Mechanical stability plays a key role in the practical applications of metal-organic frameworks (MOFs). This study provides new insight into the design of high-mechanical-stability MOFs by merging two mechanically fragile frameworks into a more robust framework. A mesoporous MOF with high mechanical stability was synthesized by combining the topological merged-net approach and the introduction of triangular rigidity. The enhancement of mechanical stability was studied by computational force field calculation and experimental AFM characterization.

**Highlights**

- Reveal mechanical enhancement of merged frameworks in reticular chemistry
- Computational calculation of three mechanisms impacts MOFs’ mechanical stability
- Synthesis of a high-mechanical-stability mesoporous mixed-linker MOF, RE-sph-MOF-5
- AFM mechanical stability study of synthesized sph-MOFs

**Understanding**

Dependency and conditional studies on material behavior
Article

Reticular chemistry for the rational design of mechanically robust mesoporous merged-net metal-organic frameworks

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SUMMARY

Access to metal-organic frameworks (MOFs) with enhanced mechanical stability is key to their successful deployment in practical applications. However, the high porosity of the material often affects mechanical stability. In this article, to achieve highly porous MOFs with enhanced mechanical stability, we explored the merged-net approach where two relatively fragile frameworks were merged into a robust MOF structure. We demonstrate the effectiveness of this approach by computationally evaluating mechanical properties of sph-MOFs with varying lengths of linkers. Prominently, we pinpoint the significance of triangular rigidity on the robustness of large-pore MOFs and, subsequently, designed and synthesized a rare earth (RE)-based RE-sph-MOF-5 by the reticulation of hexanuclear RE clusters, tritopic linkers, and unprecedentedly large planar hexatopic linkers containing 19 phenyl rings. The mechanical properties of sph-MOFs were characterized and quantified using amplitude-frequency modulation (AM-FM) bimodal atomic force microscopy (AFM) analyses. Markedly, the mesoporous RE-sph-MOF-5 expresses high mechanical stability despite its large mesoporous cavities.

INTRODUCTION

Metal-organic frameworks (MOFs) are a class of crystalline porous materials comprised of periodically linked inorganic metal ions/clusters and organic ligands.1,2 The successful deployment of the reticular chemistry based on various building-block approaches paved the way for the deliberate construction of myriad porous materials with remarkable properties.3,4 The ability of structural control and modification provides MOFs capable of a wide range of intriguing applications such as gas storage and separation,5–9 catalysis,10–12 electrochemical reduction,13,14 and energy storage.15 Markedly, prospect applications of MOFs (e.g., hydrocarbon separations, high-pressure gas storage, catalysis, etc.) depend on MOF-associated stabilities.16–19 In contrast to chemical stability and thermal stability, mechanical stability remains less explored.16,18,20,21 Advances in calculation/prediction methods22–27 and various specialized characterization techniques such as nanoindentation28,29 and atomic force microscopy (AFM) nanoindentation30 offer the potential to study and evaluate mechanical properties of extended solid-state materials, such as MOFs. Recently, the
enhancement of mechanical stability for MOFs attracted more attention, and some post-modification methods such as ligand retrofitting,\textsuperscript{31} covalent cross-linking,\textsuperscript{32} and polymer insertion\textsuperscript{33} have been reported to increase the stability of mechanically fragile MOFs. However, the direct topological design method of mechanically robust, highly porous MOFs remains less explored.\textsuperscript{14,31}

Reticular chemistry is widely used for the prediction and design of diverse types of periodic extended structures.\textsuperscript{2,3,34,35} During the past two decades of exploration, edge-transitive nets, nets with one type of edge, were found to be ideal targets of simple structures in reticular chemistry.\textsuperscript{2,36,37} Recently, we introduced a systematic design principle, named the merged-net strategy, targeting the design of more complex mixed-linker MOFs.\textsuperscript{38} The merge of two edge-transitive nets, (3,6)-c spn net (transitivity [21]) and 6-c hxg net (transitivity [11]), will lead to a merged minimal edge-transitive net,\textsuperscript{36,39} (3,6,12)-c spn net (transitivity [32]), with a relatively higher complexity (Figure S1). The merged spn net inherited the structural properties from both parent nets and encompassed the ability to be an ideal design target in reticular chemistry. Based on the spn net, two frameworks can merge through shared inorganic molecular building blocks (MBBs), thus leading to the effective design of intricate mixed-linker MOFs. Practically, utilizing the merged-net approach, we synthesized a series of highly symmetric mixed-linker MOFs, named spn-MOF-1 to -4, based on the 12-c hexanuclear rare earth (RE) clusters.\textsuperscript{38}

Here, we show the merged-net approach as an effective method to design mechanically robust and highly porous MOFs. In the merged-net MOFs, the two 3-periodic frameworks are mutually supporting each other, which gives another 3-periodic structure with enhanced mechanical stability without much loss of pore access. This phenomenon results in merged MOFs with increased mechanical stability. Although both spn and hxg nets are mechanically fragile nets, the merged spn nets are mechanically robust because of the mutual mechanical support of both parent nets. The improvement observed in the mechanical stability of merged-net MOFs set these materials among the MOFs with the highest mechanical stability based on the same size of ligand. Markedly, we report the design and synthesis of Eu-spn-MOF-5 as an example of materials owning both mesoporosity and high mechanical stability.

RESULTS

Merged nets and sph-MOF-1 to -4

Our previous reported RE-spn-MOFs (spn-MOF-1 to -4) represent the first systematically studied merge-net platform.\textsuperscript{38} All the structures are mixed-linker frameworks based on merged-net spn. These MOFs contain hexanuclear RE clusters, smaller tritopic linkers for spn frameworks, and larger hexatopic linkers (or two tritopic linkers) for hxg frameworks. By removing the smaller tritopic linker, it will be only the hxg part left, while by removing the larger hexatopic linkers, it will be only the spn part left (Figure 1).

Concretely, all the spn-MOFs are based on an RE hexanuclear cluster (Figure 1A) and contain two types of organic linkers (Figure 1B). The small-size spn-MOF-1 contains 5-(4H-1,2,4-triazol-4-yl)isophthalate (TIA) for the spn part and 4,4',4''-[(benzene-1,3,5-tricarbonyl)tris(azanediyl)]tribenzoate (BTCB) for the hxg part. The medium-size spn-MOF-2 contains benzotriphosphene carboxylate (BTTC) for the spn part and 4,4',4''-[(benzene-1,3,5-triyltris-(benzene-4,1-diyl)]tribenzoate (BTPB) for the hxg part. The spn-MOF-3 contains the same BTTC linker as spn-MOF-2 for the spn part but hexacarboxylate ligand, hexakis(4-(4-carboxyphenyl)phenyl)

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benzoate (BHPB) (Figure S2) for the hxg part. The large-size sph-MOF-4 contains 4,4',4''-s-triazine-2,4,6-triyltribenzoate (TATB) for the spn part and 4,4',4''-(benzene-1,3,5-triyltri(biphenyl-4,4'-diyl))tribenzoate (BTBPB) for the hxg part (Figures 1C–1E). In the structures of sph-MOF-1, -2, and -4, the 6-c building blocks are constructed by two tritopic linkers in a staggered stacking mode (Figure S5).

**Principles for enhancing mechanical stability of MOFs**

We use a classical force field to compute the stiffness matrix for sph-MOFs since no breaking/formation of chemical bonds, nor other quantum effects, are involved in this study (see experimental procedures for details). In our previous work, we showed that these force fields provide sufficient accuracy in predicting the mechanical properties of MOFs.22,40 For each sph-MOF, we use bulk, Young’s, and shear moduli to characterize the mechanical stability. In Figure 2, we show these metrics for the MOFs (sph-MOF-1 to -4) and their corresponding spn/hxg parts.
We found three mechanisms for the design of MOFs with higher stability: (1) topologies (nets), (2) size and flexibility of linkers, and (3) triangular rigidity.

The first mechanism is the underlying topology, and the merged-net process shows significant enhancement to the parent-net frameworks. For all the sph-MOFs, the mechanical stabilities of merged sph frameworks are significantly higher compared with the corresponding spn and hxg frameworks, especially for Young’s modulus and shear modulus (Figures 2B and 2C). With sph-MOF-2 as an example, the computed Young’s modulus increased from 2.8 (spn framework) and 2.7 (hxg framework) to 8.7 GPa (sph-MOF-2), which are 211% and 222% increases, respectively. The computed shear modulus increased from 1.0 (spn framework) and 0.9 (hxg framework) to 3.1 GPa (sph-MOF-2), which are 210% and 244% increases, respectively. As a comparison, the theoretical pore volume by volume of sph-MOF-2 is only decreased by 21.4% for the spn framework and 9.2% for the hxg framework. The increment of mechanical stability of merged nets can be attributed to two aspects. First, the merging process results in nets of higher vertex coordinates, which means that the building blocks in merged-net structures have higher connectivity than those in the parent-net frameworks. Second, compared with each parent-net framework, the added organic linkers provide extra mechanical support to the other framework.

The second mechanism is the size and flexibility of linkers. As expected, we observed a decrease in the mechanical stability by expanding the ligands, e.g., comparing sph-MOF-1 with sph-MOF-2 and sph-MOF-4. All these MOFs contain two tritopic linkers. Indeed, among these three MOFs, sph-MOF-1, with the shortest ligands, has the highest mechanical stability, and sph-MOF-4, with the largest ligands, has the lowest mechanical stability. Relatively, the stability decrease of sph-MOF-2 is...
quite small compared with sph-MOF-1. Especially, the bulk moduli of sph-MOF-1 and sph-MOF-2 are almost the same (Figure 2A), which can be attributed to the slight flexibility of the amide group in the linker of sph-MOF-1.

The third mechanism is the triangular rigidity, allowing sph-MOF-3 to stand out from this trend (Figure 3, where we observe a 50% increase of minimum (min.) shear modulus from sph-MOF-2 to sph-MOF-3). The highly connected H₂BHPB ligands of sph-MOF-3 make a very strong network with enhanced mechanical stability in contrast to all the other evaluated structures in this study. We can infer the stability of this material to the triangle rigidity. Triangles are used widely in civil and mechanical engineering for construction structures (trusses in roofs, bridges, etc.) due to their high rigidity. The angles of a triangle cannot be deformed unless the edges change length. Therefore, the deforming/shearing MOF-3 is much more difficult as it requires expansion/compression of chemical bonds, in contrast to the angle deformation in the other frameworks.

An interesting prediction is to synthesize a new sph-MOF (sph-MOF-5) with the same type of triangular connectivity as sph-MOF-3 and the same large linker size as sph-MOF-4 (Figure S6). As sph-MOF-4 is relatively unstable, we expect that this modification would afford a material adapted to higher pressures.

Design and synthesis of mechanically robust mesoporous RE-sph-MOF-5
To increase the mechanical stability of mesoporous sph-MOFs, we designed our sph-MOF-5 with hexakis(4"-1,1'-4',1"-terphenyl)-4-carboxylate)benzene (H₆BHBPB) ligand as the hxg linker (Figures 4A, S3, and S4). As far as we know, this is the first time that the H₆BHBPB compound was reported, and the linker contains 19 benzene rings, which is the highest number among all planar MOF linkers. sph-MOF-5 was designed with the same merged-net approach as other sph-MOFs. The calculated shear modulus of sph-MOF-5 is a 90% increase compared with the same-size framework sph-MOF-4.

Solvothermal reactions of Eu(NO₃)₃·5H₂O, H₃TATB, and H₆BHBPB in a N,N-diethylformamide (DEF) solution in the presence of 2-fluorobenzoic acid (2-FBA) for 48 h at 115°C yielded colorless octahedral single crystals of sph-MOF-5. Single-crystal X-ray diffraction (SCXRD) studies revealed that sph-MOF-5 crystallized in the cubic space group Fd-3m with a unit cell parameter a = 57.439(1) (Figure 4B; Table S1). The compound formulated as [(CH₃)₂NH₂][Eu₂(μ₃-OH)₂(TATB)₂(BHBPB)][H₂O]₃·x(solv). The experimental powder X-ray diffraction (PXRD) pattern of as-synthesized and
acetone-exchanged Eu-sph-MOF-5 matches the calculated PXRD pattern derived from the SCXRD data (Figure 4C).

The topological analysis of sph-MOF-5 revealed that the 12-c hexanuclear Europium clusters are linked to the 3-c TATB linkers and the 6-c BHBPB linkers to form a 3-periodic MOF based on the underlying (3,6,12)-c sph net. The carbon atoms of the center triazine in the TATB linker can be regarded as points of extension of the 3-c nodes. The carbon atoms of the center benzene in the BHBPB linker can be regarded as points of extension of the 6-c nodes. The carbon atoms of the coordinated carboxylates can be presented as points of extension of the 12-c nodes.

The unique sph net and large organic linkers provide both microporous and mesoporous cages in the structure of sph-MOF-5. The larger truncated tetrahedral cages, having diameters of about 22 Å, are delimited by four BHBPB and four TATB linkers, while the smaller tetrahedral cages, having diameters of about 13 Å, are enclosed by four TATB linkers.

The activation of sph-MOF-5 was done by solvent exchange of acetone, followed by vacuum at 105°C. The permanent porosity of sph-MOF-5 has been examined by an argon-adsorption experiment at 87 K. The uptake of argon (Ar) at P/P₀ = 0.95 is
about 940 cm³ g⁻¹ (Figure 4D). The apparent Brunauer-Emmett-Teller (BET) surface area was estimated to be 2,965 m² g⁻¹. The experimental total pore volume was estimated to be 1.21 cm³ g⁻¹ (at P/P₀ = 0.95), which is consistent with the theoretical pore volume of 1.29 cm³ g⁻¹, based on the associated crystal structure. An increase at P/P₀ = 0.17 on the Ar adsorption isotherm corresponds to a mesoporous cage with a diameter of about 2.2 nm in sph-MOF-5 (Figure 4E).

The calculated mechanical properties of sph-MOF-5 are shown and compared with the other MOFs in Table 1. The bulk modulus, Young’s modulus, and shear modulus of the spn part and the hxg part frameworks are 5.6, 1.2, and 0.4 and 8.7, 5.8, and 2.1 GPa, respectively. While the merged structure of sph-MOF-5 results in 14.5, 7.7, and 2.7 GPa, corresponding to 159%, 542%, and 575% increases, in contrast to the associated spn framework, and 66%, 33%, and 29% increases, in contrast to the associated hxg framework. Compared with sph-MOF-4, sph-MOF-5 has a similar pore size and pore volume, while the bulk modulus, Young’s modulus, and shear modulus of sph-MOF-5 are increased from 11.1, 3.9, and 1.3 to 14.5, 7.7, and 2.7 GPa, corresponding to 30%, 97%, and 108% increases. The anticipated increase in mechanical stability is mainly attributed to the triangular windows contracted by 6-c linkers in sph-MOF-5.

<table>
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<tr>
<th>Structure</th>
<th>Bulk modulus (GPa)</th>
<th>Young’s modulus (GPa)</th>
<th>Shear modulus (GPa)</th>
<th>Max. Young’s modulus (GPa)</th>
<th>Min. Young’s modulus (GPa)</th>
<th>Max. shear modulus (GPa)</th>
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<td>3.2</td>
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<td>2.7</td>
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<td>7.3</td>
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<td>10.3</td>
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Mechanical characterization of RE-sph-MOFs by amplitude-frequency modulation (AM-FM) bimodal AFM

To further confirm the conclusions obtained from the theoretical calculations, we characterized Young’s modulus of microporous Eu-sph-MOF-3, mesoporous Eu-sph-MOF-4, and mesoporous Eu-sph-MOF-5 with the AF-FM mode of AFM (Figures 5 and S6). The tested crystals are in an octahedral shape with crystal diameters ranging from 100 to 200 µm (Figure S7). All characterizations are based on at least 512 × 512 tests on the triangle surface of crystals.

The Young’s modulus of sph-MOF-4 ranges from 1 to 6 GPa with an average value of 3.7 GPa (Figure 5B), and the Young’s modulus of sph-MOF-5 ranges from 3 to 12 GPa with an average value 7.8 GPa (Figure 5C). As expected, the mechanical stability of sph-MOF-5 is enhanced compared with sph-MOF-4, although they contain similar pore environments and structure sizes. The enhancement is contributed to the hexatopic BHBPB linker, which gives triangles rather than parallelograms in the structure (Figure S6).
The comparison of Young’s moduli between sph-MOF-3 and sph-MOF-5 shows the impact of sizes on the mechanical stabilities of sph platforms. The characterized Young’s modulus of sph-MOF-3 ranges from 7 to 18 GPa with an average value of 11.3 GPa (Figure 5A). Both sph-MOF-3 and sph-MOF-5 contain triangle rigidity, resulting in a much higher Young’s modulus compared with sph-MOF-4 (Figure 5D).

The characterized Young’s modulus of sph-MOF-3 is 1.45 times that of sph-MOF-5 (11.3 versus 7.8 GPa), and the experimental pore volume of sph-MOF-5 is 1.68 times the pore volume of sph-MOF-3 (0.72 cm$^3$·g$^{-1}$ versus 1.21 cm$^3$·g$^{-1}$), which indicates that a balance of pore volume and mechanical stability should be considered in the utilization of MOFs.

**DISCUSSION**

We have explored the mechanical stability principle in merged-net materials based on isoreticular RE-sph-MOFs. The results show that the combination of the merged-net approach and triangular rigidity is an effective strategy to attain high porosity and high stability material mutually. The successful design and synthesis of mechanically robust mesoporous Eu-sph-MOF-5 demonstrate the effectiveness of this strategy. This work signifies that the merged-net approach offers great potential for the design and synthesis of highly stable porous materials, which will accelerate the discovery of functional materials for catalysis and energy storage. Markedly, this study paves the way to systematically study all the potential merged nets and their associated mechanical stability.
EXPERIMENTAL PROCEDURES

Resource availability

Lead contact
Further information and reasonable requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Mohamed Eddaoudi (mohamed.eddaoudi@kaust.edu.sa).

Materials availability
The target materials can be synthesized following the procedures under experimental procedures and data in the supplemental information.

Data and code availability
Single-crystal structures of RE-sph-MOF-5 reported in this paper have been deposited at the Cambridge Crystallographic Data Center (CCDC). The accession number for the crystal structures is CCDC: 2174677. The data can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif. All the necessary data have been presented in the main text and supplemental information. This study did not generate code.

Synthesis of Eu-sph-MOF-3 and Eu-sph-MOF-4
Eu-sph-MOF-3 and Eu-sph-MOF-4 were synthesized by a modified condition of our reported procedure. Detailed synthesis conditions can be found in the supplemental information.

Synthesis of Eu-sph-MOF-5

Eu(NO$_3$)$_3$・5H$_2$O (18.7 mg), H$_3$TATB (5.3 mg), H$_6$BHBPB (10.1 mg), 2-FBA (400 mg), and DEF (6 mL) were combined and sonicated for 10 min. The solution was evenly distributed to four 20 mL scintillation vials. Extra 2-FBA (100 mg) was added to each vial. The vials were sealed, kept in a preheated oven at 115 °C for 2 days, and cooled to room temperature. The colorless polyhedral crystals were collected and washed with DMF.

Calculations of the mechanical properties
The moduli of elasticity, including bulk, shear, and Young’s moduli, are extracted from the stiffness matrix. We follow the same procedure of our previous work to compute the stiffness matrix, and we use a classical force field (Dreiding) by fixing the metal geometry to the experimental crystal structure as implemented in the large-scale atomic/molecular massively parallel simulator (LAMMPS) interface. In our previous work, we showed that these force fields provide sufficient accuracy in predicting the mechanical properties of MOFs. All calculations were carried out within the LAMMPS molecular simulation package.

To obtain the input files of the materials, we start with the single-crystal structure of RE-sph-MOFs. All the structures were prepared based on our published CIF files of sph-MOFs by manually removing solvent molecules and disorders. The corresponding structures of single-linker spn frameworks and hxg frameworks are obtained by removing one type of linker from the sph structures. Formates were used to replace the position of carboxylates in the removed linker.

AFM mechanical properties test
Topography images, elastic modulus, and indentation were acquired in AM-FM mode using an Oxford Instruments Asylum Research MFP-3D AFM equipped with the NanoMechPro tool option. The technique exploits a dual-resonance excitation allowing the real-time measurements of surface morphology, performed in AM
mode on the fundamental resonance of the cantilever, and mechanical properties were derived from FM mode using a higher overtone. For all the measurements, we used Asylum AC160TS-R2 silicon cantilevers with a nominal tip curvature radius of 8 nm and nominal spring constant of the fundamental harmonics (nominal resonance frequency: 300 kHz) of 42 N m⁻¹. Tip radius, oscillation amplitude, and cantilever spring constant were calibrated at each measurement, and measured values were used for Young’s modulus computation. More detailed methods of AFM mechanical properties tests can be found in the supplemental information.

**SUPPLEMENTAL INFORMATION**

Supplemental information can be found online at https://doi.org/10.1016/j.matt.2022.10.004.

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**AUTHOR CONTRIBUTIONS**


**DECLARATION OF INTERESTS**

The authors declare no competing interests.

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