Zeolite Structures

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Criteria for Zeolite Frameworks Realizable for Target Synthesis**

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Zeolites containing well-defined pores in molecular dimensions have important industrial applications in the fields of catalysis, adsorption, and ion exchange.[1,2] The primary building unit of a zeolite framework is the TO_4 tetrahedron (T is usually Si, Al, or P), which is linked to four neighbors by bridging O atoms to form various strictly four-connected frameworks. To date, over 200 distinct zeolite frameworks have been discovered or synthesized,[3] and the pursuit of novel zeolites will never stop because of their important industrial applications. In particular, the function-orientated synthesis of zeolites with desired structures has become a challenging goal.[4,5] Since the 1970s, millions of hypothetical zeolite frameworks have been predicted.[6–22] Considering the very limited number of zeolites discovered in real life, one might wonder if such a tremendous number of hypothetical zeolites are really chemically feasible synthetic targets. A prerequisite for evaluating the feasibility of hypothetical zeolites is to unravel the underlying distinguishing structural features shared by all existing zeolites. Considerable efforts have been made to this end.[12,19,20,23–39] Low framework energy seemed to be the global feature that enabled the synthesis of most open-framework compounds. It explained very well the existence of conventional zeolites consisting of Al, Si, and P as the main T elements. Furthermore, a linear relationship between the framework energy (E, calculated as silica polymorphs) and the framework density (FD, defined as the number of T atoms per 1000 Å^3) was discovered for conventional zeolites.[23,24,40,41] However, with the emergence of many high-energy zeolites, especially unconventional zeolites containing T elements other than Al, Si, and P, the energy criterion has been found to not always be reliable.[30,42] Figure S1 in the Supporting Information shows the plot of E versus FD for the 200 existing zeolite frameworks, which have been optimized as silica polymorphs (see the Experimental Section). Many unconventional zeolites significantly deviate from the regression line derived from the conventional zeolites. In 2006, Thorpe and co-workers found that many existing zeolite frameworks showed a "flexibility window" over a range of densities,[32] but soon afterwards they found that several zeolites that already existed violated this criterion.[36,38,39] Up to now, there is no criterion that could universally explain the feasibility of all existing zeolites without exception.

In contrast to all previous attempts, we focused in this study on the local interatomic distances (LIDs) in four-connected zeolite frameworks; these LIDs reflect the geometries of TO_4 tetrahedra and their local linkages. We discovered that the LIDs in all existing zeolites strictly obey several rules without exception, and thus represent certain intrinsic structural features of realizable zeolites. When these features are used as new structure-evaluation criteria, the most promising synthetic candidates can be selected from the huge pool of hypothetical zeolites. This approach thus provides a valuable shortcut to future target synthesis.

In this study, we optimized all existing zeolite frameworks as silica polymorphs regardless of their true composition (see the Experimental Section). Three types of LIDs were calculated after framework optimization: T−O, O−T−O, and T−O−T distances (designated D_{TO}, D_{OO}, and D_{TT}, respectively). We found that the average LIDs (designated $\langle D_{TO}\rangle$, $\langle D_{OO}\rangle$, and $\langle D_{TT}\rangle$, respectively) in existing zeolites do not vary much ($\langle D_{TO}\rangle = 1.5967$–$1.6284$ Å; $\langle D_{OO}\rangle = 2.6071$–$2.6588$ Å; $\langle D_{TT}\rangle = 2.9435$–$3.0998$ Å; see Table S1 in the Supporting Information). More significantly, we found that the average LIDs are highly linearly correlated. Figure 1a shows the correlation between $\langle D_{TO}\rangle$ and $\langle D_{OO}\rangle$ found in 200 existing zeolites. The Pearson correlation coefficient is 0.9998, which indicates that $\langle D_{TO}\rangle$ and $\langle D_{OO}\rangle$ are highly positively correlated. The regression line has the formula $\langle D_{OO}\rangle = 1.6284 \times \langle D_{TO}\rangle + 0.0071$. The vertical deviation from this line can be calculated for each zeolite: $\varepsilon_{\langle OO\rangle} = |\langle D_{OO}\rangle - 1.6284 \times \langle D_{TO}\rangle - 0.0071|$. All existing zeolites have very small deviations, among which the largest is 0.0009 Å for the zeolite framework SOS. The smallest and the largest ratios of $\langle D_{OO}\rangle/\langle D_{TO}\rangle$ are 1.6321 and 1.6330, which correspond to average O-T-O angles of 109.39 and 109.47°, respectively. This result implies that the "average" TO_4 tetrahedron in each existing zeolite has to be close to an ideal tetrahedron. The deviation from the ideal tetrahedron is determined by $\varepsilon_{\langle OO\rangle}$, which has to be very small for each existing zeolite ($\varepsilon_{\langle OO\rangle} \leq 0.0009$ Å). This feature is our first LID criterion derived from all existing zeolites (criterion 1).

Figure 1b shows the correlation between $\langle D_{TO}\rangle$ and $\langle D_{TT}\rangle$ found in 200 existing zeolites. Strikingly, the Pearson correlation coefficient between $\langle D_{TO}\rangle$ and $\langle D_{TT}\rangle$ is −0.9981, which indicates a perfect negative linear relationship. The regression line has the formula $\langle D_{TT}\rangle = -4.8929 \times \langle D_{TO}\rangle + 10.9128$. Again, all existing zeolites are very close to the regression line. The deviation from this line can be calculated for each zeolite: $\varepsilon_{\langle TT\rangle} = |\langle D_{TT}\rangle + 4.8929 \times \langle D_{TO}\rangle - 10.9128|$. The zeolite framework EDI has a deviation of 0.0046 Å, which is the largest among all existing zeolites. The smallest and the largest ratios of $\langle D_{TT}\rangle/\langle D_{TO}\rangle$ are 1.8076 and 1.9414, which

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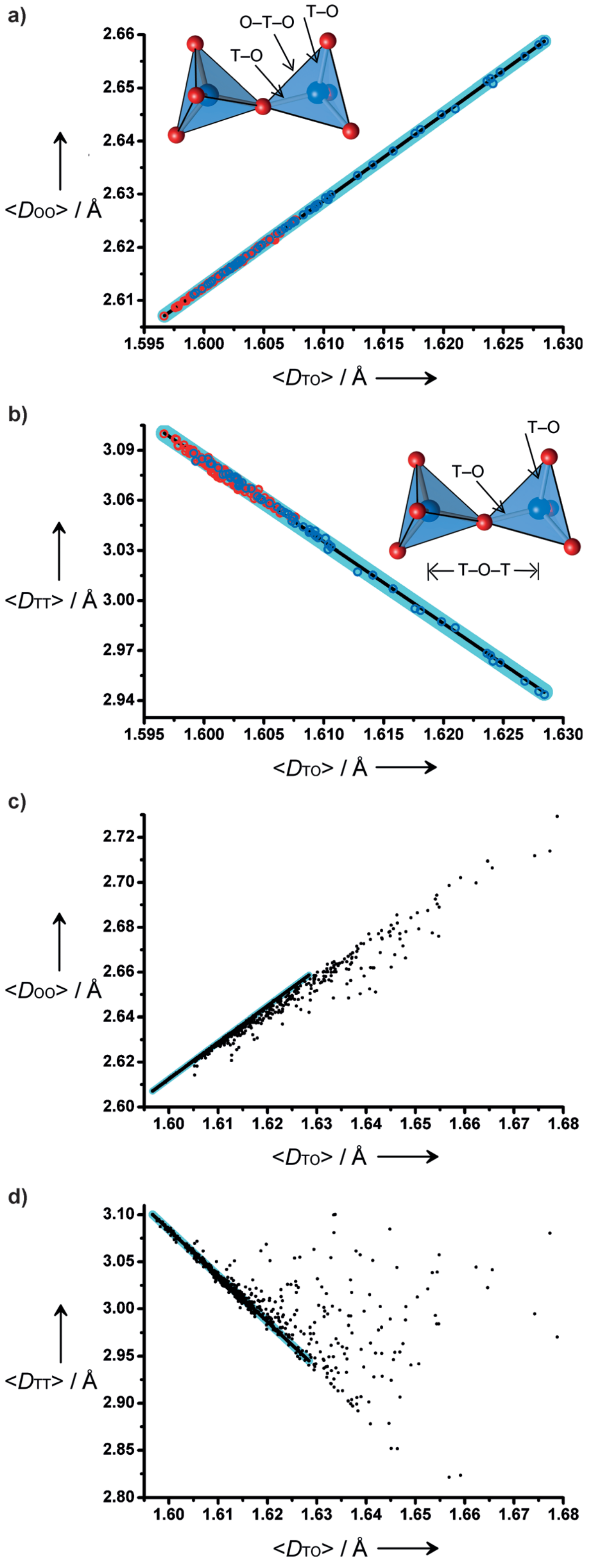

Figure 1. Linear relationships between the average LIDs in optimized zeolite frameworks. a) $\langle D_{OO}\rangle$ versus $\langle D_{TO}\rangle$ in existing zeolites; b) $\langle D_{TT}\rangle$ versus $\langle D_{TO}\rangle$ in existing zeolites; c) $\langle D_{OO}\rangle$ versus $\langle D_{TO}\rangle$ in hypothetical zeolites; d) $\langle D_{TT}\rangle$ versus $\langle D_{TO}\rangle$ in hypothetical zeolites. Red circles denote existing conventional zeolites; blue circles denote existing unconventional zeolites; black dots denote hypothetical zeolites. The regression lines derived from existing zeolites are also displayed. The regions occupied by existing zeolites are highlighted in cyan.

correspond to T-O-T angles of 129.32 and 152.20°, respectively. This relationship indicates that although the average T−O−T distances ($\langle D_{TT}\rangle$) in existing zeolites can vary within a wide range, they have to be negatively linearly related to the average T−O distances ($\langle D_{TO}\rangle$). The vertical deviation from the $\langle D_{TO}\rangle$–$\langle D_{TT}\rangle$ regression line has to be very small ($\varepsilon_{\langle TT\rangle} \leq 0.0046$ Å). This feature is our second LID criterion, which is valid for all existing zeolites (criterion 2). Criterion 1 corresponds to the tetrahedral nature of the building units in existing zeolites, whereas criterion 2 relates to the special linking mode of these building units. Criteria 1 and 2 reflect the local structure of a zeolite framework. Because no existing zeolite violates these two criteria, we conjecture that these criteria correspond to certain intrinsic structural features of realizable zeolites and can therefore be used as a new tool for the fast evaluation of the chemical feasibility of a large number of hypothetical structures.

We further calculated the average LIDs in 665 hypothetical zeolite frameworks (see the Experimental Section). Figure 1 c,d shows the plots of $\langle D_{OO}\rangle$ versus $\langle D_{TO}\rangle$ and $\langle D_{TT}\rangle$ versus $\langle D_{TO}\rangle$ for hypothetical structures. By checking the $\varepsilon_{\langle OO\rangle}$ and $\varepsilon_{\langle TT\rangle}$ values, we found that 271 of the 665 hypothetical frameworks satisfy criteria 1 and 2 simultaneously, which indicates that their synthesis might be possible (see Table S2 in the Supporting Information). The remaining 394 hypothetical frameworks violate the LID relationships, which might be a sign that they are not realizable as any oxide polymorph. The data for all existing zeolites are found at the edge regions of the data corresponding to the hypothetical zeolites in the graphs (Figure 1 c,d). Given the same $\langle D_{TO}\rangle$ value, realizable zeolites have the largest $\langle D_{OO}\rangle$ value and the smallest $\langle D_{TT}\rangle$ value. In other words, if zeolites with the same T−O distances are compared, realizable zeolites have the largest TO_4 tetrahedra and the most compact local linkages.

The average LIDs $\langle D_{TO}\rangle$, $\langle D_{OO}\rangle$, and $\langle D_{TT}\rangle$ reflect the local structural features of the whole zeolite framework. To detect local distortions of individual LIDs, we further introduced two additional criteria. We found that the standard deviations of the LIDs, designated σ_{TO}, σ_{OO}, and σ_{TT}, are all very small in the optimized framework of each existing zeolite (see Table S1 in the Supporting Information). The maximum σ_{TO}, σ_{OO}, and σ_{TT} values among all existing zeolites are 0.0196, 0.0588, and 0.0889 Å, respectively. We conjecture that all realizable zeolites should have such small σ_{TO} (≤ 0.0196 Å), σ_{OO} (≤ 0.0588 Å), and σ_{TT} values (≤ 0.0889 Å), because large variance in the LIDs will produce severe framework distortions. This feature is our third LID criterion (criterion 3). Similarly, we define the LID range (designated R_{TO}, R_{OO}, and R_{TT}, respectively) as the difference between the maximum and minimum LID in each zeolite framework. Unlike the standard deviations, which are a measure of the average variance in a particular LID, the LID ranges are more sensitive to individual extreme LIDs in each zeolite. The maximum R_{TO}, R_{OO}, and R_{TT} values among all existing zeolites are 0.0634, 0.2746, and 0.3332 Å, respectively. We conjecture that the LIDs in all realizable zeolites should have such small ranges: our fourth LID criterion (criterion 4). By applying criteria 3 and 4, we found 244 of the 665 hypothetical frameworks to be realizable, whereas only 197 of these zeolites are realizable if criteria 1–4 are all applied (see Table S2 in the Supporting Information). Although in this study we have only analyzed several hundred structures, our LID calculations are highly efficient and can be used to analyze large databases consisting of millions of structures.

In comparison with other structure-evaluation approaches, our LID criteria have three main advantages. The first advantage is the full coverage of all existing zeolites. The previously proposed energy criterion erroneously denied the feasibility of the existing zeolite frameworks BSV, CZP, JST, OBW, OSO, SOS, and WEI (among others),[19,26,28,34] whereas the flexibility criterion could not explain the existence of the zeolite frameworks ISV, RRO, and STW (and others).[36,38,39] Our LID criteria are valid for all existing zeolites, including those not allowed by other criteria. For example, JU-64 is a new gallogermanate zeolite which was recently synthesized in our laboratory.[43] Single-crystal X-ray diffraction analysis showed that the framework of JU-64 contained unprecedented 11-ring channels (Figure 2; see Table S3 in the Supporting Information). According to the energy criterion, JU-64 should be "unrealizable", because its framework energy relative to α-quartz is 49.64 kJ mol^{-1} after geometry optimization and thus much higher than 30 kJ mol^{-1}, the upper limit allowed by the energy criterion for a realizable zeolite.[28] However, we found that the optimized framework of JU-64 satisfied all four LID criteria derived from existing zeolites (see Table S1 in the Supporting Information), which verified its structural feasibility, in agreement with our experimental discovery. Another example is the recently synthesized silica polymorph of zeolite STW, the feasibility of which was denied by the flexibility criterion.[36,39,44,45] Our LID calculations again verify its structural feasibility. The optimized framework of STW satisfies all four LID criteria (see Table S1 in the Supporting Information), again in agreement with the experimental discovery.

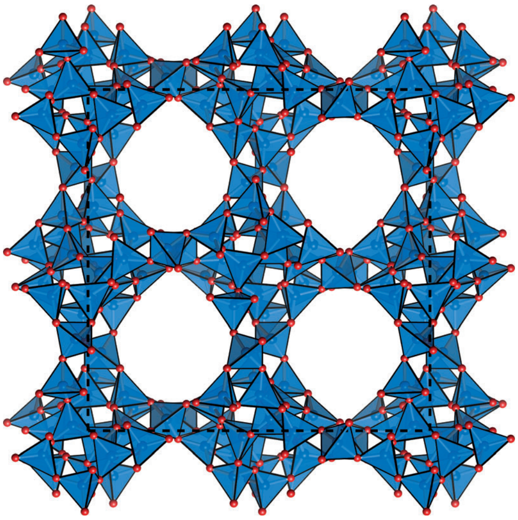

Figure 2. Optimized framework of zeolite JU-64 (space group: $Pa\bar{3}$, $a = 20.0$ Å, $FD = 12.0$ T atoms per 1000 Å^3). Atomic coordinates are listed in Table S3 of the Supporting Information. T blue, O red.

The second advantage of our LID criteria is their sensitivity to unreasonable structures. Among the 665 hypothetical structures examined in this study, 372 have framework energies lower than 30 kJ mol^{-1}. However, only 181 of these low-energy frameworks satisfy all four LID criteria. For example, the hypothetical zeolite PCOD8000012 has a framework energy of 16.20 kJ mol^{-1}. According to the energy criterion,[28] this hypothetical zeolite should be realizable. However, its optimized framework violates criteria 2–4 (see Table S2 in the Supporting Information). Visual inspection shows that although it is strictly four-connected, this framework is actually a closely packed layered structure (see Figure S2a in the Supporting Information). PCOD8000012 is clearly not a realizable three dimensionally extended zeolite framework, which verifies the validity of our LID criteria. Another example is the hypothetical zeolite PCOD8000022, the framework energy of which is 10.04 kJ mol^{-1}. According to the energy criterion, this hypothetical zeolite should also be realizable. However, our LID calculation denies its feasibility because it violates all four LID criteria (see Table S2 in the Supporting Information). Visual inspection shows that this structure consists of highly squashed 8-rings; such a structure is apparently not feasible for a zeolite framework (see Figure S2b in the Supporting Information). In contrast with the energy criterion, which reflects the average features of the whole framework, our LID criteria focus on the local bonding environment and are therefore able to pinpoint more local structural distortions and theoretical artifacts than the energy criterion.[19]

Almost all industrially important zeolites are conventional zeolites, because their framework stability is much higher than that of unconventional zeolites. Therefore, the identification of hypothetical frameworks that are realizable as conventional zeolites is also important for practical applications. The third advantage of LID criteria is their capability to directly identify potential conventional zeolites. From Figure 1 and Table S1 (see the Supporting Information), we found that the average LIDs in the optimized frameworks of conventional zeolites do not vary much ($\langle D_{\mathrm{TO}}\rangle = 1.5967$–$1.6076$ Å; $\langle D_{\mathrm{OO}}\rangle = 2.6070$–$2.6251$ Å; $\langle D_{\mathrm{TT}}\rangle = 3.0998$–$3.0490$ Å). In comparison, the average LIDs in unconventional zeolites vary within much wider ranges ($\langle D_{\mathrm{TO}}\rangle = 1.5991$–$1.6284$ Å; $\langle D_{\mathrm{OO}}\rangle = 2.6111$–$2.6588$ Å; $\langle D_{\mathrm{TT}}\rangle = 3.0882$–$2.9435$ Å). In particular, the average D_{TO} and D_{OO} values are usually longer and the average D_{TT} values are shorter in unconventional zeolites. If the average LIDs of a realizable zeolite framework fall into the regions of those of conventional zeolites, this framework might be realizable with conventional T elements; otherwise, it can only be realized with unconventional elements. By using this rule as our fifth LID criterion, we can directly pick out the most promising frameworks for synthesis as conventional zeolites. In practice, we only need to check the average D_{TO} value ($1.5967 \leq \langle D_{\mathrm{TO}}\rangle \leq 1.6076$ Å), because $\langle D_{\mathrm{OO}}\rangle$ and $\langle D_{\mathrm{TT}}\rangle$ are highly correlated to this value. For example, the $\langle D_{\mathrm{TO}}\rangle$ value in the optimized framework of JU-64 is 1.6268 Å, which indicates that JU-64 could not be realized with conventional T elements. This conclusion agrees with the fact that JU-64 was synthesized with Ge and Ga. In the zeolite STW, $\langle D_{\mathrm{TO}}\rangle =$

1.6040 Å, which indicates that this framework could be realized with conventional T elements, in agreement with the recent synthesis of STW as a pure silica polymorph.[45] Similarly, hypothetical frameworks that can be realized with conventional T elements could be predicted directly. Among the 196 hypothetical frameworks that satisfy criteria 1–4, 93 also satisfy the fifth criterion and therefore are promising targets as conventional zeolites. Figure 3 shows two such hypothetical frameworks. H123-1[22] is a hypothetical zeolite with parallel 12-ring and 8-ring channels (Figure 3a), whereas 189_2_33[21] contains 12-ring channels (Figure 3b). H123-1 is constructed from *d6r* and *d8r* building units, and 189_2_33 from *afi* and *dcc*.[3] All of these building units are frequently observed in existing conventional zeolites.

Our LID criteria are derived from optimized frameworks that assume uniform silica polymorphs. Therefore, our LID criteria are associated with the topology of a zeolitic framework, and not with its experimental crystal structure or synthetic route. Many researchers believe that the host–guest interactions between zeolite frameworks and the extra-framework species (which are usually metal cations, ammonium cations, or organic amines added during synthesis) are the driving forces that make four-connected zeolite frameworks realizable. However, these host–guest effects have been completely ignored in this study. Therefore, we believe that the feasibility of a zeolite framework should be its intrinsic structural nature. Our LID studies are based on existing structures and simple statistical theories. With the discovery of more new structures and the implementation of more sophisticated statistical tools, our LID criteria could be improved and become even more reliable.

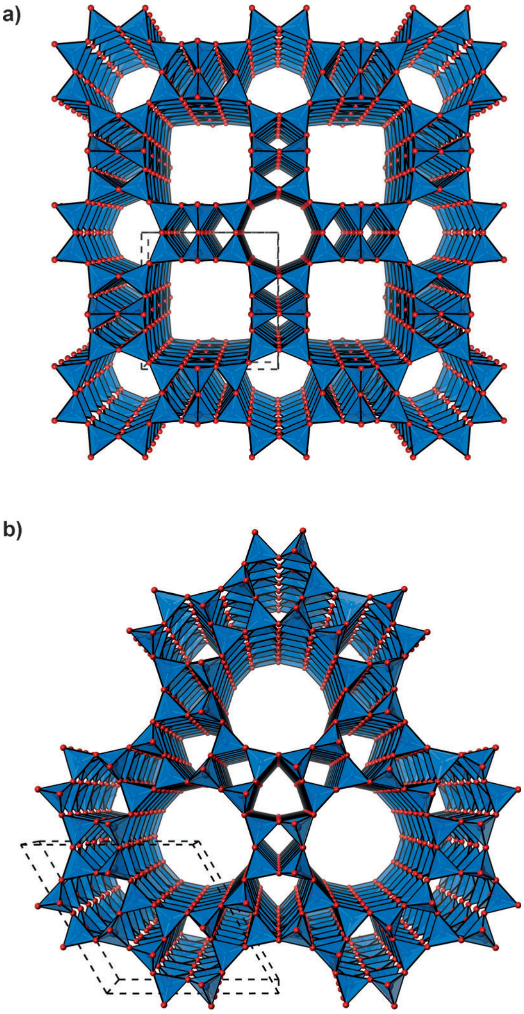

Figure 3. Framework structures of two hypothetical zeolites that might be realizable with conventional T elements. a) H123-1 (space group: $P4/mmm$, $a=12.5$, $c=9.3$ Å, $FD=16.5$ T atoms per 1000 Å^3, $E=18.41$ kJ mol^{-1}); b) 189_2_33 (space group: $P\bar{6}2m$, $a=13.6$, $c=8.8$ Å, $FD=17.1$ T atoms per 1000 Å^3, $E=13.07$ kJ mol^{-1}). T blue, O red.

In summary, we have discovered that the LIDs reflect certain intrinsic structural features of realizable zeolite frameworks. In comparison with other structure-evaluation methods, our new LID criteria are universally valid for all existing zeolites, more efficient for the screening of hypothetical structures because of their high sensitivity to unreasonable geometries, and suitable for the direct identification of feasible candidates for synthesis as conventional zeolites. The most realizable synthetic candidates can be selected on the basis of these criteria, which therefore provide a shortcut to future target synthesis.

Experimental Section

A total of 200 existing and 665 hypothetical zeolite frameworks were selected for this study. The 200 existing zeolites include 196 strictly four-connected frameworks already approved by the International Zeolite Association[3] and four recently reported frameworks awaiting approval (see Table S1 in the Supporting Information). Conventional and unconventional zeolites were classified according to the composition of the type material of each framework.[3] Interrupted frameworks were not selected because they are not strictly four-connected. The zeolite RWY was not selected because it is a sulfide compound in which the local bonding environment is dramatically different from that in all other oxide zeolites.[46] Among the 665 hypothetical zeolite frameworks selected for this study, 314 were from the Hypothetical Zeolite Database,[22] 151 were uninodal structures from the Atlas of Prospective Zeolite Structures,[21] and the remaining 200 were low-energy structures from the Deem database.[20]

All frameworks were optimized as silica polymorphs without symmetry constraints. The program GULP[47] was used with the Catlow potentials, including a core–shell polarization term.[48] All frameworks were successfully optimized and were confirmed to have no imaginary phonon mode. Framework energies were calculated relative to α-quartz, which is the most stable form of silica at ambient temperature. LID calculations were performed by using the program FraGen.[49] The Pearson correlation coefficient was calculated as the covariance of the two variables divided by the product of their standard deviations.

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