^{19}$F MAS NMR spectra of as-made PST-30. The solution $^{13}$C NMR spectrum of the dibromide salt of 13DMP-$C_4^{2+}$ in $D_2O$ (red) is given for comparison. e) The H-PST-30 structure with 10-ring and 8-ring channels viewed along the *a* (left) and *c* (right) axes. Si, blue; O, red.

## Experimental Section

The details of the computational methods, experimental procedures, characterization, and structural analysis are provided in the Supporting Information. CCDC 1919622–1919625 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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## Conflict of interests

The authors declare no conflict of interest.

**Keywords:** aluminosilicates • excess fluoride approach • hypothetical zeolites • microporous materials • targeted synthesis

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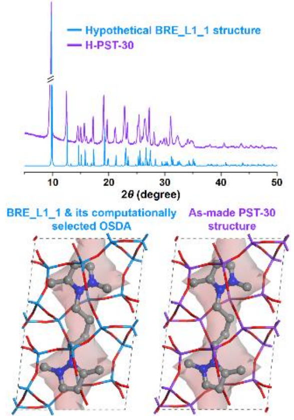
## COMMUNICATION

**Synthesis of a hypothetical structure**: A targeted hypothetical zeolite structure has been successfully synthesized by combining theoretical results with experimental insights.



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