

Porous, Crystalline Rectilinear Organic Frameworks from Linear Chain Packing

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Abstract

Porous crystalline organic materials have largely relied on macrocycles as topological rings to maintain porosity, which restricts the degree-of-freedom for structural dynamics and demands delicate synthetic control to avoid amorphous kinetic products. Here, we report rectilinear organic frameworks (ROFs) as a new class of crystalline porous materials composed of orderly packed linear polymer chains that can overcome the reliance on macrocycles. We synthesized twelve ROFs via linear polycondensation, nine of which resolved to atomic precision using electron diffraction. Their porosity emerges entirely from specific uniaxial or biaxial chain packing, governed by backbone stiffness and pendant groups that collaboratively frustrate dense packing. Linker elongation results in pore expansion, demonstrating modular material design and providing ROFs capable of gas separation. This macrocycle-free design enables efficient room-temperature scale-up, and structural transformations fundamentally unavailable to conventional frameworks. For a biaxial ROF, water adsorption triggers a coherent global rearrangement of chains, giving hydrogen-bonded water channels with high proton conductivity. Furthermore, we develop a crystal structure prediction method suitable for one-dimensional structures to analyze the energy landscape of ROFs and facilitating their rational design. Ultimately, ROFs establish a critical link between conventional linear polymers and reticular frameworks, providing a versatile platform for advanced porous materials.

Main

Porous crystalline organic materials combining the robustness of covalent linkages and the tunability of ordered pores are highly sought after for various applications^{1,2}. From covalent organic frameworks (COFs) to molecular cages, the design of these materials has relied exclusively on topological rings to maintain permanent porosity (Figs. 1a, b and c)³. While this ring-based approach imparts rigidity, it inherently restricts structural dynamics and demands delicate synthetic control to avoid the formation of amorphous kinetic products^{4,5}. Consequently, overcoming this reliance on topological rings could unlock a new material category fundamentally different from known porous polymers, cages, and frameworks, which could combine crystallinity, tunable porosity, rich structural dynamics and facile synthesis (Fig. 1d).

In this report, we design rectilinear organic frameworks (ROFs) as a new type of crystalline porous material made of orderly packed covalently linked linear polymer chains. Their chain packing geometries are governed by backbone stiffness and the interaction between pendant groups, which collaboratively frustrate dense packing to yield intrinsic void spaces. Herein, twelve ROFs are synthesized via linear (2 + 2) polycondensation, nine of which resolved to atomic precision using three-dimensional electron diffraction (3D ED). These ROFs can have uniaxial and biaxial chain packing, and their porosity emerges entirely from specific chain packing rather than covalent macrocycles. The porosity of these ROFs can be modularly tuned for gas separation and are stable under high pressure. As linear synthesis avoids kinetic fractal growth product typical of cross-linked networks, certain ROFs can be synthesized rapidly at room temperature, facilitating efficient scale-up. The macrocycle-free nature of ROFs affords a high

degree of freedom for individual chains, enabling structural transformations that are fundamentally unavailable to covalent frameworks and cages. In a ROF incorporating propanol pendant group, water adsorption triggers a coherent global rearrangement of chains, yielding an orders-of-magnitude increase in proton conductivity. This crystalline-to-crystalline structural transformation is fully elucidated by single-crystal analysis, which reveals the relative displacement between adjacent chains, specific water adsorptive sites and the hydrogen-bonded pathway in the pore for proton conduction. To facilitate the rational design of ROFs, computational methods suitable for periodic one-dimensional structures are developed based on crystal structure prediction (CSP) algorithms, which elucidate the complex interplay between intra-chain covalent bonding and inter-chain non-covalent interactions through energy calculation of a library of structures. The polymer CSP method developed here enables ROF structure determination from PXRD patterns and lower-resolution electron diffraction data, accelerating the development of new ROF architectures. The positions of the porous ROF structures on the solvent-free CSP landscape also indicate that most of them are locally stable phases with energy close to global thermodynamic minima.

ROFs represent a critical link between conventional linear polymers and reticular frameworks, where the linearity of their polymer chains and the porosity of the reticular frameworks combines to give unique guest-induced structural dynamics, synthetic scalability and associated functions. From a framework perspective, ROFs can be considered as frameworks made of genuine 1D building blocks. Notably, known “1D COFs” are ladder-type structures composed of fused macrocycles with pores similar to that of 2D COFs^{6,7}. From a polymer perspective, ROFs are crystalline porous polymers without chemical cross-linking. Conversely, crystalline 1D polymers made of flexible motifs or topochemical transformations are generally not porous^{8–10}, while porous 1D polymers such as polymers of intrinsic microporosity are generally not crystalline and have irregular void spaces¹¹. From a synthetic perspective, although crystalline polymers synthesized via condensation reactions have been sparsely reported^{12–15}, they are almost exclusively kinetic products of multidimensional “4 + 2” syntheses containing unreacted functional groups, rendering them unsuited for generalizable modular design. Therefore, ROFs establish a highly promising new class of porous materials with expansive structural scope and diverse prospective applications.

Establishment of concept prototype through “2 + 2” polycondensation

A prototypical ROF-102 is designed to demonstrate the concept of ROF, which involves using pendant groups installed along rigid 1D chains to sterically enforce an open scaffold (Fig. 2). ROF-102 was synthesized via imine condensation between 2,2'-bipyridine-5,5'-diamine (BPDA) and 2,5-bis(4-methoxyphenyl)terephthalaldehyde (MPTA) building blocks, with the methoxyphenyl pendant groups on the MPTA strategically introduced as spacer motifs between the polyimine chains (Figs. 2a and 2b, Supplementary Note 1). ROF-102 crystallizes as micron-sized blocks suitable for single-crystal electron diffraction characterization (Supplementary Fig. 1). 3D ED data and Pawley refinement of powder X-ray

diffraction pattern (PXRD) indicate a $P\bar{1}$ space group with lattice constants of $a = 9.56 \text{ \AA}$, $b = 11.51 \text{ \AA}$, $c = 12.77 \text{ \AA}$, $\alpha = 96.37^\circ$, $\beta = 95.66^\circ$, $\gamma = 90.96^\circ$ (Figs. 2c and 2d, Supplementary Table 1). Atomic-level crystal structural analysis by 3D ED reveals a strictly uniaxial packing geometry: the rigid linear chains align in parallel to form 2D layers, which subsequently stack to construct the 3D scaffold and generate continuous 1D channels along a axis (Supplementary Figs. 2 and 3). Within these layers, the methoxyphenyl pendant groups of adjacent chains mutually interlock, acting as pillars that prop open the pore. Adjacent layers are correlated by inversion centers located between them, resulting in a slight offset for the methoxyphenyl groups. Independent Gradient Model based on Hirshfeld partition (IGMH) calculations confirm that the chains interact exclusively through weak van der Waals forces¹⁶, demonstrating that backbone stiffness and pendant group geometries, rather than strong structural-directing inter-chain interactions, is the primary driver of framework formation (Supplementary Figs. 4). The resulting crystallographic largest free sphere is approximately $4.2 \text{ \AA}$, which show CO_2 uptake at 195 K (Supplementary Figs. 5). The composition and bonding of ROF-102 is also confirmed by solid-state nuclear magnetic resonance (ss-NMR), elemental analysis (EA), Thermo gravimetric analysis (TGA) and infrared spectroscopy (Supplementary Figs. 6–8).

The prototypical ROF-102 shows the ROF structures are governed by the interplay between covalent bonding within the chain and non-covalent interaction between the chains. Consequently, topological design that primarily addresses covalent connectivity of COFs is not suitable for ROFs. On the other hand, crystal structure prediction (CSP), a computational method developed for molecular crystal design that can account for noncovalent interactions is adapted to understand ROFs formation. The CSP approach involves generating a library of structures and finding the energy minima that corresponds to potential polymorphs. Standard CSP workflows treats discrete molecules as the basic building block, which cannot be directly used for extended structures. We therefore built on our previously published BOMLIP-CSP framework and extended it to enable systematic energy-density landscape sampling for the packing of infinitely long 1D polymer chains under periodic boundary conditions. For ROF-102, the packing-similarity analysis shows that the best predicted structures match the experimental packings closely (Supplementary Fig. 9). This supports that the modified CSP strategy can be used for reliable crystal structure prediction and landscape analysis in 1D polymer-chain systems. The energy-density landscape analysis shows that the uniaxial structures are relatively stable compared to those with higher dimension intercrossing (Fig. 2e). DFT calculation shows experimentally obtained ROF-102 have energy 8.96 kJ mol^{-1} higher than global minimum (Fig. 2f), which features non-accessible pockets (Supplementary Fig. 10). These findings suggest that, although the porous ROF structures are metastable on the solvent-free energy landscape, they can be stabilized under synthetic conditions by guest molecules within the porous scaffold.

Modular pore expansion of uniaxial ROFs and scalable synthesis

With the basic structural paradigm established, the capacity for modular pore expansion is then demonstrated for ROFs, which is key to the rational design of porous materials (Fig. 3). By retaining the pendant-bearing aldehyde linker MPTA of ROF-102 but substituting an extended amine linker (4,4'-Diamino-*p*-terphenyl, DAT), we synthesized and characterized ROF-105 (Supplementary Figs. 11–19).

ROF-105 also crystallize in $P\bar{1}$ space group with lattice constants of $a = 10.20 \text{ \AA}$, $b = 11.60 \text{ \AA}$, $c = 17.02 \text{ \AA}$, $\alpha = 94.68^\circ$, $\beta = 102.50^\circ$, $\gamma = 88.12^\circ$ (Supplementary Fig. 11). Crystal structure solution resolved from 3D ED confirms that ROF-105 maintains a uniaxial rod-packing geometry with one-dimensional pores along a axis, similar to ROF-102 (Figs. 3a and 3b, Supplementary Figs. 12–14, Supplementary Table 2). With the extended DAT linker, ROF-105 exhibits an expanded pore size of $5.3 \text{ \AA}$, which is accessible to N_2 and give a BET surface area of $207 \text{ m}^2/\text{g}$ (Fig. 3c). The composition and bonding of ROF-105 is also confirmed by ss-NMR, EA, TGA and infrared spectroscopy (Supplementary Figs. 15–17). Computational analysis based on CSP successfully identify the experimental ROF-105 structure and the energy landscape analysis show that it is 7.33 kJ/mol higher than the global minima (Fig. 3g, Supplementary Fig. 18), which is also a structure with non-accessible pockets (Supplementary Fig. 19).

We then harness the modular tunability of ROFs to design new architectures for proof-of-concept gas separation applications. To obtain suitable pore size for selective gas uptake, 4,4'-(anthracene-9,10-diyl)dianiline (ADA) is used to react with MPTA to form ROF-113 (Fig. 3d, Supplementary Figs. 20–34). The ADA linker has two more fused phenyl ring on the anthracene motif compared to the DAT linker of ROF-105, thus would give partitioned pore with smaller aperture. ROF-113 also crystallize in $P\bar{1}$ space group with lattice constants of $a = 6.26 \text{ \AA}$, $b = 10.72 \text{ \AA}$, $c = 15.91 \text{ \AA}$, $\alpha = 99.22^\circ$, $\beta = 97.26^\circ$, $\gamma = 102.59^\circ$ (Supplementary Fig. 20). Atomically resolved crystal structure of ROF-113 from 3D ED data shows uniaxial rod packing and one-dimensional pore along a axis, similar to ROF-102 and 105 (Supplementary Fig. 21–24, Supplementary Table 3). The interdigitation of pendant groups between adjacent offset chains gives $3.7 \text{ \AA}$ pore aperture and $5.2 \text{ \AA}$ pore cavity accessible to gases (Fig. 3e, Supplementary Fig. 25), which is suitable for the separation of CH_4 , CO_2 and C_2 hydrocarbons (Fig. 3f). The composition and bonding of ROF-113 is also confirmed by ss-NMR, EA, TGA and infrared spectroscopy (Supplementary Figs. 26–28). Remarkably, because ROF synthesis relies on discrete 1D chain elongation rather than the defect-correction processes required to close macrocycles in 2D/3D COFs, these materials exhibit high scalability. The synthesis of ROF-113 can be scaled to the gram level at room temperature in less than 10 mL of ethanol within 5 minutes, yielding highly crystalline material (Supplementary Figs. 21b and 29). The ability of scalable synthesis provides adequate material for CO_2/CH_4 breakthrough measurement at various pressures, which show separation ability consistent with the single component gas uptake (Supplementary Fig. 30). Notably, although the polyimine chains are not covalently cross-linked and interact exclusively through weak van der Waals forces (Supplementary Fig. 31), the crystallinity and separation ability of ROF-113 are maintained at 50 bar, indicating structural stability at high pressure (Supplementary Figs. 29 and 32). Computational analysis based on CSP also successfully identify the experimental ROF-113 structure (Fig. 3h, Supplementary Fig. 33). DFT calculation shows the ROF-113 structure is only 8.19 kJ mol^{-1} above the global minimum, which is also

a structure with non-accessible pockets (Supplementary Fig. 34). Considering its low relative lattice energy and the possible stabilization of the porous scaffold by solvent molecules in the pores, ROF-113 may be thermodynamically favored under synthetic conditions, consistent with its facile synthesis.

Combining the structural and computational analyses of ROF-102, ROF-105, and ROF-113 shows that all three experimentally observed structures adopt similar uniaxial rod-packing geometries with one-dimensional pores along the *a* axis and correspond to low-energy local minima on the solvent-free CSP landscapes, lying within 10 kJ mol⁻¹ of their respective global minima. Such observation indicates the noncovalent interactions associated with the methoxyphenyl pendant group, combined with the stiffness of 1D polyimine rod, have strong structure-directing effect similar to how covalent linkages and building block geometries would combine to enforce pre-determined topology in reticular frameworks. Consequently, it would also be possible to use structural-directing pendant groups to construct more complex ROF structures.

Design of biaxial ROF series with imine and hydrazone linkages

Biaxial ROFs with intercrossing chains could give much higher structural diversity and richer dynamics compared to uniaxial structures. We now harness the structural-directing role of anthracene motif to construct a series of biaxial ROFs (Fig. 4). Reacting 4,4'-(anthracene-9,10-diyl)dibenzaldehyde (ADBA) and *p*-phenylenediamine (PDA) give ROF-201 as micron size single crystals (Figs. 4a, Supplementary Fig. 35), which has a *C2/c* space group with lattice constants of *a* = 37.85 Å, *b* = 9.54 Å, *c* = 8.40 Å, β = 93.29° (Supplementary Fig. 36–37, Supplementary Table 5). ROF-201 has two set of parallel polyimine chains, with the first set going through the origin of the cell and propagating along $[11\ \bar{2}]$ and the other going through the center of the cell and propagating along $[\bar{1}\ 12]$ direction (Figs. 4b, d and e). The parallel chains within the same set are correlated by the *C*-centering translational symmetry while the intercrossing chains are correlated by rotational symmetry. The two set of chains intercross at a 25-degree angle to give interconnected open pores, which has aperture of 3.47 Å along *c* axis accessible to N₂ gas (Supplementary Fig. 38). The composition and bonding of ROF-201 is also confirmed by ss-NMR, EA, TGA and infrared spectroscopy (Supplementary Figs. 39–41). The biaxial chain arrangement of ROF-201 is driven by the non-covalent interactions and the linearity of the polyimine chain, where the anthracene motif is responsible for the steric interdigitation. CSP calculations, further adapted to evaluate biaxial structure with higher symmetry, suggest that the experimentally observed biaxial ROF-201 structure occupies an isolated, local minimum spike on the energy-density landscape, rather than belonging to the broad basin associated with the global minimum (Fig. 4c, Supplementary Figs. 42–44). This landscape feature is reminiscent of those observed in some porous organic molecular crystals¹⁷.

To obtain series of biaxial ROFs with improved chemical stability, six functionalized terephthalohydrazides (TPHZ) is used to synthesize hydrazone linked ROFs with the ADBA linker. Reacting 2,5-diethoxyterephthalohydrazide and ADBA give ROF-204 as micron size crystals

(Supplementary Figs. 45). Its crystal structure can only be partially obtained as molecular fragments from 3D ED data, which provide information that can be used to reduce the dimension of conformation search in polymer CSP (Supplementary Fig. 46). By adopting the predicted unit cell and atomic coordination, structure refinement using 3D ED data provides a reasonable model with low R values (Supplementary Table 6, Supplementary Figs. 47–49). The ROF-204 structure also has a $C2/c$ space group with lattice constants of $a = 44.85 \text{ \AA}$, $b = 9.35 \text{ \AA}$, $c = 8.04 \text{ \AA}$, $\beta = 80.94^\circ$, which has a biaxial structure with almost identical chain spatial arrangement as ROF-201 (Supplementary Figs. 50–51). Reacting 2,5-dimethoxyterephthalohydrazide and ADBA give ROF-203, whereas 3D ED fails to resolve the crystal structure due to limited resolution (Supplementary Figs. 52). Polymer fCSP is used to directly identify an energetically plausible structure that matches PXRD data, which has the same backbone structure as ROF-204 (Figs. 4h and 4i, Supplementary Fig. 53). Notably, although topology-guided modeling with PXRD validation has been applied to conventional COFs, structural modeling of ROFs pose a greater challenge because their crystal structures lack pre-defined topologies. The structural study of ROF-203 and 204 shows the power of combining experimental and computational method to expedite ROF development, and the CSP calculation provide important insight on the energy landscape of ROFs with different chain spatial arrangements (Supplementary Figs. 54–56).

Hydrazone-linked Biaxial ROFs with more flexible pendant groups can also be obtained. Reacting 2,5-bis(2-methoxyethoxy)terephthalohydrazide and ADBA give ROF-211 as single crystals that can be solved by 3D ED with atomic resolution (Fig. 4c and 4f, Supplementary Figs. 57–58). ROF-211 also has a $C2/c$ space group with lattice constants of $a = 45.87 \text{ \AA}$, $b = 9.43 \text{ \AA}$, $c = 8.34 \text{ \AA}$, $\beta = 98.44^\circ$ and the same biaxial chain spatial arrangement as ROF-203, 204 and 201 (Fig. 4f, Supplementary Table 7, Supplementary Fig. 59). ROF-211 is also confirmed by ss-NMR, EA, TGA and infrared spectroscopy (Supplementary Figs. 60–62). Notably, although the methoxyethoxy side chains of ROF-211 are highly flexible and can give hydrogen bonding, it did not alter the specific biaxial chain packing geometry, which indicates the stiffness of extended 1D chain enable ADBA to play an important structural directing role as supramolecular registry between adjacent intercrossing chains. The generality of biaxial ROF structure design is further demonstrated by the synthesis of ROF-205 and 206, which is made by reacting 2,5-bis(allyloxy)- and 2,5-bis(prop-2-yn-1-yloxy)terephthalohydrazide with ADBA, respectively. Both ROF-205 and 206 show similar PXRD patterns as ROF-203, 204 and 211, indicative of similar structural backbone (Supplementary Fig. 63). All ADBA based ROFs show photoluminescence under UV light with quantum yield from few to 20%, and the photophysical properties are affected by the pendant groups (Supplementary Fig. 64).

Structural dynamics of biaxial ROFs and proton conductivity

Compared to higher dimensional covalent frameworks, ROFs can show unique dynamics associated with the degree-of-freedom of individual chains, which can bring new functions (Fig. 5). To demonstrate such dynamics, ROF-212 is synthesized by reacting 2,5-bis(3-hydroxypropoxy)terephthalohydrazide and ADBA as micron sized crystals (Fig. 5a, Supplementary Figs. 65). ROF-212, in its hydrated phase

(denoted as ROF-212-h), shows a similar structure as ROF-211, having a $C2/c$ space group, lattice constant of $a = 45.10 \text{ \AA}$, $b = 9.72 \text{ \AA}$, $c = 8.05 \text{ \AA}$, $\beta = 99.59^\circ$ and the same biaxial chain arrangement resolved by 3D ED with atomic resolution (Figs. 5b, 5c, Supplementary Table 8, Supplementary Figs. 66–67). The adsorbed water molecules are clearly identified by cryo-3D ED, which align along c axis in the channel, forming a hydrogen-bonded pathway with the hydroxypropoxy pendant groups (Fig. 5d). Such water chain gives high room temperature proton conductivity of $3.3 \times 10^{-4} \text{ S/cm}$ without any additional acidic proton source, which is corroborated with conductivity measurement on D_2O hydrated sample and a micron-size single crystal sample (Supplementary Figs. 68–69)^{18–20}. Upon dehydration, ROF-212-h show phase transformation to give ROF-212-v structure which is also resolved by 3D ED with atomic resolution (Fig. 5e, Supplementary Figs. 70–71). In this crystal-to-crystal transformation, the chains move with respect to each other, changing the inter-chain distance and slide offset accompanied by conformational change within the chain (Fig. 5f). Such dynamic process results in overall reduction in symmetry, leading to $P\bar{1}$ space group for ROF-212-v (Supplementary Table 9). Such transformation is only possible when chains that are not restricted by covalent bonding and can undergo global structure rearrangement, which is a unique feature for ROFs. The phase change is reversible and can be triggered by water adsorption and desorption, which gives a stepwise water adsorption isotherm (Supplementary Fig. 72). The dehydration induced phase change is accompanied by a change in photoluminescence and loss of proton conductivity, potentially applicable for humidity sensing (Supplementary Fig. 73). ROF-212 is also confirmed by ss-NMR, EA, TGA and infrared spectroscopy (Supplementary Figs. 74–76).

The generality of biaxial dynamic structure design is further demonstrated with linkers without the anthracene motif. ROF-301, synthesized by reacting 2',5'-dimethoxy-[1,1':4',1''-terphenyl]-4,4''-dicarbaldehyde (DMTDA) with 2,5-bis(2-methoxyethoxy)terephthalohydrazide, also show a biaxial structure characterized by 3D ED with atomic resolution (Supplementary Figs. 77–79, Supplementary Table 10), which is characterized by ss-NMR, IR, TGA and water adsorption isotherm (Supplementary Figs. 80–84). Another dynamic biaxial structure ROF-302 is synthesized with DMTDA and 2,5-diethoxyterephthalohydrazide, which is resolved by 3D ED with atomic resolution and characterized by NMR, IR, TGA techniques (Supplementary Figs. 85–90, Supplementary Table 11). ROF-302 shows a stepwise water adsorption isotherm and change in PXRD pattern upon hydration, which indicates structural dynamics triggered by water adsorption (Supplementary Figs. 91–92).

In summary, we have reported rectilinear organic frameworks as a new type of porous crystalline organic material made of covalently linked linear chains, which shows permanent porosity by order chain packing. The ROFs can be modularly designed with uniaxial and biaxial structures and have tunable and stable pores applicable for gas separation. The macrocycle-free feature of ROFs not only make them fundamentally different from known COFs and cages, but also endows facile synthesis and unique global dynamics giving rise to tunable proton conductivities and fluorescence. Computational methods are developed to understand the formation of ROFs and facilitate their structure design and determination, which would enable rational and efficient ROF development in the future.

Method

Synthesis of ROF-102. 2,2'-bipyridine-5,5'-diamine (BPDA, 11.1 mg, 0.06 mmol) and 2,5-bis(4-methoxyphenyl) terephthalaldehyde (MPTA, 17.3 mg, 0.05 mmol) were weighed and placed in a 10 mL glass vial. A solvent mixture (1,4-dioxane : mesitylene = 1:2, 3 mL) was added, and the mixture was ultrasonically dissolved at room temperature to form a uniformly dispersed suspension. Then, 0.2 mL of acetic acid (12 M) was added. The solution was subsequently placed in an oven at 80°C for 3 days, the orange-colored solid was separated by centrifugation, and washed with tetrahydrofuran (THF) for three times. The solid was then evacuated at 80°C overnight to obtain ROF-102. Elemental analysis calcd (%) for $C_{32}H_{24}N_4O_2 \cdot 2H_2O$: C 72.18, H 5.26, N 10.53; found: C 72.24, H 4.81, N 9.33.

Synthesis of ROF-113. MPTA (17.3 mg, 0.05 mmol) and 4,4'-(anthracene-9,10-diyl)dianiline (ADA, 18 mg, 0.05 mmol) were weighed and placed in a 10 mL glass vial. A solvent mixture (1,4-dioxane: mesitylene = 1:2, 3 mL) was added, and the mixture was ultrasonically dissolved at room temperature to form a uniformly dispersed suspension. Then, 0.2 mL of acetic acid (12 M) was added. The solution was subsequently placed in an oven at 80°C for 3 days, the solid was separated by centrifugation, and washed with THF for three times. The solid was then evacuated at 80°C overnight to obtain ROF-113. Elemental analysis calcd (%) for $C_{24}H_{17}NO$: C 85.97, H 5.07, N 4.18; found: C 84.3, H 4.9, N 4.04.

Scalable Synthesis of ROF-113. MPTA (346 mg, 1 mmol) and 4,4'-(anthracene-9,10-diyl)dianiline (ADA, 360 mg, 1 mmol) were weighed and placed in a 100 mL glass vial. 60 mL ethanol (EtOH) was added, and the mixture was ultrasonically dissolved at room temperature to form a uniformly dispersed suspension. Then, 2 mL of acetic acid (12 M) was added. The solution was subsequently placed in fume hood at room temperature for 30 minutes, the solid was separated by centrifugation, and washed with EtOH for three times. This solid was then evacuated at 80°C overnight to obtain scalable prepared ROF-113.

Synthesis of ROF-201. A 1,4-dioxane/mesitylene (0.4 mL/0.8 mL) mixture of 4,4'-(anthracene-9,10-diyl)dibenzaldehyde (ADBA, 9.7 mg, 0.025 mmol) and p-phenylenediamine (PDA, 3.2 mg, 0.03 mmol) and 0.1 mL of acetic acid (12 M) were added to an ampoule (2 mL). The ampoule was degassed by three freeze-pump-thaw cycles and sealed by flame. The ampoule was subsequently placed in an oven at 80°C for 3 days, the solid was separated by centrifugation, and washed with THF for three times. The solid was then evacuated at 80°C overnight to obtain ROF-201. Elemental analysis calcd (%) for $C_{17}H_{11}N$: C 89.08, H 4.8, N 6.11; found: C 87.19, H 5.723, N 5.09.

Synthesis of ROF-211. 2,5-bis(2-methoxyethoxy)terephthalohydrazide (TPHA-OCH₂CH₂OCH₃, 17.1 mg, 0.05 mmol) and ADBA (17.3 mg, 0.05 mmol) were weighed and placed in a 10 mL glass vial. A solvent mixture (1,4-dioxane : mesitylene = 1:2, 3 mL) was added, and the mixture was ultrasonically dissolved at room temperature to form a uniformly dispersed suspension. Then, 0.2 mL of acetic acid (12 M) was added. The solution was subsequently placed in an oven at 80°C for 3 days, the solid was separated by centrifugation, and washed with THF for three times. The solid was then

evacuated at 80°C overnight to obtain ROF-211. Elemental analysis calcd (%) for C₂₁H₁₈N₂O₃·H₂O: C 69.23, H 5.49, N 7.69; found: C 70.68, H 5.4, N 7.9

Synthesis of ROF-105, 212, 203, 204, 205, 206, 301, 302 can be found in Supplementary Information.

Three-dimensional electron diffraction (3D ED). The data were collected either on a JEOL JEM-2100 Plus transmission electron microscope (TEM) using a TVIPS camera or a JEOL JEM-F200 using an ASI Cheetah 1800 hybrid pixel detector. For the sample preparation of most ROF specimens, one drop of THF dispersion containing the ROF sample was dropped onto a carbon film-supported TEM copper grid. After the evaporation of the solvent in air, the grid was transferred to a TEM high-tilt holder (+ 70° rotation) and loaded into the TEM for 3D ED data collection. For ROF-212-H, the sample was prepared by a plunge freezing method^{21,22}. A drop of H₂O containing the ROF sample was deposited onto a carbon film-supported TEM copper grid. After removal of excess H₂O, the grid was transferred under water-vapor-saturated conditions to a Gatan 914.6 cryogenic holder in a Gatan cryo-sample preparation workstation. After insertion into the workstation, the sample-containing part of the cryogenic holder was immersed in liquid nitrogen. The Dewar tank was then cooled with liquid nitrogen until the cryogenic holder stabilized at liquid-nitrogen temperature. The cryogenic holder was subsequently loaded rapidly into the TEM for cryo-3D ED data collection.

The 3D ED datasets were collected through a modified INSTAMATIC software²³. The 3D ED datasets were processed using an XDS data processing software²⁴. The initial structure was resolved by either a direct method using SIR2019 software²⁵ or an intrinsic phasing method using a SHELXT²⁶ program in an OLEX2 software²⁷, followed by a refinement least-square procedure using SHELXL²⁸. 3D ED reconstruction was processed by a PETS2 software²⁹.

Overall Workflow of Crystal Structure Prediction for Polymer (Polymer CSP). The crystal structure prediction strategy employed in this study uses a quasi-random search algorithm, which was adapted and further developed from the protocol previously established BOMLIP-CSP³⁰ by our group for molecular crystals. Similar to conventional CSP workflows, the procedure begins with the identification of conformers of the minimum repeating unit, followed by the generation of a large number of potential crystal structures using a quasi-random sampling approach. The candidate structures are then geometrically optimized and ranked according to their lattice energies. After the removal of duplicate structures, low-energy candidates are further re-optimized using density functional theory (DFT)-level calculations. Where possible, the predicted structures are subsequently validated against the target structures by comparing their PXRD patterns. Details of computational methods involved in Polymer CSP can be found in Supplementary Information.

Gas adsorption. Ultrahigh-grade gases (99.999%) such as He, N₂, CO₂, C₂H₂, C₂H₆, CH₄ were used throughout the experiments. Low-pressure gas adsorption isotherms were measured volumetrically using a Microtac BELsorp Max gas sorption analyzer. Liquid nitrogen bath and dry ice-methanol baths

was used for the temperatures controlled at 77K and 195K. Water bath with circulator were used for temperatures controlled at 298 K.

Proton Conductivity Characterizations. After the ground powder sample (ROF-212) was fully exposed to an aqueous environment, it was loaded into a 10-mm test mold and pressed under high pressure for 1 min to form a pellet. Then, the proton conductivities were determined using a.c. impedance spectroscopy (Solartron SI 1260 Impedance/Gain-Phase analyser) over the frequency range 1 Hz–10 MHz and with an input voltage amplitude of 100 mV. ZView software was used to extrapolate impedance data results by means of an equivalent circuit simulation to complete the Nyquist plot and obtain the resistance values. The proton conductivity (σ) was calculated using the following equation: $\sigma = L/(R \cdot S)$, where L is the pellet thickness, R is the pellet resistance, and S is the pellet area.

Details of other characterizations methods can be found in Supplementary Information.

Declarations

Contribution

Q. C., Y. L. synthesized and characterized the ROFs; S. W. and Y. Ma carried out 3D ED and determined the structure; C. Z, D. F., L. C. and J.J developed polymer CSP and conducted computational analysis. Y. Z. conceived the project and the concept of ROFs and led the writing of the manuscript with contributions from all co-authors

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Data Availability

All data supporting the findings of this study are available within the paper and its Supplementary Information files. Crystallographic data for the ROFs in this Article have been deposited at the Cambridge Crystallographic Data Centre (CCDC) (CCDC 2539225 for ROF-102, CCDC 2539303 for ROF-

105, CCDC 2539226 for ROF-113, CCDC 2539307 for ROF-201, CCDC 2547691 for ROF-204, CCDC 2539308 for ROF-211, CCDC 2540426 for ROF-212-h, CCDC 2543345 for ROF-212-v, CCDC 2539874 for ROF-301, CCDC 2539875 for ROF-302). Copies of the data can be obtained free of charge at <https://www.ccdc.cam.ac.uk/structures/>.

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Figures

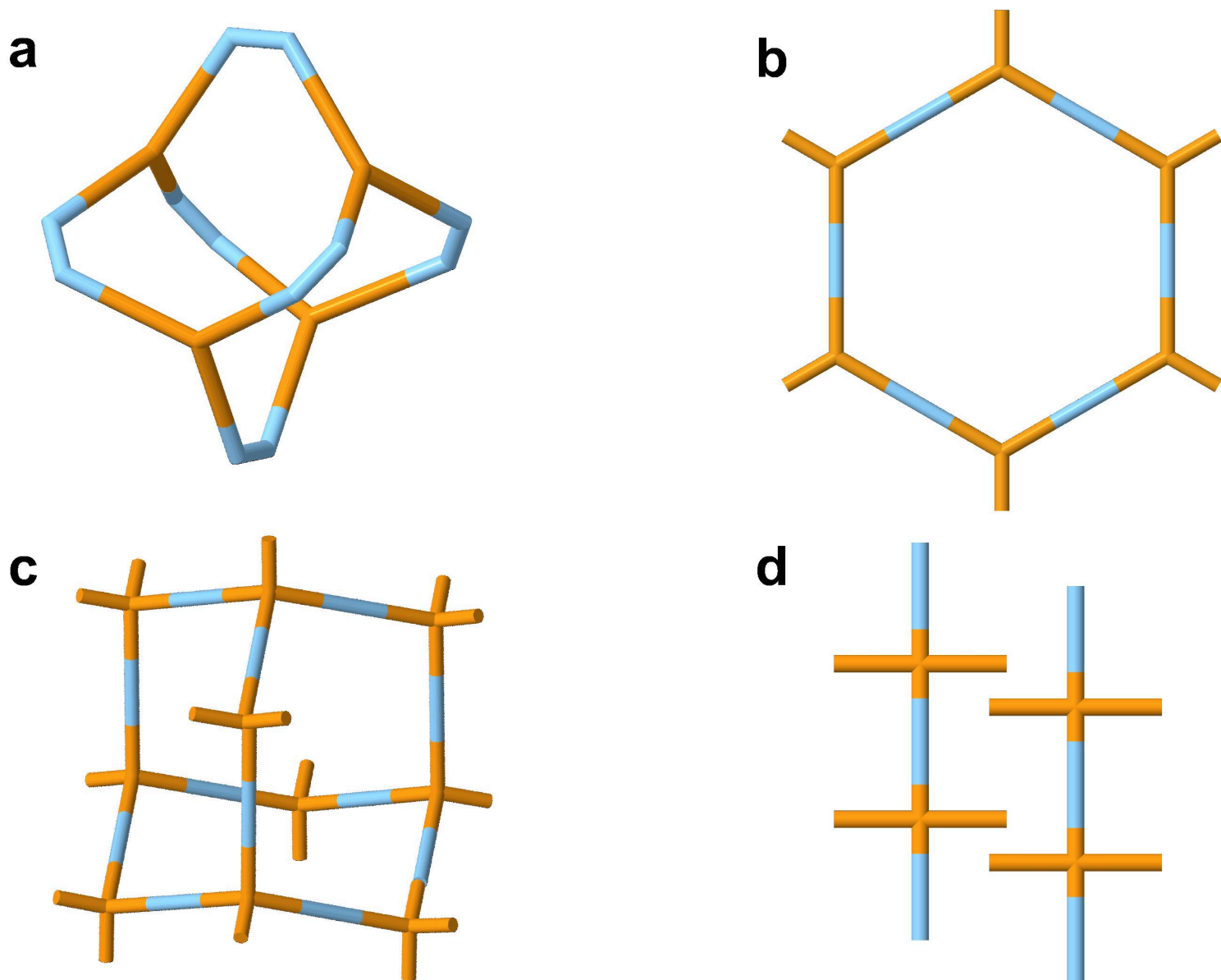


Figure 1

Macrocycle-free pore construction of ROFs compared to COFs and cages. The porosity of cages (a), layered and ladder-type COFs (b) and 3D COFs (c) are based on macrocycles whereas the porosity of ROFs is based on linear chain packings (d).

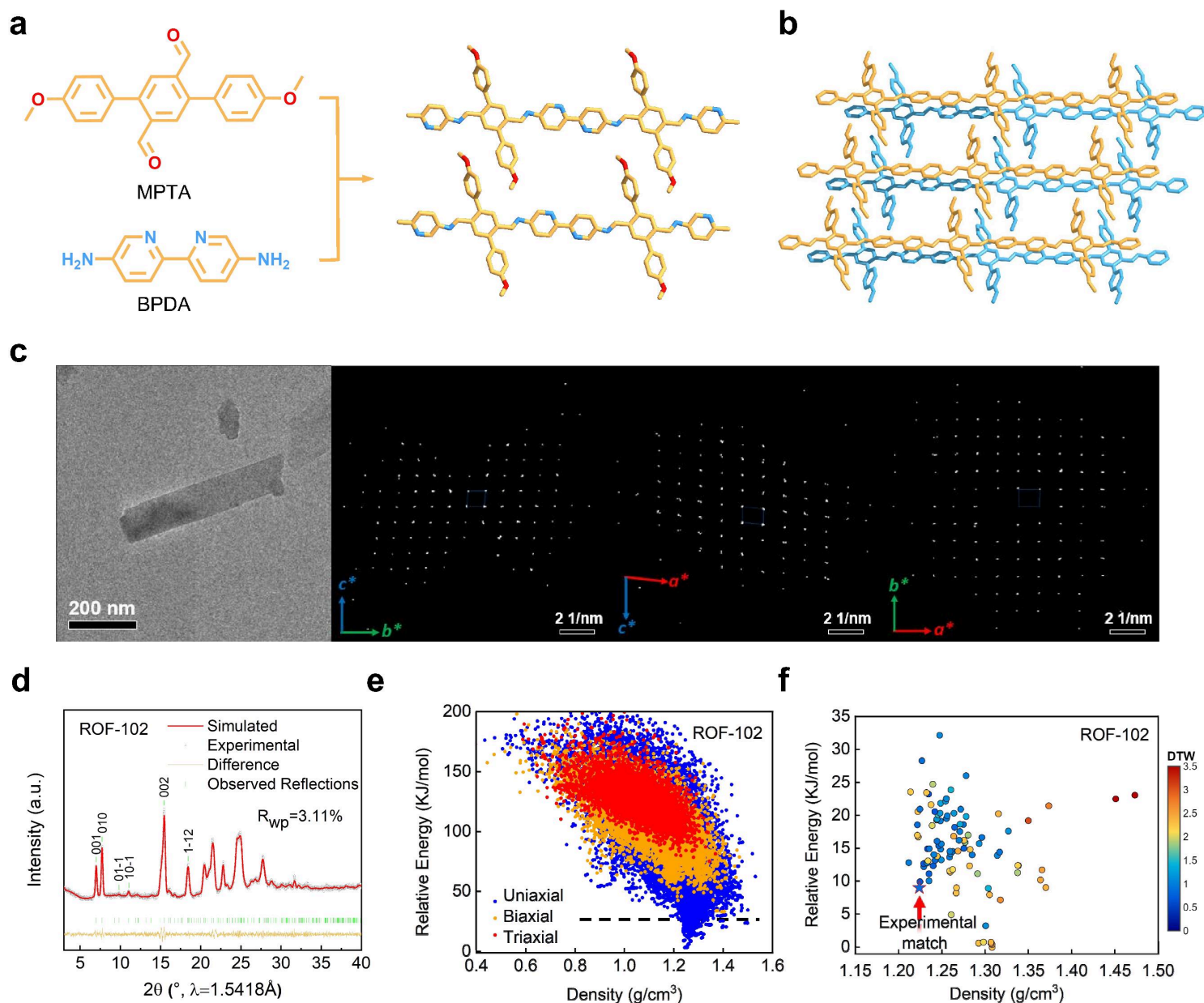


Figure 2

Construction and analysis of ROF-102 as a concept prototype. ROF-102 is synthesized through imine condensation of MPTA and BPDA where polyimine chains first pack into layers (**a**) and then stack to give 3D open frameworks (**b**). The crystal structure is determined with atomic resolution by 3D ED (**c**) and the phase purity is confirmed by Pawley refinement of PXRd pattern (**d**). The CSP energy landscape of ROF-102 is evaluated using a machine-learning potential with structures colored according to their axial dimensionality (**e**), where the dashed line indicates the top 100 lowest-energy structures. These structures are selected for DFT re-optimization that gives energy landscape (**f**), where the points are colored according to the dynamic time warping score between the simulated and experimental PXRd patterns. The red arrow marks the structure identified as the experimental match.

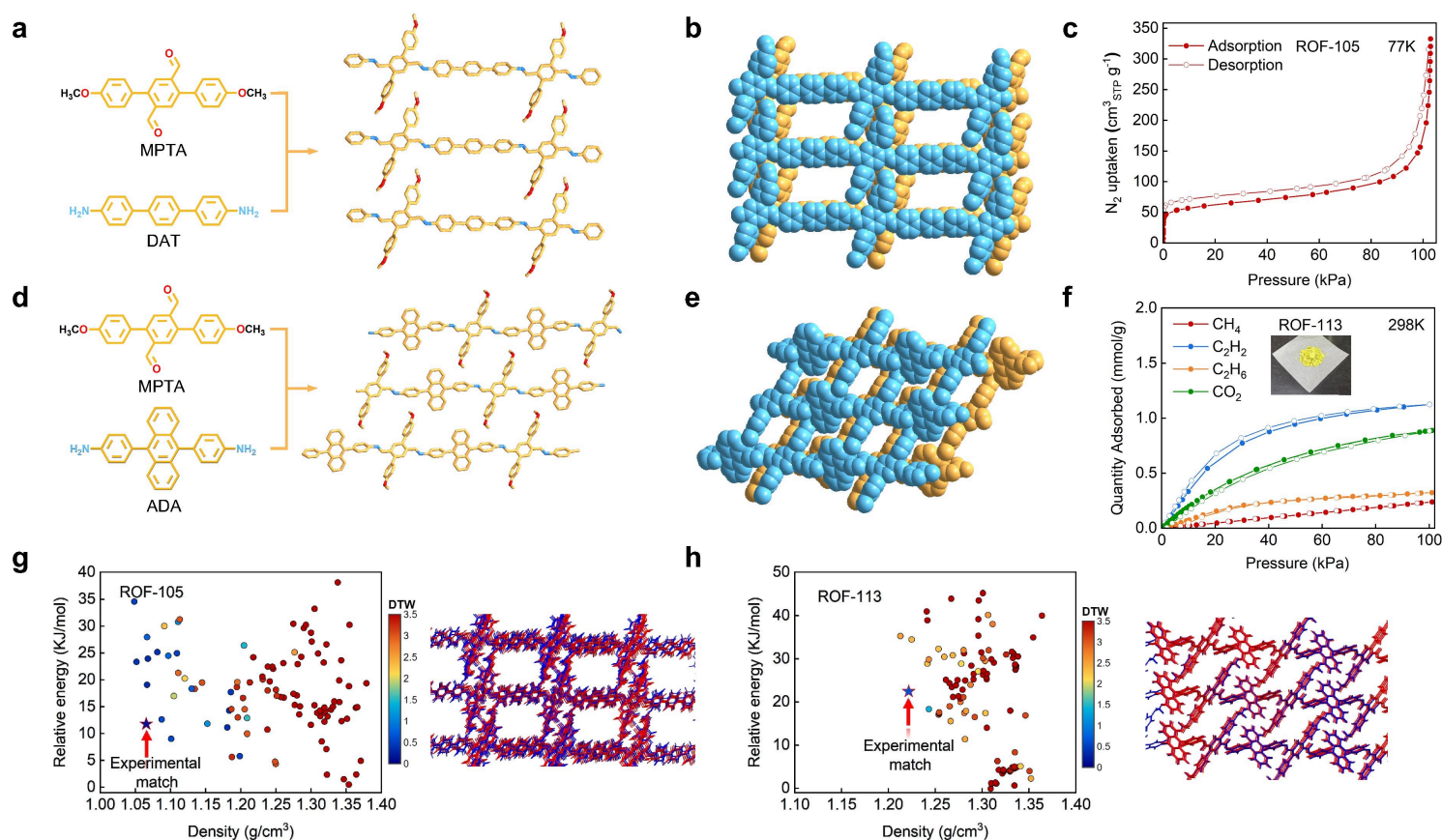


Figure 3

Modular design and pore expansion of uniaxial ROFs. ROF-105 is synthesized with MPTA and an elongated diamine building block DAT (**a**), which has a similar uniaxial structure as ROF-102 with expanded 1D pores (**b**). 77 K N_2 adsorption isotherm of ROF-105 showing surface area of $207 m^2/g$ (**c**). ROF-113 is obtained by reacting MPTA with an anthracene-based diamine ADA (**d**), which gives smaller pore opening compared to ROF-105 (**e**) suitable for separating CO_2 , CH_4 and C_2 hydrocarbons (**f**). Gram scale ROF-113 can be synthesized in 10 ml ethanol at room temperature within 5 min (**f**, inset). **g**, **h**, Energy landscape of the selected low-energy structures after DFT re-optimization for ROF-105 and ROF-113 with overlays of predicted and experimental structures. The points are colored according to the dynamic time warping (DTW) score between the simulated and experimental PXRD patterns. The red arrow marks the structure identified as the experimental match.

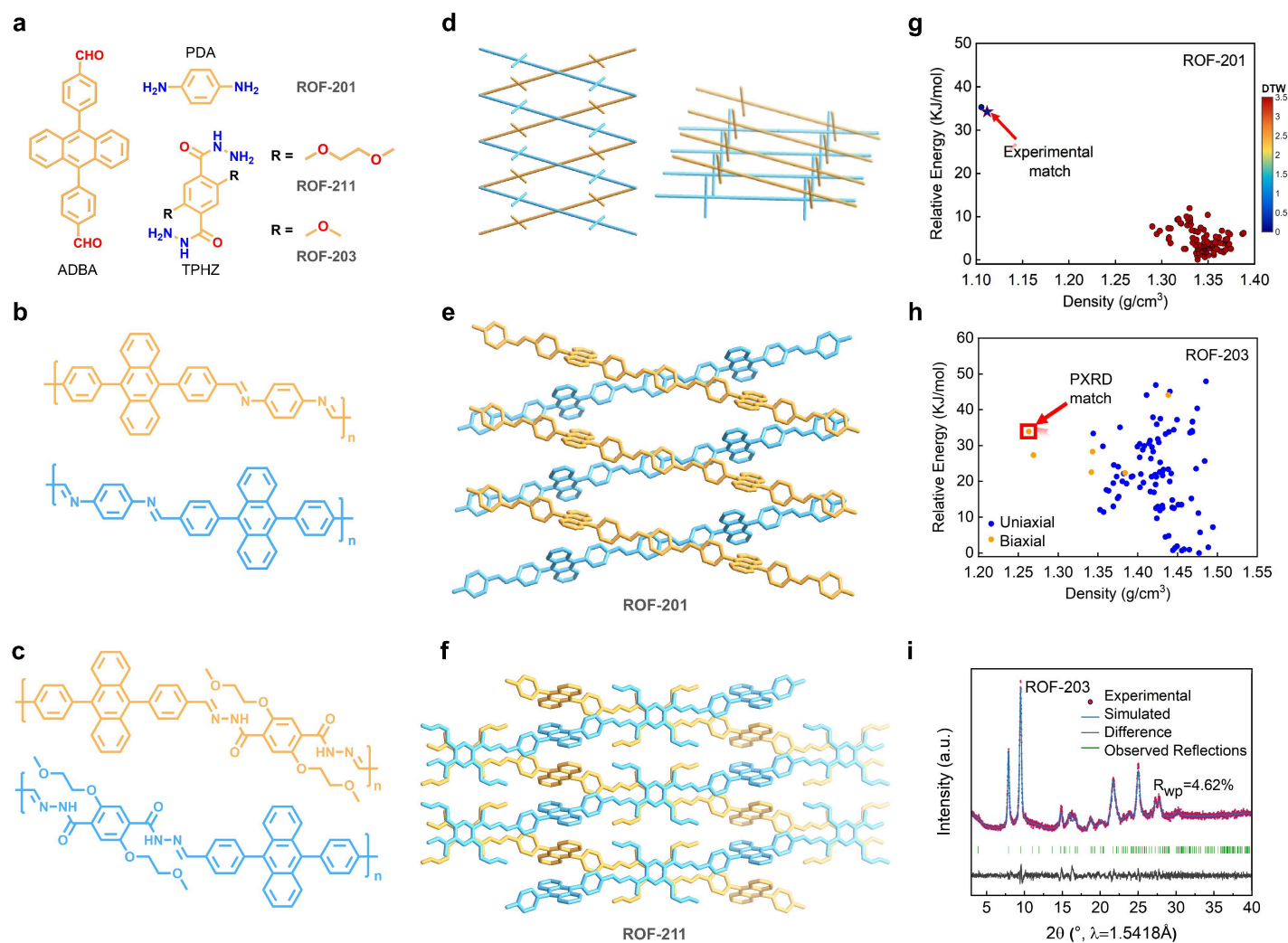


Figure 4

Modular design of biaxial ROFs. ADBA linker is used to construct biaxial ROFs with PDA and terephthalohydrazide linkers (**a**), which gives imine-based ROF-201 (**b**) and hydrazone-linked ROF-203 and ROF-211 (**c**). All three ROFs have biaxial structure with two set of mutually intercrossing chains (**d**). The structures of ROF-201 and ROF-211 are determined by 3D ED with atomic resolution (**e**, **f**). CSP calculations suggest ROF-201 structure occupies an isolated, local minimum spike on the energy-density landscape (**g**). The points are colored according to the dynamic time warping (DTW) score between the simulated and experimental PXRD patterns. Polymer CSP for ROF-203 identified a biaxial structure in the energy landscape matching the experimental PXRD (**h**), which is used as structure model for Pawley refinement to give the ROF-203 structure (**i**).

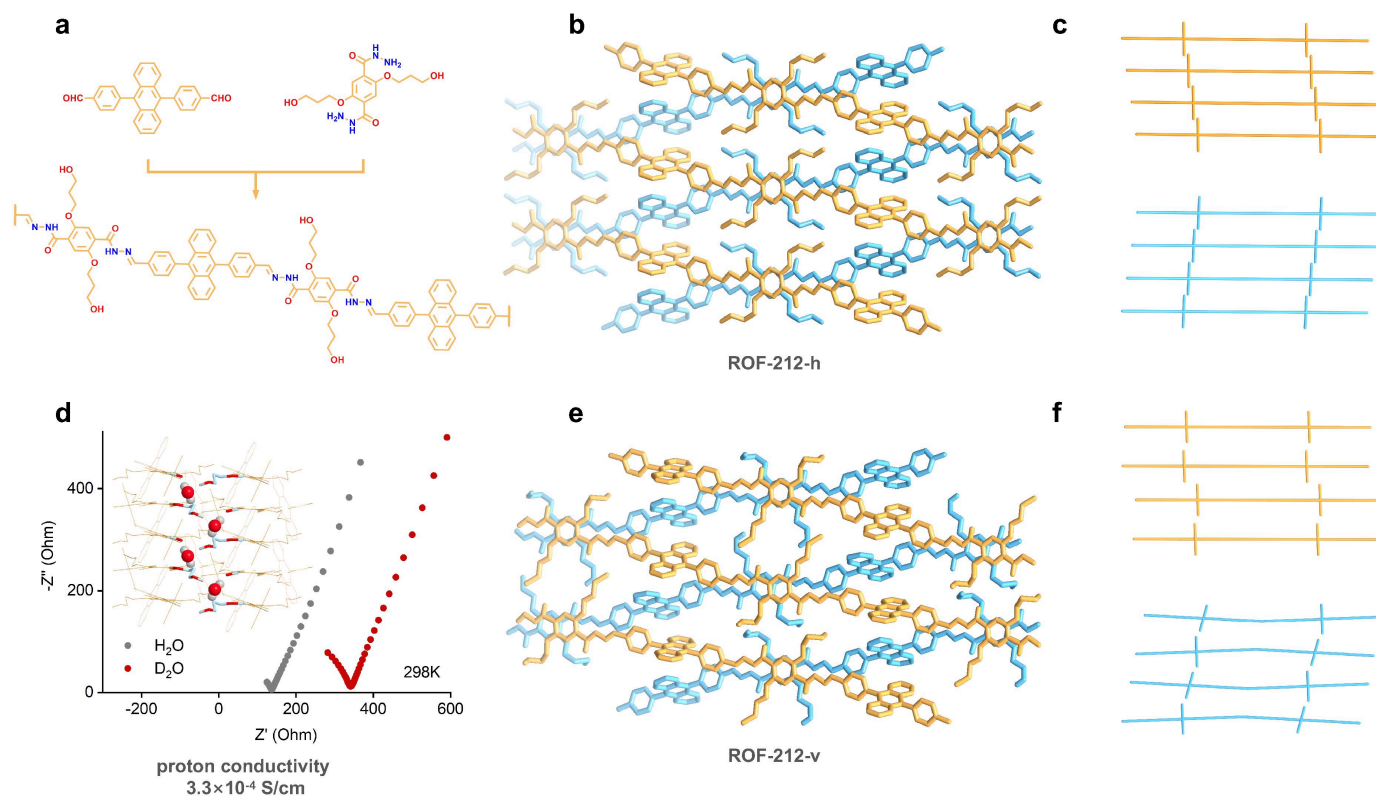


Figure 5

Global dynamics of biaxial ROF-212 and resulting proton conductivity. ROF-212 is synthesized with ADBA and 2,5-bis(3-hydroxypropoxy)terephthalohydrazide (**a**). Its hydrated phase ROF-212-h has similar structure as ROF-211 (**b**) with two set of regularly spaced, mutually intercrossing chains correlated by two-fold rotational symmetry (**c**). The adsorbed water molecules ROF-212-h, resolved by 3D ED, form hydrogen-bonded water channels with the hydroxypropoxy pendant group to give high proton conductivity (**d**). Upon dehydration, ROF-212 undergo global structural rearrangement (**e**) with individual chains moving with respect to each other to give the ROF-212-v phase with reduced symmetry (**f**).

Supplementary Files

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