Supporting Information

Supramolecular Proton Conductors Self-Assembled by Organic Cages

Zhenyu Yang,[a] Ningjin Zhang,[b] Lei Lei,[c] Chunyang Yu,[a] Junjie Ding,[a] Pan Li,[a] Jiaolong Chen,[a] Ming Li,[c] Sanliang Ling,[c] Xiaodong Zhuang[a] and Shaodong Zhang[a]*

[a] School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road
Shanghai 200240, China
[b] Instrumental Analysis Center, Shanghai Jiao Tong University, 800 Dongchuan Road
Shanghai 200240, China
[c] Advanced Materials Research Group, Faculty of Engineering, University of Nottingham, Nottingham NG7 2RD, United Kingdom
*E-mail: sdzhang@sjtu.edu.cn
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1 Materials

Tris(4-bromophenyl)methanol 1a was synthesized according to the literature.\textsuperscript{51} 4-(Tris(4-bromophenyl)methyl)phenol 1b was prepared according to the literature.\textsuperscript{52} Scandium(III) trifluoromethanesulfonate, sodium tris(acetoxy)hydroborate were purchased from Shanghai Adamas-Beta Co. Ltd. Tris(2-aminoethyl)amine (TREN), tris(3-aminopropyl)amine (TRPN), 2-formylbenzeneboronic acid, 1,4-phenylenediboronic acid were purchased from Beijing InnoChem Co. Ltd. All other reagents were bought from commercial sources and used without any purification unless otherwise stated. Tetrahydrofuran was dried over sodium/benzophenone under nitrogen atmosphere before use. The reaction evolution was monitored by thin-layer chromatography (TLC) and flash column chromatography was performed on silica gel (200-300 mesh) with indicated eluent.

2. Techniques

2.1 Solution nuclear magnetic resonance (NMR)

\(^1\text{H}\) NMR and \(^{13}\text{C}\) NMR spectra were recorded on a Bruker Advance III HD (400/500 MHz) NMR spectrometer at room temperature. Proton and carbon chemical shift values (\(\delta\)) and coupling constants (\(J\)) are reported in ppm and Hertz (Hz) respectively. The resonance multiplicity of the \(^1\text{H}\) NMR spectra are denoted as “s” (single), “d” (doublet), “t” (triplet), “quint” (quintet), “m” (multiplet) and broad resonances are described as “br”. Residual protic solvent of CDCl\(_3\) (\(^1\text{H}\), \(\delta = 7.26\) ppm; \(^{13}\text{C}\), \(\delta = 77.16\) ppm), CD\(_2\)Cl\(_2\) (\(^1\text{H}\), \(\delta = 5.32\) ppm; \(^{13}\text{C}\), \(\delta = 53.84\) ppm), CD\(_3\)OD (\(^1\text{H}\), \(\delta = 3.31\) ppm; \(^{13}\text{C}\), \(\delta = 49.00\) ppm) were used as the internal standard in the \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra.

2.2 Fourier-transform infrared spectroscopy (FT-IR)

Fourier-Transform Infrared Spectroscopy (FT-IR) spectra were recorded on a Perkin-Elmer Paragon 1000 spectrometer at frequencies ranging from 4000 to 500 cm\(^{-1}\) at room temperature. The signal intensity was denoted as “s” (strong), “m” (medium), “w” (weak) and “br” (broad).
2.3 High performance liquid chromatography (HPLC)

HPLC analysis was performed on a Shimadzu LC-20 AD instrument at room temperature using a Daicel Chiralcel IA column.

2.4 Matrix-assisted laser desorption and ionization time-of-flight mass spectrometry (MALDI-TOF MS)

Matrix-assisted laser desorption and ionization time-of-flight mass spectrometry (MALDI-TOF MS) was performed on a solariX XR 7.0 T hybrid quadrupole-FTICR mass spectrometer equipped with an ESI/APCI/MALDI ion source (Bruker Daltonics, Bremen, Germany). The MS instrument was tuned and calibrated with ESI-L low concentration tuning mix (Agilent Technologies, Santa Clara, CA, USA) and sodium formate. The analytical sample was prepared by mixing the reaction mixture (2.0 mg/mL in CHCl₃) with the matrix solution (10 mg/mL DCTB in CHCl₃) in a v/v ratio of 1/5, and then loaded onto the MALDI plate. The sample on the plate was thoroughly dried prior to analysis. The mass spectra were analyzed using Compass Data Analysis 5.0 (Bruker).

2.5 Single crystal X-ray diffraction (SC-XRD)

The crystals were kept at 170.0 K during data collection. Using Olex2, the structures were solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation. Some solvent molecules were highly disordered and could not be reasonably located. The voids in the crystal lattice were treated with Platon squeeze program.

2.6 Powder X-ray diffraction (PXRD)

Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 advance diffractometer with Cu–Kα1 radiation (λ = 1.5406 Å). The detailed procedure of sample preparation for PXRD measurements are as follows: The as-synthesized bulk powder samples were firstly dispersed in distilled THF solvent with a concentration at 30 mg/mL, followed by sonication until thorough dispersion. Then, additional TFA was added until the mixture became clear, which was subsequently subjected to filtration
with 0.45 µm PTFE springe filter to remove the undissolved residue. Slow evaporation of the settled solution could obtain high-quality single crystals, which were then loaded into a 0.7 mm diameter quartz glass capillary without mother liquor. PXRD data were collected at ambient temperature with a capillary setup.

**2.7 Thermal gravimetric analysis (TGA)**

TGA was performed with a STA449C integration thermal analyzer under flowing N\textsubscript{2} with 10 °C/min ramp rate. Samples were heated in a Platinum pan (800 °C) under N\textsubscript{2} flux (60 mL/min).

**2.8 Alternating current impedance measurement**

The sample preparations for proton conductivity measurements are as follows: the freshly prepared crystal samples were air dried at room temperature and then weighed using an analytical balance, followed by grounding to a fine powder with a pestle and motor. Press the samples into tablets using a tablet press.

The proton conductivity was measured with an EC Labs Bio-Logic (SP-300) potentiostat using banana plug cables. The 2 probe (quasi four probe) electrochemical impedance spectroscopy was measured using a sinusoidal amplitude of 10.0 mV over the frequency range 100 mHz-7 MHz.
3. Theoretical calculations

![Diagram showing theoretical calculations for cages 1 to 4 with SE values]

**Figure S1.** The strain energy (SE) of Cage-1 to Cage-4 determined by DFT calculations (B3LYP-D3 in PCM with chloroform as solvent).

The strain energy (SE) of cages were also studied by DFT calculation (M06-2X-D3) in PCM with chloroform as solvent) (Figure S1), which were computed to evaluate the possibility of forming a cage structure. SE is defined as the energy difference between the cage and optimized precursor. It should be noted that the end groups of cages were reduced to aldehyde structures to maintain the equality of the calculations. All of the calculations reported here were performed with the Gaussian09 program.

It was found from the results of DFT calculations that the cages fabricated with small-sized TREN exhibits a higher SE than the cages constructed by large-sized TRPN. In addition, Cage-1 and Cage-2 have suitable SE with 188.9 kJ mol\(^{-1}\) for Cage-1, and 191.0 kJ mol\(^{-1}\) for Cage-2, respectively. However, Cage-3 and Cage-4 show the highest and lowest SE value, which are 224.4 kJ mol\(^{-1}\) for Cage-3, and 176.5 kJ mol\(^{-1}\) for Cage-4, respectively. Considering no formation of Cage-3 and Cage-4 were observed experimentally, we assume that a threshold effect might play a significant role that determines the formation of cage structures in the current study.
4. Synthesis

4.1 Design and synthesis of organic cages

Aided by density functional theory (DFT) calculations, we synthesized Cage-1 and Cage-2 in a controlled fashion (Figure S2). We first rationally designed the paw-shaped molecule 1 with triformal groups, which could react with small-sized tris(2-aminoethyl)amine (TREN) and large-sized tris(3-aminopropyl)amine (TRPN) via cycloimination and subsequent reduction, while Cage-3 is the by-product (trace amount). By contrast, the reaction with large-sized tris(3-aminopropyl)amine (TRPN) molecule yields Cage-2 and -4 as major and side product (trace amount), respectively. (b) and (d) are MALDI-TOF MS spectra of the reaction mixture, corresponding to the reduced reaction mixture of triformal precursor 1 with TREN and TRPN molecules, respectively. M1–M4 represent the calculated molecular weight of Cage-1 to -4. (c) and (d) are partial $^1$H NMR spectra of purified Cage-1 and -2, which are collected in CD$_3$OD and CD$_2$Cl$_2$ (400 MHz, 25 ºC), respectively.
cycloimination, respectively. Due to the dynamic nature, we assumed that two products, i.e., [1+1] and [2+2] nanocages, are accessible for each reaction (Figure S2a). On the other hand, as determined by DFT calculation, the reaction with TREN prefers the formation of the [2+2] product Cage-1 to that of the [1+1] product Cage-3; while in the reaction with TRPN, the [1+1] product Cage-2 is thermodynamically more favored over the [2+2] product Cage-4. This product distribution results from different strain energies of the hypothetical products (see detailed DFT calculation in Figure S1), which we coin strain-discrimitive strategy.

Accordingly, the triformyl precursor molecule 1 was synthesized by Pd(PPh₃)₄ catalyzed Suzuki-Miyaura cross-coupling reaction using commercially available molecule (2-formyl phenyl)boronic acid as reactant (41% three-step overall yield, see Figure S3 for details). Small-sized TREN was then employed to react with molecule 1 using Sc(OTf)₃ as catalyst. The molar ratio of the reactants was TREN:1: Sc(OTf)₃ = 1:1:0.3 in chloroform (CHCl₃), followed by reduction with NaHB(OAc)₃ (7.5 equiv.), yielding Cage-1 in amine form (56% two-step overall yield, see Figure S4 for details). The chemical structure of Cage-1 was confirmed by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS, Figure S2b) and nuclear magnetic resonance (NMR, Figure S2c). As the structure of Cage-1 exhibits a torsional configuration, one of the three alphatic chains is independent from the other two, its ¹H NMR spectrum shows two sets of resonances with an integral area ratio of 1:2 (H₈:H₈’, H₆:H₆’ and H₁₀:H₁₀’). However, the formation of Cage-3 could only be detected by mass spectrometry (Figure S2b) but not by NMR spectroscopies, indicating only trace amount of Cage-3 was formed during the reaction. This product distribution is in line with the DFT calculation based on the strain energy difference (Figure S1).

Similarly, amine-containing product Cage-2 was formed as the dominating species by cycloimination between molecule 1 and large-sized TRPN (with one more carbon atom at each arm as compared to TREN, Figure S2a), followed by reduction with NaH(OAc)₃ (52% two-step overall yield, see Figure S4 for details). Its structure was confirmed by MALDI-TOF MS (Figure S2d) and NMR (Figure S2e) spectroscopy.
As discriminated by strain energy, Cage-4 was only produced in trace amount, as confirmed by mass spectrometry (Figure S2d). In contrast to Cage-1, the chemical structure of Cage-2 manifests a highly symmetric configuration with each flexible chain stretching in the same manner, which is consistent with its simple splitting pattern in the $^1$H NMR spectroscopy (Figure S2e).

4.2 Synthesis route of Tri-formyl precursor 1

Figure S3. Synthesis route of Tri-formyl precursor 1.

Tris(4-bromophenyl)methanol (1a): 1,4-Dibromobenzene (11.8 g, 50.0 mmol, 3.0 equiv.) was dissolved in anhydrous THF (100.0 mL) and cooled to -78 °C, followed by dropwise addition of $n$-BuLi (1.6 M in Hexane) (31.2 mL, 50.0 mmol, 3.0 equiv.). The mixture was stirred for 1 h, after which diethyl carbonate (2.0 g, 16.6 mmol, 1.0 equiv.) was added slowly. The solution was stirred for another 0.5 h at -78 °C and then allowed to room temperature for 12 h. Saturated NH$_4$Cl aqueous solution (50.0 mL) was added to quench the reaction, which was then extracted with DCM (3×50.0 mL), dried over anhydrous Na$_2$SO$_4$, and concentrated to give the crude product. Purification by flash column chromatography (Hex/DCM = 1:3, v/v) yielded the title compound 1a (5.2 g, 63%) as a white solid. $^1$H NMR (400 MHz, CDCl$_3$), $\delta$ = 7.45 (dd, $J$ = 8.0, 4.0 Hz, 6H), 7.12 (dd, $J$ = 8.0, 4.0 Hz, 6H), 2.70 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$), $\delta$ = 144.99, 131.47, 129.60, 122.11, 81.24.

4-(Tris(4-bromophenyl)methyl)phenol (1b): Tris(4-bromophenyl)methanol (1a) (2.0 g, 4.0 mmol, 1.0 equiv.) and phenol (2.0 g, 21.9 mmol, 5.5 equiv.) were charged into a
25 mL Schlenk flask, which was degassed by evacuating and refilling with argon three times. Sulfuric acid (250 µL) was then added, and the system was heated to 80 °C for 4 h under argon. After cooling to room temperature, an aqueous solution of NaOH (10 wt%, 25.0 mL) was added and stirred for 0.5 h to remove the excess phenol. The mixture was then extracted with DCM (3×50.0 mL), dried over anhydrous Na₂SO₄, and concentrated to give the pure product 1b (2.2 g, 96%) as a white solid. 

**¹H NMR (400 MHz, CDCl₃), δ = 7.38–7.41 (dd, J = 8.0, 4.0 Hz, 6H), 7.04–7.07 (dd, J = 8.0, 4.0 Hz, 6H), 6.98–7.01 (dd, J = 8.0, 4.0 Hz, 2H), 6.72–6.75 (dd, J = 8.0, 4.0 Hz, 2H).**

**¹³C NMR (101 MHz, CDCl₃), δ = 154.55, 145.73, 137.92, 132.93, 132.37, 131.20, 120.69, 115.01, 63.73.**

**Tri-formyl precursor 1:** Into a 250 mL Schlenk flask was charged with 4-(tris(4-bromophenyl)methyl)phenol 1b (1.9 g, 3.3 mmol, 1.0 equiv.), (2-formylphenyl)boronic acid (2.9 g, 19.5 mmol, 6.0 equiv.), Pd(PPh₃)₄ (563.0 mg, 0.5 mmol, 0.15 equiv.), K₂CO₃ (6.7 g, 48.8 mmol, 15.0 equiv.), which was degassed by evacuating and refilling with nitrogen three times. Dioxane (130.0 mL) and water (32.5 mL) were then added successively under N₂ atmosphere. The reaction mixture was refluxed at 95 °C for 2 days. After cooling to room temperature, dioxane was removed by rotary evaporator and the left mixture was extracted with DCM (3×70.0 mL), dried over anhydrous Na₂SO₄, and concentrated to give the crude product. Purification by flash column chromatography (PE/EA = 1:1, v/v) yielded the title compound 1 (1.4 g, 67%) as a white solid. 

**¹H NMR (400 MHz, CDCl₃), δ = 10.06 (s, 3H), 8.02–8.04 (d, J = 8.0 Hz, 3H), 7.63–7.67 (t, J = 16.0, 8.0 Hz, 3H), 7.49–7.52 (m, 6H), 7.40 (d, J = 8.0 Hz, 6H), 7.34 (d, J = 8.0 Hz, 6H), 7.17 (d, J = 8.0 Hz, 2H), 6.83 (d, J = 8.0 Hz, 2H).**

**¹³C NMR (101 MHz, CDCl₃), δ = 192.73, 154.21, 146.75, 145.66, 138.31, 135.72, 133.82, 133.80, 132.42, 131.15, 130.92, 129.68, 127.99, 127.77, 114.90, 64.21. FT-IR (KBr, cm⁻¹): ν = 3361.5 (br), 2956.4 (s), 2924.5 (s), 2852.4 (s), 1692.7 (s), 1596.4 (m), 1509.1 (w), 1493.0 (w), 1473.9 (m), 1378.1 (w), 1363.3 (w), 1254.9 (m), 1193.3 (m), 1081.6 (m), 1004.2 (w), 968.5 (m), 829.4 (s), 767.3 (s), 652.1 (m), 597.6 (m), 536.5 (w). HR-MS (MALDI): C₃₃H₂₃O₃⁺ [M]⁺, Calculated: 467.1642; Found: 467.1658, which
corresponds to the cationic fragment of the title molecule with one arm, i.e., two benzene units, stripped off by laser.

4.3 Synthesis of Cage-1 and -2

**Figure S4.** Synthesis of Cage-1 and -2.

**Cage-1:** Into a 500 mL flask was charged with 0.005 mol/L tri-formyl precursor 1 (492.7 mg, 0.76 mmol, 1.0 equiv.) in 152 mL of CHCl₃, then a 0.005 mol/L solution of tris(2-aminoethyl)amine (TREN) (214.5 mg, 1.2 mmol, 1.5 equiv.) in 228.0 mL of CHCl₃ was added dropwise followed by addition of Sc(OTf)₃ (113.0 mg, 0.3 mmol, 0.3 equiv.) directly. The reaction mixture was stirred at room temperature for 4 h. Then, the product was reduced by NaBH(OAc)₃ (2.4 g, 11.4 mmol, 15.0 equiv.) overnight, the solution was quenched with NaOH solution (2.0 M, 200 mL). The precipitates were filtered under vacuum and washed with DCM (100 mL), dried in the low pressure oven to give the Cage-1 (315 mg, 56%) as a white solid. NMR spectroscopy was conducted with additional trifluoroacetic acid (TFA) for better solubility in CD₃OD. $^1$H NMR (400 MHz, CD₃OD), δ = 7.63–7.20 (m, 52H), 6.75–6.73 (d, $J = 8.0$ Hz, 4H), 4.30 (s, 4H), 8.01 (s, 8H). $^{13}$C NMR (101 MHz, CD₃OD), δ = 156.87, 148.40, 148.23, 143.93, 143.88, 138.72, 138.65, 138.20, 132.95, 132.19, 132.09, 131.98, 131.02, 130.71, 129.99, 129.60, 129.44, 115.80, 65.38, 45.84. FT-IR (KBr, cm$^{-1}$): ν = 3315.38 (br), 3023.87 (w), 2935.13 (w), 2827.78 (w), 1509.30 (s), 1578.44 (m), 1481.00 (m), 1408.00 (m), 1408.00 (m), 130.71, 129.60, 129.44, 115.80, 65.38, 45.84. FT-IR (KBr, cm$^{-1}$): ν = 3315.38 (br), 3023.87 (w), 2935.13 (w), 2827.78 (w), 1509.30 (s), 1578.44 (m), 1481.00 (m), 1408.00 (m), 1262.12 (m), 1178.54 (m), 1107.42 (w), 1006.19 (m), 830.23 (s), 763.59 (s), 707.11
(w), 649.53 (s), 597.90 (m), 539.48 (w). HR-MS (MALDI): C$_{104}$H$_{101}$N$_8$O$_2^+$ [M+H]$^+$. Calculated: 1494.8076; Found: 1494.8153. Elemental analysis (%) Calculated for C$_{104}$H$_{100}$N$_8$O$_2$: C 83.61, H 6.75, N 7.50; Found: C 81.38, H 7.07, N 6.87.

**Cage-2:** Into a 500 mL flask was charged with 0.005 mol/L tri-formyl precursor 1 (492.7 mg, 0.76 mmol, 1.0 equiv.) 152 mL in CHCl$_3$, then a 0.005 mol/L solution of tris(3-aminopropyl)amine (TRPN) (214.5 mg, 1.2 mmol, 1.5 equiv.) 228.0 mL in CHCl$_3$ was added dropwise followed by addition of Sc(OTf)$_3$ (113.0 mg, 0.3 mmol, 0.3 equiv.) directly. The reaction mixture was stirred at room temperature for 4 h. Then, the product was reduced by NaBH(OAc)$_3$ (1.2 g, 5.7 mmol, 7.5 equiv.) overnight, the excess reductant NaBH(OAc)$_3$ was filtered off under vacuum and the solution was quenched with NaOH solution (2.0 M, 200 mL), extracted with CHCl$_3$ (3×200 mL), dried over anhydrous Na$_2$SO$_4$, and concentrated to give the crude product. Purification by flash column chromatography (DCM/MeOH/NH$_3$(aq) = 50:2:3, v/v/v) afforded the Cage-2 (312.0 mg, 52%) as a white solid. $^1$H NMR (400 MHz, CD$_2$Cl$_2$), $\delta$ = 7.38 (d, $J$ = 8.0 Hz, 6H), 7.26–7.32 (m, 18H), 7.20 (d, $J$ = 8.0 Hz, 2H), 6.2 (d, $J$ = 8.0 Hz, 2H), 7.36 (s, 6H), 2.43–2.47 (t, $J$ = 16.0, 8.0 Hz, 6H), 2.26–2.30 (d, $J$ = 16.0, 8.0 Hz, 6H), 1.27–1.41 (m, 6H). $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$), $\delta$ = 155.27, 146.79, 142.18, 139.26, 138.12, 132.84, 131.43, 130.79, 130.04, 128.53, 127.89, 127.70, 114.99, 64.08, 52.74, 52.26, 47.71, 27.04. FT-IR (KBr, cm$^{-1}$): $\nu$ = 3024.2 (w), 2925.2 (s), 2852.8 (m), 1664.9 (w), 1609.2 (m), 1509.3 (s), 1481.0 (s), 1446.7 (m), 1376.7 (w), 1263.9 (s), 1178.3 (s), 1108.7 (m), 1006.1 (m), 828.4 (s), 762.1 (s), 737.3 (s), 597.0 (m), 570.5 (w), 537.6 (m). HR-MS (MALDI): C$_{55}$H$_{57}$N$_4$O$^+$ [M+H]$^+$, Calculated: 789.4527; Found: 789.4511. Elemental analysis (%) Calculated for C$_{55}$H$_{56}$N$_4$: C 83.72, H 7.15, N 7.10; Found: C 82.97, H 7.24, N 6.59.

### 4.4. HPLC analysis of Cage-1 and -2

As the Cage-1 had a poor solubility in common organic solvents, we performed the HPLC analysis of Cage-1 and -2 using their fully protonic products with additional trifluoroacetic acid. The elution was employed within 15 min with 5% MeOH in THF at
a flow rate of 0.6 mL/min. The sample concentration was 5.0 mM in methanol, and the injection volume was 20 µL. The absorbance was monitored at 254 nm.

Figure S5. Stacked HPLC traces of TFA doped Cage-1 (upper panel) and TFA doped Cage-2 (lower panel).
5. Kinetic experiments of the formation of Cage-1’ and -2’ as well as their transformation

Figure S6. $^1$H NMR (400 MHz, CDCl$_3$, 25 °C) monitoring the formation process of Cage-2’, which is the imine form of Cage-2 for differentiation.
Figure S7. $^1$H NMR (400 MHz, CDCl$_3$, 25 °C) monitoring of the formation process of Cage-1' as well as its transformation to Cage-2'. (a) Partial $^1$H NMR spectra evolution profile of the generation process of Cage-1' as a function of time over 5.0 h (bottom panel) and the rapid transformation to Cage-2' within 0.5 h (upper panel) triggered by adding additional TRPN. The bottom trace at 0 h represents the start of the reaction existing only the precursor molecule 1 in CDCl$_3$. The characteristic resonances of Cage-1' (at 5.0 h) and Cage-2' (at 12 h) are colored in blue and green, respectively. (b) The corresponding molecular structures with labeled protons.

The kinetic investigation of the transformation from Cage-1' to Cage-2'. In order to further verify the selective formation mechanism of the strain-discriminative effect that high strain energy cage products could be ultimately transformed into low strain energy cage products due to the dynamic nature of DCC, $^1$H NMR spectra monitoring experiments were performed to investigate the dynamic transformation behavior between Cage-1' and Cage-2' (Figure S6-7). For easy distinguishing, we named the imine form of Cage-1 and Cage-2 as Cage-1' and Cage-2', respectively. At the beginning of the reaction (Figure S7a, at 0 h), the reaction system only exists the precursor molecule 1, where $H_A$ indicates the protons of aldehyde groups and $H_B$
represents the adjacent protons on the periphery benzene ring. Upon adding an equal stoichiometric ratio of TREN in the reaction system with a catalytic amount of Sc(OTf)_3 as the catalyst, the resonances of H_A and H_B gradually disappeared with the characteristic peaks of Cage-1' (H_C–H_D') appeared with time until 1.0 h reaches its steady-state, indicating the highly selective and efficient formation of Cage-1' (Figure S7a, at 1 h). As the chemical structure of Cage-1' exhibits a torsional configuration, one of the three alkane chains is independent of the other two in terms of its chemical and geometric environment, leading to the formation of two sets of peaks with different chemical shifts (Figure S7a, at 5.0 h), which have an integral area ratio of 1:2 using the relative resonances (e.g., H_C : H_C'). Here, H_C indicates the protons on the Schiff base of the independent chain and the other two are represented as H_C'. Meanwhile, the corresponding protons adjacent to the imine bonds on the rigid arms are denoted as H_D and H_D', respectively. At this time, additional TRPN, with a molar ratio at 3:1 to the precursor molecule 1, was charged into the reaction mixture to induce the transformation. As shown in the ^1^H NMR spectrum (Figure S7a, at 5.5 h), the resonances of H_C and H_C' completely disappeared within 0.5 h, moving to H_E and H_E' with a higher chemical shift, which are the characteristic peaks of Cage-2' (Figure S6). The above results clearly indicate that Cage-2' is thermodynamic more stable than Cage-1', which is the driving force of cage structures’ reconstruction as well as the rapid transformation to the lower strain energy product.
6. X-ray crystallography

Single crystals of Cage-1 suitable for X-ray crystallography were obtained by slow evaporation its hydrous THF solution containing pristine cage molecules and additional trifluoroacetic acid (TFA), it therefore yielded single crystals that encapsulate TFA and H₂O molecules. CCDC deposition number 2109831.

Table S1. Crystal data and structure refinement for Cage-1

| Identification code | Cage-1 |
|---------------------|--------|
| Empirical formula   | C₁₂₀H₁₂₂F₁₈N₈O₁₉ |
| Formula weight      | 2322.25 |
| Temperature         | 170.0 K |
| Wavelength          | 1.34139 Å |
| Crystal system, space group | Monoclinic, C2/c |
| Unit cell dimensions | \(a = 26.6620(5)\) Å, \(\alpha = 90°\) \(b = 33.2105(6)\) Å, \(\beta = 95.8680(10)°\) \(c = 15.1850(3)\) Å, \(\gamma = 90°\) |
| Volume              | 13375.2(4) Å³ |
| Z, Calculated density| 8, 1.153 g/cm³ |
| Absorption coefficient | 0.517 mm⁻¹ |
| F (000)             | 4848 |
| Crystal size        | 0.08 × 0.06 × 0.05 mm³ |
| Theta range for data collection | 3.267 to 54.988° |
| Limiting indices    | -32 <= h <= 32, -40 <= k < 39, -17 <= l <= 18 |
| Reflections collected / unique | 71107 / 12695 [R(int) = 0.0369] |
| Completeness to theta = 53.594° | 99.6 % |
| Absorption correction | Semi-empirical from equivalents |
| Max and min. transmission | 0.7508 and 0.5224 |
| Refinement method   | Full-matrix least-squares on F² |
| Data / restraints / parameters | 12695 / 234 / 842 |
| Goodness-of-fit on F² | 1.040 |
| Final R indices [I>2 sigma (I)] | R₁ = 0.1084, wR₂ = 0.2691 |
| R indices (all data) | R₁ = 0.1190, wR₂ = 0.2763 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.900 and -0.860 e.A⁻³ |
Single crystals of **Cage-2** suitable for X-ray crystallography were obtained by slow evaporation its hydrous THF solution containing pristine cage molecules and additional trifluoroacetic acid (TFA), it therefore yielded single crystals that encapsulate TFA and H$_2$O molecules. CCDC deposition number 2109832.

**Table S2. Crystal data and structure refinement for Cage-2**

| Identification code | **Cage-2** |
|---------------------|------------|
| Empirical formula   | C$_{124}$H$_{128}$F$_{21}$N$_8$O$_{20}$ |
| Formula weight      | 2449.34 |
| Temperature         | 173.0 K |
| Wavelength          | 1.54178 Å |
| Crystal system, space group | Triclinic, P-1 |
| Unit cell dimensions | $a = 16.537(4)$ Å, $a = 80.954(9)^\circ$ |
|                     | $b = 20.414(5)$ Å, $\beta = 78.753(7)^\circ$ |
|                     | $c = 21.298(5)$ Å, $\gamma = 87.090(15)^\circ$ |
| Volume              | 6962(3) Å$^3$ |
| Z, Calculated density | 2, 1.168 Mg/m$^3$ |
| Absorption coefficient | 0.837 mm$^{-1}$ |
| F (000)             | 2554 |
| Crystal size        | $0.16 \times 0.06 \times 0.06$ mm$^3$ |
| Theta range for data collection | 2.139 to 68.471° |
| Limiting indices    | $-19 \leq h \leq 19$, $-24 \leq k \leq 24$, $-25 \leq l \leq 25$ |
| Reflections collected / unique | 103156 / 25511 [R(int) = 0.0772] |
| Completeness to theta = | 100.0 % |
| Absorption correction | Semi-empirical from equivalents |
| Max and min. transmission | 0.7446 and 0.7179 |
| Refinement method   | Full-matrix least-squares on F$^2$ |
| Data / restraints / parameters | 25511 / 172 / 1666 |
| Goodness-of-fit on F$^2$ | 1.067 |
| Final R indices [I>2 sigma (I)] | R1 = 0.0793, wR2 = 0.2270 |
| R indices (all data) | R1 = 0.1034, wR2 = 0.2507 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 1.092 and -0.702 e.A$^{-3}$ |
Figure S8. The detail information of hydrogen-bonds formed in the supramolecular proton conductors. (a) TFA doped Cage-1 with the chemical formula of Cage-1·6TFA·4H$_2$O. (b) TFA doped Cage-2 with the chemical formula of Cage-2·4TFA·2H$_2$O.

For clear presentation of detail information of the hydrogen bonds formed in the supramolecular proton conductors, we mapped out the figures showing all hydrogen atoms participated in forming the hydrogen bonds (Figure S8). It was found that eight TFA (①-⑧) and four H$_2$O (①-④) molecules are in the vicinity of Cage-1, where TFA (③, ⑤) and H$_2$O (②, ③) located inside the cage cavity and the other proton carriers (TFA and H$_2$O) distributed outside (Figure S8a, left). In addition, TFA (①,④,⑦,⑧) molecules share half to Cage-1, which indicates Cage-1 contains six TFA and four water molecules. The results are coincident with its chemical formula Cage-1·6TFA·4H$_2$O. The zoom-in view of its asymmetric unit shows that TFA (①-③) and
H₂O (①) participated in forming hydrogen bonds, while TFA (④) and H₂O (②) are free from the cage framework (Figure S8a, right). The results suggest that five TFA (①-③, ⑤-⑦) and two H₂O (①, ④) participated in generating the hydrogen bonds, the other proton carriers did not in the solid crystalline phase. Interestingly, the tertiary amines on the aliphatic chains of Cage-1 were not protonated, which is assumably due to the electrostatic repulsion of the neighbouring TFA molecules as well as the steric hindrance of the irregularly stretched amine moiety caused by the rigid strain conformation.

In contrast to Cage-1, Cage-2 exhibits four TFA (①-④) and two water (①-②) molecules distributed outside the cage cavity (Figure S8b, left), which are in accordance with its chemical formula Cage-2·4TFA·2H₂O. The zoom-in view shows TFA (①-③) and H₂O (②) participated in forming the hydrogen bonds, while TFA (④) and H₂O (①) are free (Figure S8b, right). The ellipse and sticks model of TFA (④) indicates it is highly disorder, further validated its mobility, which are essential for proton conductivity.⁸⁸ On the other hand, the refinement during the crystal analysis always leads to an unrealistic model, we therefore have applied solvent masking to eliminate the electronic contribution of this TFA molecule to avoid alert level A in checkCIF/PLATON report and deposited its corresponding CIF file in CCDC. In addition, the tertiary amine of Cage-2 was protonated due to the less steric hindrance and electrostatic repulsion of the neighboring TFA.
7. Powder X-ray diffraction pattern

**Figure S9.** Powder X-ray pattern of TFA doped Cage-1, experimental pattern (grey line), Pawley refinement (blue circles), simulated pattern (red line) and difference (black line). Profiles for Pawley refinement ($R_{wp} = 1.24 \%$, $R_p = 0.59 \%$) at 298 K ($a = 26.660062$, $b = 33.208877$, $c = 15.184484$ Å, $C2/c$). The reflection positions are marked with green.

**Figure S10.** Powder X-ray pattern of TFA doped Cage-2, experimental pattern (grey line), Pawley refinement (blue circles), simulated pattern (red line) and difference (black line). Profiles for Pawley refinement ($R_{wp} = 0.29 \%$, $R_p = 0.15 \%$) at 298 K ($a = 16.536734$, $b = 20.414427$, $c = 21.296873$ Å, P-1). The reflection positions are marked with green.
Figure S11. Powder X-ray pattern of TFA doped Cage-1 after conductivity measurement (light blue line) and simulated pattern (red line).

Figure S12. Powder X-ray pattern of TFA doped Cage-2 after conductivity measurement (light blue line) and simulated pattern (red line).
8. Thermal gravimetric analysis

Figure S13. Thermogravimetric curve of air-dried sample of (a) TFA doped Cage-1, (b) TFA doped Cage-2 under N₂ flow with 10 °C/min ramp rate. The samples were heated in a Platinum pan from room temperature to 800 °C under the N₂ flux of 60 mL/min.

**Thermal stability of the supramolecular proton conductors.** To clarify the thermal stability of TFA doped Cages, we conducted their thermogravimetric analysis under nitrogen gas flow. It was found from the TGA result of TFA doped Cage-1 that there are three major weight loss processes with heating before its decomposition temperature (Figure S13a). The first stage is before 94 °C, losing about 4% weight, which corresponds to the evaporation of solvent molecule THF. The following stage is from 94 °C to 157 °C with a roughly weight loss of 3%, which is attributed to the desorption of four water molecules per formula from the crystalline sample of Cage-1·6TFA·4H₂O. The last stage is from 157 °C to 315 °C, which has a weight loss of 31%, corresponding to the desorption of TFA molecules from the crystalline sample.

Similarly, the first stage of crystalline sample of TFA doped Cage-2 (Cage-2·4TFA·2H₂O) is before 77 °C with a weight loss of 7%, which corresponds to the evaporation of solvent molecule THF (Figure S13b). Its second stage is from 115 °C to 165 °C with losing 3% weight, which is attributed to the desorption of two water molecules. The last stage is from 165 °C to 313 °C with a weight loss of 32%, corresponding to the desorption of TFA molecules.

As the proton carriers (TFA and H₂O) are essential for proton conductivity, we therefore performed the proton conductivity experiments under 80 °C to strictly ensure the thermal stability of proton carriers during the measurements.
9. Proton conductivity

Figure S14. Nyquist plots of (a) Cage-1 and (b) Cage-2 without doping of TFA.

Table S3. Proton conductivities at different temperatures under the air humidity (48% RH) (a), and under different relative humidity at 303 K (b).

|       | Temperature (K) | 303  | 313  | 323  | 333  | 343  | 353  |
|-------|----------------|------|------|------|------|------|------|
|       | R (Ω)          |      |      |      |      |      |      |
| TFA doped Cage-1 |                  |      |      |      |      |      |      |
| σ (S cm⁻¹) | 1.59×10⁻⁴     | 1.70×10⁻⁴ | 1.80×10⁻⁴ | 2.60×10⁻⁴ | 2.88×10⁻⁴ | 3.75×10⁻⁴ |     |
| R (Ω)   | 32725          | 22451 | 16499 | 10448 | 5137 | 2881 |     |
| TFA doped Cage-2 |                  |      |      |      |      |      |      |
| σ (S cm⁻¹) | 9.19×10⁻⁷     | 1.34×10⁻⁶ | 1.82×10⁻⁶ | 2.88×10⁻⁶ | 5.85×10⁻⁶ | 1.04×10⁻⁵ |     |

|       | Relative Humidity (RH) | 48%  | 58%  | 76%  | 86%  | 98%  |
|-------|------------------------|------|------|------|------|------|
|       | R (Ω)                  |      |      |      |      |      |
| TFA doped Cage-1 |                  |      |      |      |      |      |
| σ (S cm⁻¹) | 1.59×10⁻⁴     | 2.86×10⁻⁴ | 3.40×10⁻⁴ | 3.90×10⁻⁴ | 1.60×10⁻⁵ |     |
| R (Ω)   | 32725          | 19573 | 16279 | 10933 | 575.1 |     |
| TFA doped Cage-2 |                  |      |      |      |      |      |
| σ (S cm⁻¹) | 9.19×10⁻⁷     | 1.54×10⁻⁶ | 1.85×10⁻⁶ | 2.75×10⁻⁶ | 5.23×10⁻⁶ |     |
Figure S15. Nyquist plots of TFA doped Cage-1 at different temperatures (303-353 K) under the air humidity (48% RH).
Figure S16. Nyquist plots of TFA doped Cage-1 under different humidity (58-98%) at 303 K.
Figure S17. Nyquist plots of TFA doped Cage-2 at different temperatures (303-353 K) under the air humidity (48% RH).
Figure S18. Nyquist plots of TFA doped Cage-2 under different humidity (58-98%) at 303 K.
Figure S19. Recycle tests of TFA doped Cage-1 (a) and -2 (b) under RH of 48% at different temperatures.

Table S4. Comparison of proton conductivities of similar crystalline solid-state proton conductors.

| Material | Name                  | Conditions | Proton Conductivity (S cm⁻¹) | Eₜ (eV) | Ref.                  |
|----------|-----------------------|------------|-------------------------------|---------|-----------------------|
| MOF      | MOF-74(Mg)-Urea       | 323 K, 95% RH | $3.7 \times 10^{-2}$          | >0.4    | J. Am. Chem. Soc. 2020, 142, 6861. |
|          | [Pt₃(MPC)₃Cl₂]Co(DMA)- | 333 K, 95% RH | $2.2 \times 10^{-2}$          | 0.67    | JACS Au. 2022, 2, 109. |
|          | guest]₁               |             |                               |         |                       |
| COF      | H3PO4@TPB-DMeTP-COF   | 433 K, 0% RH | $1.91 \times 10^{-1}$         | 0.34    | Nat Commun. 2020, 11, 1981. |
| COF      | COF-F6-H              | 143 K, 0% RH | $4.2 \times 10^{-2}$          | 0.09–0.54 | J. Am. Chem. Soc. 2020, 142, 14357. |
| HOF      | CPO2-2                | 333 K, 98% RH | $2.2 \times 10^{-2}$          | 0.61    | Angew. Chem. Int. Ed. 2018, 57, 5345. |
|          | GTUB5                 | 348 K, 75% RH | $3.0 \times 10^{-3}$          | 0.26    | Nat Commun. 2020, 11, 3180. |
| Organic  | CC1-HCI               | 303 K, 95% RH | $1.1 \times 10^{-3}$          | 0.35    | Nat Commun. 2016, 7, 12750. |
| Cage     | Cage-1-TFA            | 303 K, 98% RH | $1.6 \times 10^{-3}$          | 0.16    | This work             |
10. *Ab initio* molecular dynamics simulations

10.1 Simulation methods

All simulations were performed with the CP2K code, which uses a mixed Gaussian/plane-wave basis set.\(^\text{59}\) Double polarization quality Gaussian basis sets\(^\text{10}\) and plane-wave cutoff of 400 Ry for the auxiliary grid were used. The density functional theory (DFT) calculations including geometry relaxation, single point energies and *ab initio* molecular dynamics (AIMD) simulations were conducted using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional,\(^\text{11}\) with Grimme’s D3 van der Waals correction (PBE+D3).\(^\text{12}\) AIMD simulations within the Born-Oppenheimer approximation were performed in the canonical (NVT) ensemble. A timestep of 0.5 fs was used for the integration of the equation of motion, and the simulations were run for 50 ps (100,000 AIMD steps following 2,000 steps of equilibration run that has a strong thermostat coupling). The temperature of the AIMD simulation was 500 K, which was controlled by the canonical sampling through velocity rescaling thermostat\(^\text{13}\) using a time constant of 50 fs. The initial structures of Cage-1 and Cage-2 were taken from their crystal structures.

10.2 Mean square displacement and diffusion coefficient calculation

Before analyzing the data, the AIMD trajectories of Cage-1 and Cage-2 were calibrated by fixing the center of masses (CoMs) of the systems, which is defined by:

\[
\text{CoM}(t) = \frac{\sum_{i=1}^{n} m_i r_i(t)}{\sum_{i=1}^{n} m_i}
\]

Where \(m_i\) is the mass of atom \(i\), \(r_i(t)\) is the position of atom \(i\) at time \(t\) and \(n\) is the number of atoms in the system.

Because of the relatively slow proton hopping rates, especially in Cage-2, the motion of proton carriers, i.e., water molecules were tracked. The positions of water molecules, which is just their CoMs, were first calculated. Then, the mean square displacements (MSDs) of the water molecules were calculated according to the following definition:
\[
MSD(m) = \frac{1}{N - m} \sum_{k=0}^{N-m-1} (r(k + m) - r(k))^2
\]

Where \( r(m) \) is the position of water molecule at frame \( m \) in the trajectory and \( N \) is the total number of frames in the trajectory. The above calculation was performed for each water molecule and the average values can be used to calculate the diffusion coefficient \( D \) for long enough \( t \) according to the Einstein relation:

\[
MSD(t) = 2nDt
\]

Where \( n \) is the degree of freedom of the system. The instantaneous diffusion coefficients \( D \) calculated by the above equation were plotted in main text Figure 5. The average diffusion coefficients \( D \) was calculated by fitting the MSD-\( t \) data with a linear function, where the slope is \( 2n \) times \( D \).

10.3 Hydrogen bond analysis

The hydrogen bonds in each frame were characterized by geometry criteria: (i) the separation between the hydrogen bond donor and acceptor is less than 1.02(\( R_D + R_A \)) where \( R_D \) and \( R_A \) are the van der Waals radii of the donor and acceptor and (ii) the D-H-A angle is larger than 90°. The number of hydrogen bonds \( n(H\text{-bonds}) \) were divided by the total number of available donor acceptor pairs \( N(d\text{-a}) \) to evaluate the probability of hydrogen bond formation.

The lifetime \( \tau \) of hydrogen bonds in Cage-1 and Cage-2 were analyzed as well to investigate the forming and breaking dynamics of hydrogen bonds. A time autocorrelation function was used to describe the hydrogen bond dynamics\(^{S14}\):

\[
C_t = \left( \frac{\sum \delta_{ij}(t_0)\delta_{ij}(t_0 + t)}{\sum \delta_{ij}(t_0)^2} \right)
\]

Where \( \delta_{ij} \) is a binary function which takes one if a hydrogen donor-acceptor pair \( i-j \) forms a hydrogen bonding according to the geometry criteria and otherwise takes zero. The summation counts the number of hydrogen bonds formed for the start time \( t_0 \) and the time \( t_0 + t \). The squared angle denotes the average of different start time \( t_0 \). A continuous method was used to calculate the autocorrelation function, where once a
hydrogen bond breaks, the corresponding donor-acceptor pair is removed from the list and will not be counted even if they form hydrogen bonds again.

The autocorrelation function of hydrogen bonds in Cage-1 and Cage-2 are plotted in Figure S26. The function describes the breaking rate of hydrogen bonds in average, and the hydrogen bond lifetime can be obtained by integration of the function$^{15}$:

$$\tau = \int_0^\infty (C(t) - \langle C(t = \infty) \rangle) dt$$

Figure S20. The time autocorrelation function $C_t$ of hydrogen bonds in (a) Cage-1 and (b) Cage-2, the solid lines are the biexponential function fittings of the autocorrelation function. The hydrogen bond lifetime $\tau$ were obtained by integrating the fitted line from zero to infinity.

To calculate the hydrogen bond lifetime, the autocorrelation functions were fitted by a biexponential function:$^{15}$

$$C_t = A e^{-\frac{t}{\tau_1}} + (1-A) e^{-\frac{t}{\tau_2}}$$

Where $A$ is the amplitude factor, $\tau_1$ and $\tau_2$ are the characteristic lifetimes of the biexponential function. The obtained biexponential function were then integrated from zero to infinity to obtain the hydrogen bond lifetime $\tau$. 

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11. Spectra

11.1 Mass spectra

Figure S21. MALDI-TOF-MS of *Tri-formyl precursor 1*. (positive-reflector mode, DCTB as matrix).

Figure S22. MALDI-TOF-MS of *Cage-1*. (positive-reflector mode, DCTB as matrix).
Figure S23. MALDI-TOF-MS of Cage-2. (positive-reflector mode, DCTB as matrix).
11.2 IR spectra

Figure S24. FTIR spectrum of \textit{Tri}-formyl precursor 1.

Figure S25. FTIR spectrum of Cage-1.
Figure S26. FTIR spectrum of Cage-2.
11.3 NMR spectra

Figure S27. $^1$H NMR (top, 400 MHz) and $^{13}$C NMR (bottom, 101 MHz) spectra of tris(4-bromophenyl)methanol 1a in CDCl$_3$. 

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Figure S28. $^1$H NMR (top, 400 MHz) and $^{13}$C NMR (bottom, 101 MHz) spectra of 4-(tris(4-bromophenyl)methyl)phenol 1b in CDCl$_3$. 
Figure S29. $^1$H NMR (top, 400 MHz) and $^{13}$C NMR (bottom, 101 MHz) spectra of *Tri*-formyl precursor 1 in CDCl$_3$. 
Figure S30. $^1$H NMR (top, 400 MHz) and $^{13}$C NMR (bottom, 101 MHz) spectra of Cage-1 in CD$_3$OD.
Figure S31. $^1$H NMR (top, 400 MHz) and $^{13}$C NMR (bottom, 101 MHz) spectra of Cage-2 in CD$_2$Cl$_2$. 
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