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RESEARCH ARTICLE

# An Aluminosilicate Zeolite Containing Rings of Tetrahedral Atoms with All Odd Numbers from Five to Eleven

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**Abstract:** Herein we report the synthesis, structure solution, and catalytic properties of PST-31 with an unprecedented framework topology. This high-silica (Si/Al = 16) zeolite was synthesized using a pyrazolium-based dication with a tetramethylene linker as an organic structure-directing agent (OSDA) in hydroxide media. The PST-31 structure is built from new building layers containing 4-, 5-, 6-, and 7-rings, which are connected by single 4-rings in the interlayer region to form a two-dimensional pore system. Its channels consist of [$4.5^6.6.9.11$] and [5.6.7.9.10.11] cavities and are thus delimited by 9-, 10-, and 11-rings. The OSDA cations in as-synthesized PST-31 were determined to reside without disorder in the large [$4^2.5^{14}.6^4.7^2.9^4$] cavities composed of smaller [$4.5^6.6.9.11$] and [5.6.7.9.10.11] ones, leading to a symmetry coincidence between the OSDA and the surrounding zeolite cavity. The proton form of PST-31 was found to be selective for the cracking of *n*-hexane to light olefins.

## Introduction

Aluminosilicate zeolites are steadily increasing in use as industrial catalysts and adsorbents, mainly due to their structural and chemical stability.[1] Therefore, the discovery of novel zeolite structures is highly desirable to expand their applications to more challenging tasks. Regardless of the composition, a total of 253 framework type materials have so far been approved by the Structure Commission of the International Zeolite Association (IZA-SC) and are conventionally classified as small-, medium-, large-, and extra-large pore structures which have 8, 10, 12, and over 12 tetrahedral atoms (T-atoms) in the largest pore opening, respectively.[2]

Zeolite structures containing rings of odd numbers of T-atoms higher than 6, although scarce, are also known. According to IZA-SC, there are only five, twelve, and two structures that contain 7-, 9-, and 11-rings, respectively.[2] It is worth noting that SSZ-23 (IZA code STT) is the only one which simultaneously has 7- and 9-rings.[3] This scarcity of zeolite structures with odd-membered rings is extended in the hypothetical structure database, the reason for this is still unclear.[4] On the other hand, Li and Deem have analyzed a huge number of hypothetical structures in terms of their framework energy and density, they found that the probability of frameworks containing 7-rings decreases when approaching the low-density edge of the structure distribution.[5]

Since the first use of organic structure-directing agents (OSDAs) by Barrer in zeolite synthesis,[6] the OSDA design has dominated the discovery of many interesting new zeolite structures.[7] Despite the great success of this approach, however, the geometric correspondence between the encapsulated OSDA molecule and the pore structure of the crystallized zeolite is generally far from close. Apart from the case of ZSM-18 (MEI) where its cavity and the triquaternary OSDA employed are characterized by the same symmetry element (threefold rotation),[8] most, if not all, OSDAs have been found to remain disordered within the zeolite pores.

Here we present the synthesis and structure of a new aluminosilicate (Si/Al = 16) zeolite containing rings of T-atoms with all odd numbers from five to eleven, denoted PST-31, and its catalytic properties for the cracking of *n*-hexane. This new zeolite has been synthesized using a pyrazolium-based dication as an OSDA, together with $Na^+$ or $K^+$, in hydroxide media. We also demonstrate that the OSDA in as-synthesized PST-31 not only ends up in an ordered fashion, although highly flexible due to its central tetramethylene chain, but also shows symmetric matching (inversion center) with the host zeolite cavity. This may in our view be responsible for directing the unique PST-31 structure.

## Results and Discussion

Recently, we have reported that PST-22 (PWW), a new medium-pore zeolite with intersecting 10- and 8-ring channels, can be synthesized using 1,1'-(1,4-butanediyl)bis(2,4-dimethyl-1H-pyrazol-2-ium) dications, denoted 14DMP-$C_4^{2+}$, as an OSDA under excess fluoride conditions ($HF/OSDA^{2+}$ = 4 and Si/Al = 10).[9] This stimulated us to examine whether its synthesis is possible in the presence of the same OSDA, but without using toxic fluoride anions. As can be found in Table S1, we were able to crystallize PST-22 by heating synthesis gels with $SiO_2/Al_2O_3$ = 20 and $NaOH/SiO_2$ = 0.30-0.35 at 175 °C for 7 days. Detailed characterization results of this PST-22 in comparison to the identical zeolite obtained in fluoride$^-$ media will be given elsewhere. Of particular interest is that when the $SiO_2/Al_2O_3$ ratio in the gel was slightly increased to 30, a novel zeolite, denoted PST-31 was the phase formed at $NaOH/SiO_2$ = 0.30-0.35. We note that like the case of PST-22, the gel composition range leading to pure PST-31 was also narrow. However, the replacement of NaOH with the equivalent amount of KOH under the conditions described above was found to again produce pure PST-31, although the use of the other alkali cations, i.e., $Li^+$, $Rb^+$, and $Cs^+$, was not successful (Table S2).

Field emission scanning electron microscopy shows that as-synthesized PST-31 always appears as very small (< 30 nm) nanospheres (Figure S1), regardless of the type and amount of alkali cations employed in its synthesis. $^{13}C$ magic-angle-spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy reveals that its OSDA molecules remain intact (Figure S2). When PST-31 was calcined at 600 °C to remove the occluded OSDAs (Figure S3) and then converted to its proton form (H-PST-31), there were no significant changes in the powder X-ray diffraction (PXRD) pattern (Figure 1a), indicating its high structural stability. However, while the $^{27}Al$ MAS NMR spectrum of as-synthesized PST-31 shows one resonance around 55 ppm assigned to tetrahedral Al, an additional weak signal around 0 ppm due to octahedral Al is observable in the spectrum of H-PST-31 (Figure S4). The $^{29}Si$ MAS NMR spectra of both as-synthesized and proton forms of PST-31 are dominated by a broad and asymmetric signal around -110 ppm. The difference in the line shape indicates that a portion of framework Al atoms has been removed during the calcination step for OSDA removal, which can be further supported by the existence of an IR band at 3655 cm$^{-1}$, corresponding to the OH group of extraframework Al species (Figure S5). On the other hand, since we were not able to determine the structure of this new zeolite from PXRD data, we applied three-dimensional electron diffraction tomography (3D-EDT) for solving the PST-31 structure.[10]

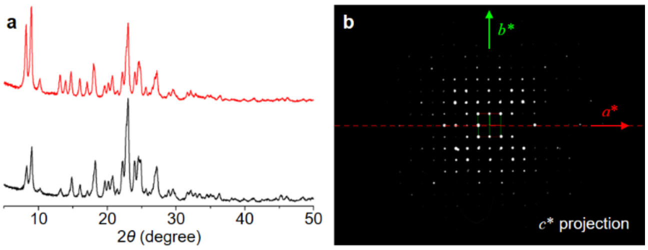

*Figure 1.* a) PXRD patterns of the as-synthesized (black) and proton (red) forms of PST-31. b) Projection of reciprocal space reconstructed from 3D-EDT data of H-PST-31 along the c* direction.

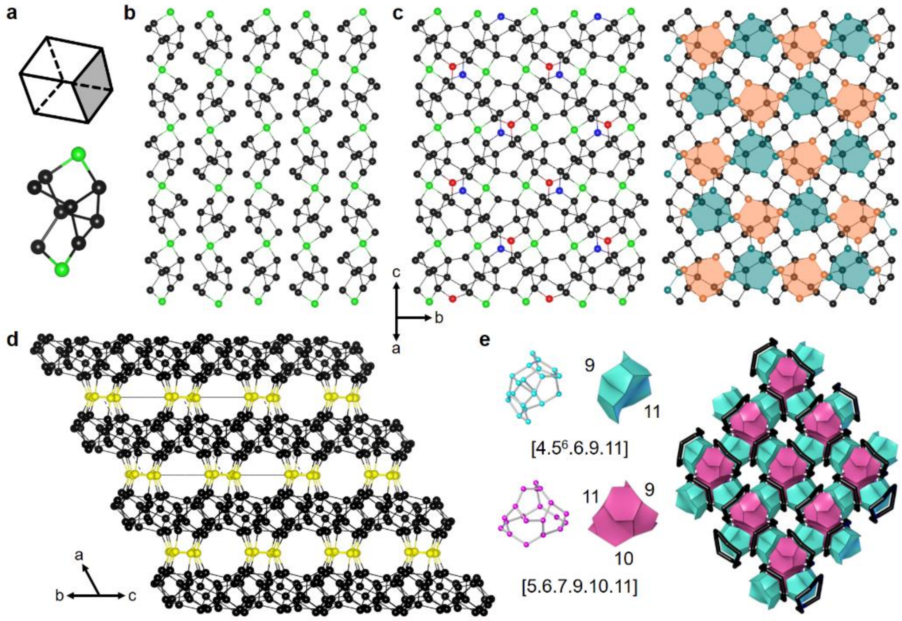

*Figure 2.* a) Double 4-ring unit (top) and its 1,3-stellated-5-open unit (bottom; [$4.5^3.7$]). The T-atoms in stellated points and in the other ones are indicated by light green and black balls, respectively. Bridging O atoms have been omitted for clarity. b) PST-31 building chains. These chains, made up of [$4.5^3.7$] units by sharing T-atoms in stellated points, are arrayed along the *b*-axis to construct a PST-31 building layer. The [$4.5^3.7$] units in each chain are arranged by glide reflection, and two adjacent PST-31 chains are related to each other by inversion. c) Top views of the PST-31 layer consisting of PST-31 chains and extra T-atoms. (Left) The extra T-atoms in top and bottom sides are indicated by red and blue balls, respectively. (Right) The T-atoms in top and bottom sides, which will be involved in interlayer connection, are indicated by orange and turquoise blue balls, respectively. The 7-rings including these T-atoms are marked in the same colors. d) The PST-31 structure viewed along [011]. Its building layers and interlayer single 4-ring units are marked in black and yellow, respectively. Two adjacent PST-31 layers are related to each other by translation (*1/2*c). e) Tiling presentation of the 2D pore structure of PST-31: the 9-rings are highlighted by thick black lines. Notice that its channels, consisting of [$4.5^6.6.9.11$] and [$5.6.7.9.10.11$] cavities, are delimited by 9-, 10-, and 11-rings.

The 3D reciprocal lattice of H-PST-31, reconstructed from 3D-EDT data, shows a mirror plane, as marked by a dashed line in Figure 1b, which indicates the 2/*m* Laue symmetry and thus a monoclinic space group. The unit cell parameters obtained using the 3D-EDT data were *a* = 13.699 Å, *b* = 14.375 Å, *c* = 17.188 Å, *β* = 128.7°. The 2D slices from the reconstructed reciprocal space (Figure S6) allowed us to deduce that the reflection conditions were *h*0*l*: *l* = 2*n* and 0*k*0: *k* = 2*n*, for which the space group with the highest symmetry is $P2_1/c$ (no. 14). The H-PST-31 structure was solved and refined from the 3D-EDT data using this space group and the program Sir2014.[11] Rietveld refinement was also carried out using synchrotron PXRD data with the standardized lattice parameters (Figure S7 and Tables S3-S6).[12] The final refined unit cell parameters determined were *a* = 13.8222(7) Å, *b* = 14.3797(5) Å, *c* = 17.2724(9) Å, *β* = 128.9719(21)° for hydrated H-PST-31.

The structure of PST-31 has 12 crystallographically distinct T-sites. Its framework is built up of 1,3-stellated-5-

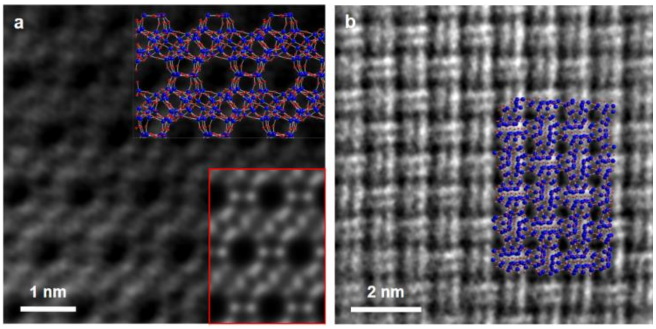

***Figure 3.*** $C_s$-corrected ADF-STEM images of H-PST-31 along the a) [011] and b) [101] directions, which are superimposed with its structure model. Si, blue; O, red. The simulated micrograph, indicated by a red box in a), is given for comparison.

open cubic ([$4.5^3.7$]) units as a key building unit (Figure 2a). These modified double-4 ring (*d4r*) units are connected one another by sharing the T-atoms in stellated points (in green), with glide arrangement, to form the PST-31 building chain (Figure 2b). The PST-31 building layer is then created by a combination of PST-31 chains and extra T-atoms, where the two adjacent chains are related by inversion symmetry (Figure 2b,c). It should be noted that the PST-31 layer contains one type of 7-ring~~s~~, as well as 4-, 5-, and 6-rings, which consist of four T-atoms with three (not four) intralayer connections and are equally distributed in both top and bottom sides. Also, there is the other type of 7-ring~~s~~ in the middle of the layer (Figure S8). Regardless of the size of these 7-rings, however, the PST-31 layer itself is nonporous in nature due to the presence of 6-rings between 7-rings connected along the direction perpendicular to the layer.

On the other hand, the PST-31 layers are stacked along the *a*-axis via the connection between intralayer 7-rings (Figure 2c, right) and interlayer single 4-ring (*s4r*) units, where two adjacent layers are related to each other by translation of 0.5*c* (Figure 2d). The *s4r* units at the same height, which are located in the nodes of the (4,4) net topology, act as pillars. This leads to the formation of a 2D pore system, which consists of mutually intersecting channels, made up of [$4.5^6.6.9.11$] and [5.6.7.9.10.11] cavities. As a result, the intersecting channels of PST-31 have multiple delimiting rings, i.e., 9-, 10-, and 11-rings with dimensions 3.7 × 4.9, 4.5 × 6.2, and 5.0 × 6.7 Å, respectively (Figures 2e, S9, and S10). As such, they have the ring sequence 9-11-10-11-9-10 and are thus undulating in nature. This feature is particularly intriguing because the pure-silica UZM-55 is the only example of the existence among all zeolite structures of multiple delimiting rings (10- and 12-rings) in a single channel.[13] The framework density (defined as the number of T-atoms per 1000 Å$^3$) of PST-31 was calculated to be 18.0.

Spherical aberration corrected annular dark field scanning transmission electron microscopy ($C_s$-corrected ADF-STEM) supports the reliability of the H-PST-31 structure determination (Figure 3). In particular, the image of H-PST-31 observed along [011] allows clear observation of the channels surrounded by the building layers and interlayer *s4r* units, consistent with Figure 2d. It is also remarkable that the [$4.5^6.6.9.11$] and [5.6.7.9.10.11] tiles in the tiling presentation of the PST-31 structure (Figure 2e) have a 'weak' ring (one face larger than all the other faces in a tile; here, the 11-ring).[14] This means that both tiles are not 'natural' tiles.[14] Furthermore, the tiling arrangement for the entire structure, calculated using the program package ToposPro,[15] was found to be [$4.5^2.6$] + [4.5.6.7] + [$5^2.6^2$] + [$5.6^2.7$] + [$4^2.5^3.7$] + [5.6.7.9.10.11] + [$4.5^6.6.9.11$]; only [$5^2.6^2$] (*t-pes*) is a natural tile (Figure S11). Consequently, unlike all zeolite structures known to date,[2] constructing the natural tiling (with only strong rings) for the PST-31 framework was not possible since an edge is simultaneously adjacent to the weak rings. If so, merging small tiles through weak rings would lead the larger tile to contain the edge inside itself, thus not allowing natural tiling of the PST-31 structure.

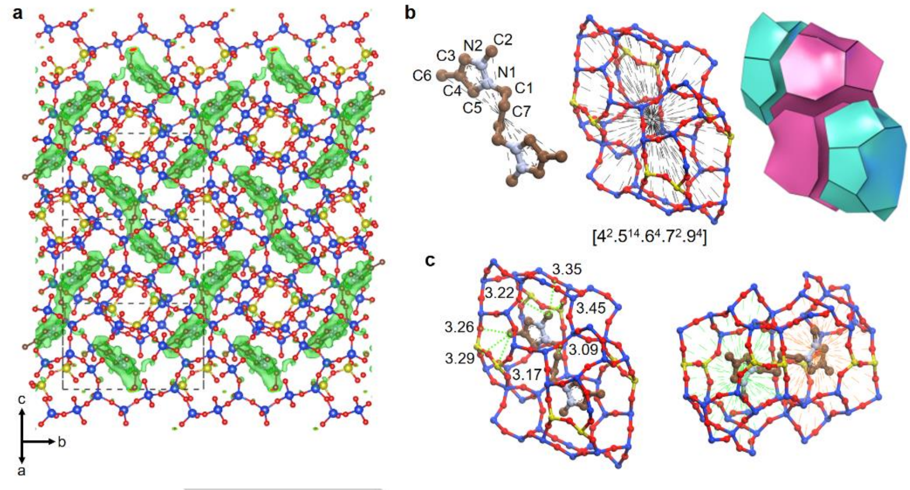

***Figure 4.*** a) Refined structure of as-synthesized PST-31 with occluded 14DMP-$C_4^{2+}$. Si, blue and yellow in PST-31 layers and single 4-ring units, respectively; O, red; C, brown; N, pale blue. The regions marked in translucent green indicate the positive difference electron density maps visualized using the whole data set, after refining the framework atoms only against the high-angle (d-space < ~2 Å) data. b) The configuration (left) of 14DMP-$C_4^{2+}$ encapsulated within the large [$4^2.5^{14}.6^4.7^2.9^4$] cavity (middle). Both the OSDA and [$4^2.5^{14}.6^4.7^2.9^4$] cavity have an inversion center at the same crystallographic position. Their inversion center, indicated by a black dot, is guided with dashed lines. The [$4^2.5^{14}.6^4.7^2.9^4$] cavity (right) consisting of two [$4.5^6.6.9.11$] and two [5.6.7.9.10.11] cavities. c) Two different views of the [$4^2.5^{14}.6^4.7^2.9^4$] cavity containing 14DMP-$C_4^{2+}$. (Left) The distances between the host cavity and guest molecule, shorter than 3.5 Å, are marked. (Right) The centroids of adjacent [$4.5^6.6.9.11$] and [5.6.7.9.10.11] cavities are indicated by green and orange dots guided with dashed lines, respectively. These centroids are located close to those of the pyrazolium rings in the OSDA, respectively.

We next carried out PXRD and Rietveld analyses on the dehydrated, as-synthesized PST-31 to determine the OSDA location (Figure S12 and Tables S8-S11). A piece of the positive electron density remaining after initial scaling,[16] corresponding to a 14DMP-$C_4^{2+}$ molecule, was determined to be located within the large [$4^2.5^{14}.6^4.7^2.9^4$] cavity consisting of two [$4.5^6.6.9.11$] and two [5.6.7.9.10.11] ones (Figure 4a). We also note that this OSDA spans the 10- and 11-rings, but not the 9-rings (Figure S13). The centroids of adjacent [$4.5^6.6.9.11$] and [5.6.7.9.10.11] cavities, halves of the [$4^2.5^{14}.6^4.7^2.9^4$] one, were found to be near those of the pyrazolium rings, respectively. More interestingly, the dication exactly follows the space group symmetry of the PST-31 framework without disorder: both the OSDA and [$4^2.5^{14}.6^4.7^2.9^4$] cavity have same inversion center (Figure 4b), unlike the case of PST-22 that can be synthesized using the same OSDA.[9] This suggests that the point group symmetry of the host

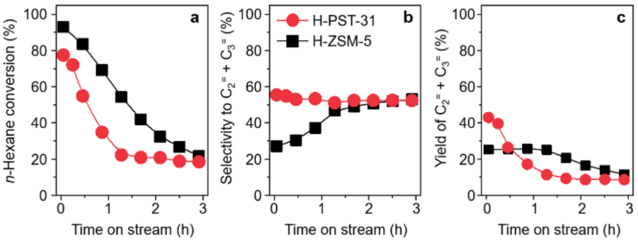

***Figure 5.*** a) *n*-Hexane conversion and b) selectivity to and c) yield of ethylene and propylene as a function of time on stream in the *n*-hexane cracking over H-PST-31 and H-ZSM-5 at 650 °C and 12.45 $h^{-1}$ WHSV.

cavity is dictated by that of the guest molecule. Their close relation can be further supported by the multiple short distances (< 3.5 Å) between the C atoms in the OSDA and the framework O atoms (Figure 4c).

We compared the experimentally determined crystal structures of a series of diazolium-based dication salts with different head groups and methylene chain lengths (Table S12),[17] referred to as “diazole acronym”-$C_n^{2+}$, where *n* is the methylene chain length (3-6). Most of the dications with *n* = 3-5 had no molecular symmetry. However, we note that while some cations with odd-numbered chain lengths are characterized by a 2-fold rotational axis, some with *n* = 4 and all with *n* = 6 possess an inversion center, like 14DMP-$C_4^{2+}$ in as-synthesized PST-31. In fact, these two symmetries are the highest ones theoretically possible for the corresponding cations. The conformation of 14DMP-$C_4^{2+}$ was also found to be reasonable when compared to that of other cations, for example, 1MI-$C_4^{2+}$, where 1MI is 1-methylimidazole (Figure S14 and Table S12). In particular, its stabilization energy in the PST-31 structure was calculated to be -11.2 kJ (mol Si)$^{-1}$, which is lower than the values of any of the other dications with different head groups and chain lengths (Table S13).[18] Given both the molecular symmetry and shape, therefore, a combination of the 14DMP head group and the tetramethylene linker appears to provide an optimum OSDA for the crystallization of PST-31. In addition, the fact that the gel composition range yielding pure PST-31 with abundant odd-membered rings is narrow (Tables S1 and S2) suggests that the structure-directing effect of 14DMP-$C_4^{2+}$ may be specific rather than strong. This is because the conformation of flexible OSDAs, which affects the phase selectivity of the crystallization, can be altered by the type and concentration of inorganic components in synthesis mixtures.[19]

From a structural point of view, on the other hand, we were aware that the tetrahedrality of the resulting structures could be maintained, although the interlayer *s4r* units in PST-31 are eliminated or replaced by *d4r* units (Figure S15 and Table S14). The same result was obtained when the symmetry operations relating the two adjacent PST-31 layers are other than translation along the *c*-axis (i.e., translation along *b*-axis, reflection, and glide reflection). As a result, we were able to generate a total of 11 new hypothetical structures built from PST-31 layers (Tables S14 and Figure S16). The largest ring size in these structures was found to vary with the size of the interlayer unit: 7-8 for no unit, 9-11 for *s4r*, and 11-13 for *d4r* (Table S16). Nine of them meet the local interatomic distance criteria (Table S15) and are thus synthesizable.[20] It is interesting to note that despite its chemical feasibility, we were unable to describe the PST-31_H8 structure with 11- and 13-membered delimiting rings in a single channel by natural tiling, like the PST-31 case.

The Ar adsorption data reveal that H-PST-31 with a bulk Si/Al ratio of 16 has a micropore volume of 0.13 $cm^3$ $g^{-1}$ (Figure S17). While the pore size distribution curve of H-PST-31 calculated using the Horvath-Kawazoe formalism is characterized by one sharp maximum at 4.4 Å, the curve calculated using density functional theory shows not only a sharp band at 5 Å, but also a broad one centered at ca. 400 Å, indicative of the presence of interparticle pores (Figure S18). $NH_3$ temperature-programmed desorption and IR spectroscopy with adsorbed pyridine reveal that its acidic properties are similar to those of H-ZSM-5 with Si/Al = 15 (Figure S19 and Table S17). From competitive cracking of *n*-hexane and 3-methylpentane, H-PST-31 were calculated to have a constraint index of 9.7, falling within the values for medium-pore zeolites (Figure S20).[21] We also reacted H-PST-31 with *n*-hexane at 650 °C and 12.45 $h^{-1}$ weight hourly space velocity and compared the results with those of H-ZSM-5 with a similar Si/Al ratio (15). The catalytic cracking of *n*-hexane is a test reaction of naphtha cracking to assess the performance of zeolite catalysts and the reaction mechanism.[22] Interestingly, H-PST-31 is characterized by a higher yield of ethylene and propylene at early time on stream than H-ZSM-5 (Figure 5). Given that the commercial naphtha cracking plant is run in a fluidized bed due to rapid coke deposition, the initial catalytic performance is of prime importance. This renders H-PST-31 attractive as a fluidized catalytic cracking additive, which deserves further study.

## *Conclusion*

In summary, we have synthesized a novel high-silica zeolite PST-31 with abundant odd-membered rings (all from five to eleven), using an OSDA consisting of two pyrazolium moieties linked by a tetramethylene chain in the hydroxide media. In contrast to all 253 zeolite structures recognized by the IZA-SC, we were not able to describe the PST-31 framework structure by natural tiling. The intersecting channels in its 2D pore system are composed of two types of tile, both of which possess a weak 11-ring. Consequently, they are delimited by rings of three different sizes (i.e., 9-, 10-, and 11-rings). Structural analysis reveals the transmission of symmetry (inversion) from the OSDA to the host zeolite cavity in as-synthesized PST-31. We also found that H-PST-31 is promising for catalytic cracking applications.

## Acknowledgements

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**Keywords:** aluminosilicates • electron diffraction • odd-membered rings • structure elucidation • zeolites

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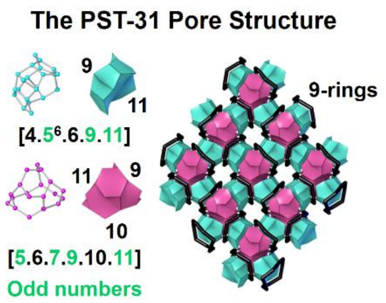
**Entry for the Table of Contents**



**Abundant odd-membered rings**: PST-31, a novel aluminosilicate zeolite with all odd-membered rings from five to eleven, has been synthesized in hydroxide media.