Electronic Supplementary Information (ESI) for

Structure Direction towards the New Large Pore Zeolite NUD-3

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S1 Experimental Section

S1.1 Synthesis of SDA1



Scheme 1 Synthesis of SDA1

In a 500-mL round-bottom flask, 14.12 g (80.66 mmol) of 1,2-bis(chloromethyl)benzene and 14.60 g (177.8 mmol, 1.10 e.q.) of N-methylimidazole in 300 mL MeCN were stirred overnight and then refluxed for 2 d. After the reaction finished, the white solid was filtrated and then washed with 300 mL ethyl ether. The product was collected and dried overnight at 80 °C in an oven to get 26.72 g (78.76 mmol) 1,1'-(1,2-phenylenebis(methylene))bis(3-methylimidazol-3-ium) chloride **SDA1** (yield: 97.64 %). ¹H NMR (300 MHz, D₂O) δ 3.79 (s, 6H), 5.44 (s, 4H), 7.31 (t, 2H), 7.41 (m, 4H), 7.53 (m, 2H), 8.56 (t, 2H); ¹³C NMR (300 MHz, D₂O) δ 131.52, 131.07, 130.68, 123.87, 122.26, 49.96, 35.80.

S1.2 Anion exchange

26.08 g (76.87 mmol) **SDA1Cl** was dissolved into 300 mL of deionized water and then added on a column with around 400 mL anion exchange resin. The type of resin is Cl⁻form 717 anion exchange resin (Sinopharm Chemical Reagent Co., Ltd), which should be firstly treated with concentrated NaOH solution to get the OH⁻form resin, with the exchange capacity of 3.6 mmol per gram of wet resin. The obtained solution of **SDA1OH** was titrated with 0.1 M HCl solution. (Yield: 99 %; treatment with acidified AgNO₃ (diluted) showed absence of halides).

S1.3 Synthesis of zeolite

NUD-3 was synthesized using a gel of composition $0.5 \text{ SiO}_2 : 0.5 \text{ GeO}_2 : 0.25 \text{ SDA1}(OH)_2 : 0.5 \text{ HF} : 1.5 H_2O at 150 °C for 15 d within a static autoclave. The procedure was as follows: 0.4168 g (3.98 mmol) GeO₂ was introduced in a 5.6824 g SDA(OH)₂ solution with [OH⁻] = 0.3524 mmol/g (1.00 mmol SDA(OH)₂) until complete dissolution. Additionally, 895 <math>\mu$ L (4.01 mmol) of TEOS was added and stirred until totally hydrolyzed and then ethanol was totally evaporated. After that, 89 μ L 40 % HF (2.01 mmol) was added. [CAUTION: HF is corrosive and toxic, handle with care inside a fume hood.] Then, the gel was put into an oven at 85 °C until it reached the goal ratio of H₂O/T. Finally, the gel was transferred into a Teflon lined autoclave and crystallized at 150 °C for 15 d.

After the crystallization, the content was filtrated, washed with water $(2 \times 20 \text{ mL})$ and acetone (20 mL), and then dried to get 0.146 gram of as-made NUD-3 zeolite. (Yield: 15.1 %)

Similar procedures were performed on all gels with their related gel composition in Tab. S1.

S2 Characterization Methods

The synchrotron powder X-ray diffraction (PXRD) pattern of as-made NUD-3 was collected in Debye-Scherrer geometry at beamline BL04-MSPD (Material Science Powder Diffraction) of the Spanish synchrotron, ALBA, with a wavelength of $\lambda = 0.619274$ Å. In situ PXRD patterns at various temperatures were collected on a Bruker D8 Advance diffractometer equipped with an MRI high-temperature attachment. Laboratory general PXRD patterns for phase identification were recorded on a Rigaku Dmax 2400 X-ray diffractometer with Cu Kα radiation at 40 kV and 100 mA. The Si/Ge ratios of as-made NUD-3 were obtained by inductively coupled plasma (ICP) emission spectrometry on an ESCALAB2000 analyzer. The zeolite sample was dissolved in a diluted HF solution and a plastic tube was used as the sample injection line of the ICP machine to prevent corrosion by HF. ¹³C, ¹⁹F and ²⁹Si solid state NMR spectra were carried out on a Varian model VNMRS-400WB spectrometer under one pulse condition and the experiments details have already been listed in a previous article.^[S1] ¹H and ¹³C liquid NMR spectra were performed on a Bruker Avance 300. Gas adsorption measurements of nitrogen and argon were carried out with calcined NUD-3 samples on a Micromeritics ASAP 2020 at 77 K and 87 K, respectively. Scanning electron microscopy (SEM) images were taken in a Hitachi S-4800 microscope. In order to determine the organic content in the as-made zeolite sample, CHN elemental analysis was performed on an Elementary Vario EL III micro-analyser. Thermogravimetric (TG) analysis experiment was carried out in an SDT Q600 TA instrument under air flow (100 mL/min) heating from 25 °C to 1000 °C at a heating rate of 10 °C/min. Fourier transform infrared (FT-IR) spectra were registered in the transmission mode at 4 cm⁻¹ resolution using a Thermo Nicolet Nexus 670 spectrometer provided with an MCT detector, in which the sample was prepared as a self-supporting wafer and treated under vacuum at 180 °C for 2 hrs.

S3 cRED Data Collection, Data Process, Structure Solution and Rietveld

Refinement

cRED data on as-made NUD-3 were collected using the continuous rotation method (cRED) using a JEOL JEM2100 TEM (LaB₆ filament) operating at 200 kV as described previously.^[S2] Shortly, the goniometer was rotated continuously during the data collection, while the selected area electron diffraction (SAED) patterns were captured from the crystal simultaneously by a quad hybrid pixel detector (Timepix). Three datasets were collected on individual crystals of NUD-3. The reciprocal space reconstruction was carried out using the program REDp,^[S3] and the reflection intensity extraction was conducted by the program XDS^{.[S4]} The data were scaled and merged based on unit cell consistency, correlation coefficients between the datasets, and resolution using XSCALE.^[S4] *Ab initio* structure solution was performed using the program ShelxT.^[S5] All Si/Ge and O atoms were located directly with the *P4/mmm* symmetry. The structure model was initially refined against the cRED data using the program Olex 2 without employing any bond and angle restraints. All symmetry independent T-atoms were refined as mixed Si/Ge sites and all framework atoms were refined anisotropically and the PLATON/SQUEEZE procedure was conducted to deduct the contribution of diffraction from the disordered SDA molecules in the pores.^[S6] The refinement converged with $R_1 = 19.1\%$, $wR_2 = 48.5\%$. These relatively high residuals are normal for cRED data because of the multiple scattering of the electrons. The experimental parameters and crystallographic details of the structure refinement are shown in Tab. S2.

To achieve a more precise framework structure and information on the location of the SDAs, the final structure of as-made NUD-3 was refined against the synchrotron powder X-ray diffraction (SPXRD) using TOPAS-V6.^[S7] Initially, a Pawley fit was performed to optimize the unit cell dimensions, background, and peak profile. The background was modeled with a 15-term shifted Chebyshev polynomial, and the peak profile was modeled with the Pearson VII peak-shape function. The model from cRED data was used as initial model. Before the refinement, an optimization of the framework geometry was performed by using the distance-least-squares algorithm in the program DLS-76.^[S8] The position of SDAs was determined by using a combination of simulated annealing (global optimization) and Rietveld refinement as described previously.^[S9] Soft geometric restraints were applied on the bond distances and angles of the framework atoms. These restraints were imposed throughout the refinement, but their relative weighting with respect to the SPXRD data was reduced as the refinement progressed. Finally, the unit cell dimensions, background, and peak profile were further refined. The refinement converged to $R_p = 5.99\%$ and $R_{wp} = 8.12\%$ with $R_{exp} = 7.72\%$ (Fig. S3). More crystallographic information about NUD-3 can be found in Tab. S3 and S4.

S4 Computational Details

Molecular mechanics simulations were carried out in order to study the structure-directing effect of **SDA1** towards the ordered tetragonal NUD-3 or the disordered cubic ITQ-21 frameworks; simulations were carried out using the Forcite module implemented in Materials Studio software.^[S10] The geometry of the NUD-3 zeolite structure (as obtained from Rietveld analysis, in a SiO₂ version including Si, O and F atoms occluded in D4R units; disordered F not found by XRD were not included in the calculations) was kept fixed during all the molecular simulations. Molecular structures and the interaction energies of the organic SDA cations with the framework are described with the Dreiding forcefield.^[S11] The atomic charge-distribution of the SDA cations was obtained from DFT+D calculations, using the B3LYP hybrid functional and the ESP charge calculation method, setting the total net charge to +2; framework Si, O and F charges were kept fixed to +0.6, -0.3 and -1.0, respectively.

Due to the large size of the cations, $2 \times 2 \times 2$ supercells were built as zeolite models in order to allow for the different organic long-range packing arrangements. Starting from the location found by Rietveld refinement, the organic cations were manually inserted in the framework in different relative orientations, and the energy of the systems was calculated by geometry-optimization. The interaction energy was calculated by subtracting the energy of the dications in vacuo to the total energy of the system; all the energy values are given in kcal/mol SDA.

DFT quantum mechanics calculations of selected systems were also performed; in this case, atomic positions of the zeolite framework as well as unit cell parameters were allowed to vary during geometry optimization. Calculations were carried out with the CASTEP code,^[S12] using the PBE generalized gradient approximation.^[S13]

In order to explain the structure directing effect of **SDA1** to form the tetragonal NUD-3 instead of the cubic ITQ-21, we firstly performed a DFT geometry optimization of a SiO₂ NUD-3 framework starting with either the tetragonal NUD-3 or the isometric ITQ-21 unit cell parameters, removing any symmetry and unit cell constraints: in both cases the optimization resulted in the same tetragonal cell with a shorter 'c' parameter. This shows that the tetragonal symmetry is inherent to the NUD-3 topology because of the ordered orientation of the S4Rs perpendicular to the *c*-axis, reducing the 'c' parameter and hence making slightly elliptical the [100] and [010] channels.

Ge/T	0	Dof								
H_2O/T	1	Kel.								
SDA/T	0.5	0.25								
SDA1	NUD-3	NUD-3	This work							
SDA2	BEC	LAY	[S14]							
SDA3	ITQ-21	ITQ-21	[S15]							
SDA4	Am	ITQ-21	[S15]							

Tab. S1 Synthesis results using the 4 SDAs in Fig. 1.

Remark: Crystallization temperature = 150 °C, time = 15 days.

Tab. S2 cRED: Experimental parameters and crystallographic details of the structure refinement of as-synthesized NUD-3.

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Identification code	NUD-3
Number of datasets	3
Tilt range	-57.05°~58.45°/-52.76°~63.81°/-60.39°~42.18°
Tilt step	0.23°
Radiation	electron
Wavelength	0.0251 Å
Program for data procession	XDS
Program for structure determination	ShelxT
Crystal system	Tetragonal
Unit cell dimensions	a = b = 14.793(2) Å c = 13.330(3) Å $\alpha = \beta = \gamma = 90 ^{\circ}$
Volume	2917.1(1) Å ³
space group	P4/mmm
Resolution	0.8 Å
$I/\sigma(I)$	6.4
Completeness	100%
No. of total reflections	35835
No. of unique reflections	1772
No. of parameters	70
No. of restraints	0
Dataset (h, k, l)	18→-18, 18→-18, 16→-16
$R_{int}/R_1/WR_2/GoF$	0.3821 / 0.1909 / 0.4854 / 1.407
$\rho_{min}, \rho_{max} (e^{-/} Å^3)$	0.26, -0.37

Identification code	NUD-3				
Composition	$[Ge_{16.53}Si_{19.47}O_{72}F_3] (C_{16}N_4H_{20})_{2.76}$				
Wavelength	0.619274 Å				
Radiation	Synchrotron				
Crystal system	Tetragonal				
Space group	P4/mmm				
Unit cell dimensions	a = b = 14.3055(1) Å c = 12.8455(2) Å $\alpha = \beta = \gamma = 90 \circ$				
Volume	2628.79(8) Å ³				
2θ range for data refinement	2-40°				
Number of parameters	83				
Number of reflections	1141				
Number of data points	12667				
Number of restrains	16 for (Si,Ge)-O, 33 for O-(Si,Ge)-O				
Refinement method	Rietveld refinment				
$R_p/R_{wp}/R_{exp}$	5.99% / 8.12% / 7.72%				

Tab. S3 Crystal data and Rietveld refinement for as-synthesized NUD-3.

Tab. S4 T-O bond distances (Å) for calcined NUD-3.

T1-O9	1.659(7)	T2-O1	1.624(8)	T3-O5	1.669(1)	T4-O5	1.631(2)
T1-O8	1.666(6)	T2-O1	1.624(8)	T3-O4	1.676(6)	T4-O6	1.651(2)
T1-O7	1.667(9)	T2-O6	1.621(2)	T3-O4	1.676(6)	T4-O2	1.666(1)
T1-O2	1.687(1)	T2-O6	1.621(2)	T3-O3	1.678(1)	T4-O2	1.666(1)

Tab. S5 Crystallographic data and framework information of the zeolites relevant to this work.

Zeolite ^[a]	SG	a(Å)	$b(\text{\AA})$	$c(\text{\AA})$	β(°)	U.C. Volume (Å ³)	<i>n</i> (T)/u.c. ^[b]	FD (T*nm ⁻³)	Ref.
NUD-3-as	P4/mmm	14.3055	14.3055	12.8455	90	2629	36	13.69	This work
NUD-3-cal	P4/mmm	14.1787	14.1787	12.7019	90	2554	36	14.10	This work
ITQ-21-as	Fm-3c	27.6980	27.6980	27.6980	90	21249	288	13.55	[S16]
PKU-14-as	I2/m	19.8075	26.7538	19.8127	90.48	10499	128	12.19	[S17]
PKU-14-deh	Fm-3c	27.7683	27.7683	27.7683	90	21412	256	11.96	[S17]

Remarks: [a] "-as" means the as-made zeolite; NUD-3-cal means NUD-3 calcined at 550 °C while PKU-14-deh means the PKU-14 dehydrated by heating at 180 °C. [b] Number of T atoms in each unit cell.

per unit cell (calculated with Dreiding forcefield).										
	Interactio	on Energy (per SDA)	Relative l	Energy (p	er SDA)				
Configuration	1	2	3	1	2	3				
Tetragonal	-101.7	-105.3	-108.4	6.7	3.2	0.0				
Cubic	-98.3	-104.1	-105.4	10.1	4.3	3.0				

Tab. S6 Interaction energy and relative energy (in kcal/mol SDA) of the different **SDA1** configurations in the real tetragonal or a hypothetical pseudocubic unit cell, with a loading of 2 SDAs per unit cell (calculated with Dreiding forcefield)

Tab. S7 C, H, N chemical analyses of as-made NUD-3.

Experimental Weight			Experi	mental	Theoretical		
An	Amount (<i>wt</i> %)			Ratio	Mole Ratio		
N	С	Н	C/N	C/N H/N		H/N	
4.06	14.59	1.73	4.19	5.92	4	5	

T-atom	Coordination Sequences											
Name		N_1 to N_{12}										
T1	4	9	17	28	41	61	90	118	143	174	219	273
T2	4	9	18	30	42	60	89	122	149	172	209	267
Т3	4	12	18	27	46	63	83	116	150	181	213	258
T4	4	11	20	24	34	66	96	105	124	172	220	253
T-atom Name	Mult	iplicity	F	Extended Point Symbol					Ver	tex Syı	nbol	
T1		16		4.	5.4.62	·4·7			4.5	$\cdot 4 \cdot 6_2 \cdot 4$	·12 ₂	
T2		8		$4.6_2 \cdot 4 \cdot 6_2 \cdot 4 \cdot 8_4$					4.62	2·4·6 ₂ ·4	·12 ₂	
Т3		8	$5 \cdot 6 \cdot 5 \cdot 6 \cdot 6_2 \cdot 6$						5.6	5.5.6.62	2.12	
T4		4		4.5	$2 \cdot 6_2 \cdot 6_2$	$\cdot 6_2 \cdot 6_2$			$4 \cdot 5_2$	$\cdot 6_2 \cdot 6_2 \cdot$	$6_2 \cdot 6_2$	

Tab. S8 Topology table of the framework of NUD-3.

Ge/T	SDA/T	H ₂ O/T	<i>T</i> (°C)	<i>t</i> (d)	Product
0.167	0.4167	2.5	150	15	UWY
0.167	0.4167	4.17	150	15	AST
0.167	0.4167	8.33	150	15	UWY
0.167	0.8333	2.5	150	15	UWY
0.167	0.8333	4.17	150	15	LTA
0.167	0.8333	8.33	150	15	UWY
0.333	0.3333	2	150	15	UWY
0.333	0.3333	3.33	150	15	UWY
0.333	0.3333	6.67	150	15	UWY
0.333	0.6667	2	150	15	UWY + LTA
0.333	0.6667	3.33	150	15	UWY + LTA
0.333	0.6667	6.67	150	15	AST
0.333	1	2	150	15	UWY
0.333	1	3.33	150	15	LTA
0.333	1	6.67	150	15	UWY + LTA
0.5	0.15	1.5	150	15	UWY
0.5	0.15	2.5	150	15	UWY
0.5	0.15	5	150	15	UWY
0.5	0.25	1.5	150	15	NUD-3
0.5	0.25	2.5	150	15	NUD-3 + UWY
0.5	0.25	5	150	15	UWY
0.5	0.375	1.5	150	15	NUD-3
0.5	0.375	2.5	150	15	NUD-3
0.5	0.375	5	150	15	UWY
0.5	0.5	1.5	150	15	NUD-3
0.5	0.5	2.5	150	15	NUD-3
0.5	0.5	5	150	15	UWY
0.5	0.75	1.5	150	15	LAY + LTA
0.5	0.75	2.5	150	15	LAY + LTA
0.5	0.75	5	150	15	NUD-3 + UWY
0.6	0.12	1.2	150	15	UWY
0.6	0.12	2	150	15	UWY
0.6	0.12	4	150	15	UWY
0.6	0.2	1.2	150	15	NUD-3
0.6	0.2	2	150	15	UWY
0.6	0.2	4	150	15	UWY
0.6	0.3	1.2	150	15	NUD-3
0.6	0.3	2	150	15	NUD-3
0.6	0.3	4	150	15	UWY
0.6	0.4	1.2	150	15	NUD-3
0.6	0.4	2	150	15	NUD-3
0.6	0.4	4	150	15	NUD-3 + UWY
0.6	0.6	1.2	150	15	LAY + LTA

Tab. S9 High-throughput synthesis results at 150 °C and 175 °C with SDA1.

Ge/T	SDA/T	H_2O/T	<i>T</i> (°C)	<i>t</i> (d)	Product
0.6	0.6	2	150	15	LAY + NUD-3
0.6	0.6	4	150	15	NUD-3
0.167	0.4167	2.5	175	15	UWY
0.167	0.4167	4.17	175	15	UWY
0.167	0.4167	8.33	175	15	AST
0.167	0.8333	2.5	175	15	AST
0.167	0.8333	4.17	175	15	AST
0.167	0.8333	8.33	175	15	AST
0.333	0.3333	2	175	15	UWY
0.333	0.3333	3.33	175	15	UWY
0.333	0.3333	6.67	175	15	AST
0.333	0.6667	2	175	15	UWY
0.333	0.6667	3.33	175	15	UWY
0.333	0.6667	6.67	175	15	UWY
0.5	0.25	1.5	175	15	NUD-3 + UWY
0.5	0.25	2.5	175	15	UWY
0.5	0.25	5	175	15	UWY
0.5	0.5	1.5	175	15	LTA
0.5	0.5	2.5	175	15	UWY
0.5	0.5	5	175	15	UWY
0.5	0.25	1.5	150	30	NUD-3 + LAY
0.5	0.375	1.5	150	30	NUD-3
0.5	0.375	2.5	150	30	NUD-3
0.5	0.5	2.5	150	30	NUD-3
0.6	0.3	2	150	30	NUD-3
0.6	0.4	2	150	30	NUD-3 + LAY

Tab. S9 (continues) High-throughput synthesis results at 150 °C and 175 °C with SDA1

Remark: All the OH anion is provided by the anion-exchanged SDA solution and the HF/SDAOH ratio is 1. A "+" refers to the mixture of 2 phases (characterized by PXRD), while "LAY" refers to an unstable layer material after the calcination. **AST, LTA** and **UWY** are zeolite framework type codes provided by IZA-SC.















Fig. S2 Reconstructed 3D cRED data of NUD-3: (a) overview of 3D reciprocal lattice, and selected 2D slices cut from 3D reciprocal lattice which correspond to (b) *hk*0, (c) *h0l* and (d) 0*kl*.



Fig. S3 Rietveld refinement plot of as-synthesized NUD-3 ($\lambda = 0.619274$ Å).



Fig. S4 Size of the diffusion limiting rings (*i.e.* smallest rings along the channel) of 12MR pores in the Rietveld refined NUD-3 framework, viewed along *a*- and *c*- axes. The O van der Waals radius (1.35 Å) has been subtracted.



Fig. S5 Nitrogen adsorption and desorption curves of calcined NUD-3, showing the Ia type isotherm.



Fig. S6 Argon adsorption and desorption curves of calcined NUD-3, showing the Ia type isotherm.



Fig. S7 Calcined NUD-3 pore size distribution *via* Horvath-Kawazoe differential pore volume plot derived from Ar adsorption.

Nitrogen adsorption (Fig. S5) gives a BET surface area of $392 \text{ m}^2/\text{g}$ and a micropore volume of $0.12 \text{ cm}^3/\text{g}$. When considering the lighter formula weight of silica, the equivalent values for a SiO₂ composition are $530 \text{ m}^2/\text{g}$ and $0.16 \text{ cm}^3/\text{g}$. These values are similar and slightly smaller, respectively, than those reported for silica-based large pore zeolites such as Beta. The lower than expected micropore volume of NUD-3 may be due to a decreased stability of this Ge-rich material. Argon adsorption indicates that the mean pore size of NUD-3 is 6.8 Å, based on the maximum value of the smoothed differential pore volume in the Horvath-Kawazoe graph (Fig. S6, S7).



Fig. S8 *In situ* PXRD patterns of NUD-3 from 30 to 600 °C. The black pattern at the top was collected after heating and then cooling down to 40 °C.



Fig. S9 FT-IR spectra in self-supported wafer of NUD-3 (a) as-made and (b) dehydrated at 180 $^{\rm o}{\rm C}$ for 2 hrs.



Fig. S10 Location of **SDA1** (1 dication per unit cell) in the NUD-3 framework, as obtained from Rietveld refinement; F anions are displayed as balls.



Fig. S11 Two views of the three possible long-range arrangements of **SDA1** (2 cations per unit cell) in the position obtained from Rietveld refinement; F anions are displayed as balls, while O atoms have been omitted for clarity.

After an intensive search, three different long-range arrangements for packing the organic cations in the position obtained from the Rietveld refinement while avoiding short-contacts were found; in the three cases, SDAs in the *ab* plane in adjacent [001] channels orient perpendicular to each other to avoid overlapping (Fig. S11-left). In the first configuration (1), the two SDAs pack by rotating 180° around the *c*-axis, and orienting one of their imidazolium rings towards [00-1] direction (Fig. S11-top); this configuration involves a π - π stacking between the imidazolium rings sited aligned along the [001] channels (dashed vellow rectangle). The second configuration (2) (Fig. S11-middle) is similar to (1), but is built with an inverted SDA where the imidazolium rings aligned with the [001] channels point in opposite directions, preventing an effective π - π stacking between the imidazolium rings. Finally, we found another alternative packing orientation (3) (Fig. S11-bottom); in this case, the two SDAs in the same [001] channel are rotated 180° around b-axis, orienting their imidazolium rings along the [001] channel towards opposite directions, again preventing an effective π - π stacking of the imidazolium rings. Geometry optimization (with Dreiding forcefield) of the three arrangements (in the tetragonal NUD-3 unit cell obtained by Rietveld) (Tab. S6) showed a higher stability for configuration '3' (Interaction energy = -108.4 kcal/mol SDA), followed by '2' (-105.3) and then by '1' (-101.7) (repetition of the calculations but without charges also showed a lower stability for '1', but those for '2' and '3' were similar). DFT calculations for '1' and '2' configurations showed results in line with Dreiding conclusions.



Fig. S12 Interaction energy (in kcal/mol SDA, calculated with Dreiding forcefield) of the three **SDA1** packing arrangements (1, 2 and 3) in NUD-3 tetragonal unit cells with varying *c* parameter.



Fig. S13 Photoluminescence of diluted (left) and concentrated (middle) **SDA1** solutions, and of **SDA1**-NUD-3 (right).

A study of the fluorescence behavior of the cations in aqueous solution at increasing concentration (Fig. S13) shows a unique band at 280 nm when the cation is at low concentration (left), characteristic of phenyl rings arranged as monomers; this also shows that imidazolium rings do not display emission bands at low concentrations, at least in aqueous solution. At high concentrations, two bands emerge, one between 300 and 350 nm and another broad band between 400 and 520 nm (middle). The latter could be assigned to π - π stacked phenyl rings, while the origin for the former is not clear at the moment. The fluorescence spectrum of NUD-3 (right) shows that phenyl rings of adjacent cations do not develop π - π interactions because of the lack of a band at 450-500 nm, in agreement with the Rietveld results. The photoluminescence spectra of NUD-3 in Fig S10 show a relatively strong band at ~300 nm and a weak band at ~450 nm; these two bands could be assigned to the emissions of the monomer and excimers, respectively. Even though no π - π stacking interactions between the phenyl rings are found in the three configurations, interactions such as CH- π (phenyl or imidazolium ring) between the neighboring SDAs may still generate excimers upon excitation. Possibly because of the less efficient charge transfer in these weakly-interacted SDAs, the intensities of the excimers are weaker and the emission of the monomer remains strong.



Fig. S14 ¹⁹F solid state NMR spectrum of as-synthesized NUD-3. Spanning sidebands were marked as "*". A resonance around -125 ppm marked as "x" is assigned to F in hexacoordinated species ^[S18] possibly in the surface of the zeolite ^[S19] or as an impurity phase.



Fig. S15 ¹³C NMR spectrum of (a) solid state NMR of as-made NUD-3, (b) liquid NMR of **SDA1**.



Fig. S16 TG curve of NUD-3.

Based on ¹³C solid state NMR, CHN elemental analysis, Ge/Si ICP analysis, and TG analysis, the unit cell empirical formula of as-synthesized NUD-3 could be determined as $[Ge_{16.73}Si_{19.27}O_{72}]|(C_{16}H_{20}N_4F_2)_{2.80}(H_2O)_{5.14}$.



Fig. S17 Topology figures of NUD-3.

	Fig. S18 Tiling of NUD-3 framework.									
Name & SG	NU	JD-3, <i>P</i> 4/ <i>mm</i>	т	Transitiv	ity	491	28			
Tiling	8[6	3]+4[4.5 ² .6 ²]+	$-3[4^6]+2[4^2.6^4]$	$+[12^6]+2[4^4.6]$	$[4.12^2]+$	$[4^4.5^8.12^2]$				
	A	> <					\sum			
Face Smb.	[6 ³]		$[4.5^2.6^2]$	[4 ⁶]		[4 ² .6	⁶⁴]			
(V, E, F)	(8, 9, 3)	(1	0, 13, 5)	(8, 12, 6	5)	(12, 16	5, 6)			
Symmetry	<i>.m</i> .		m2m	4/ <i>mmm</i> , n	n2m	4mr	п			
Wyckoff	16 <i>n</i>		8 <i>i</i>	2b, 8i		4 <i>e</i>				
Label	t-kah	t-me	el	t-cub		t-lau				
		D	R							
Face Smb.	[12	⁶]	[4 ⁴ .6'	$^{4}.12^{2}]$		$[4^4.5^8.12^2]$				
(V, E, F)	(32, 3	6, 6)	(24, 3	2, 10)		(28, 40, 14)			
Symmetry	4/ <i>m</i> r	nm	mn	nm		ттт				
Wyckoff	21)	1	8		1 <u>g</u>				
Label	-		t-sty							

Remark:

A "-" in Label indicates that this tiling was not found in IZA tiling database.

Supporting References

- S1 L. Xu, L. Zhang, J. Li, K. Muraoka, F. Peng, H. Xu, C. Lin, Z. Gao, J.-G. Jiang, W. Chaikittisilp, J. Sun, T. Okubo and P. Wu, *Chem. Euro. J.*, **2018**, *24*, 9247-9253.
- S2 Z. R. Gao, J. Li, C. Lin, A. Mayoral, J. Sun and M. A. Camblor, *Angew. Chem. Int. Ed.*, 10.1002/anie.202011801.
- S3 W. Wan, J. Sun, J. Su, S. Hovmöller and X. Zou, J. Appl. Cryst., 2013, 46, 1863-1873.
- S4 (a) W. Kabsch, Acta Cryst. 2010, D66, 125-132; (b) W. Kabsch, Acta Cryst. 2010, D66, 133-144.
- S5 G. M. Sheldrick, Acta Cryst. 2015, A71, 3-8.
- S6 A. L. Spek, Acta Cryst. 2009, D65, 148-155.
- S7 A. A. Coelho, J. Appl. Cryst. 2018, 51, 210-218.
- S8 Ch. Baerlocher, A. Hepp and W. M. Meier, DLS-76. A program for the simulation of crystal structures by geometric refinement, 1976. https://www.xray.cz/ecm-cd/soft/xray/refine/dls/dls76manual.html (accessed Oct 29, 2020).
- S9 S. Smeets, L. B. McCusker, Ch. Baerlocher, S. Elomari, D. Xie and S. I. Zones, J. Am. Chem. Soc. 2016, 138, 7099-7106.
- S10 Forcite Module, Material Studio 2019, BIOVIA.
- S11 S. L. Mayo, B. D. Olafson and W. A. Goddard, J. Phys. Chem. 1990, 94, 26, 8897-8909.
- S12 S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. J. Probert, K. Refson and M. C. Payne, Z. *Kristallogr.* 2005, 220, 567-570.
- S13 J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett. 1996, 77, 3865-3868.
- S14 B. W. Boal, M. W. Deem, D. Xie, J. H. Kang, M. E. Davis and S. I. Zones, *Chem. Mater.* 2016, 28, 7, 2158-2164
- S15 F.-J. Chen, The Design of Structure-Directing Agents in the Synthesis of Novel Zeolite and Its Application. Ph.D. Thesis, Nanjing University, Nanjing, March 2014.
- S16 (a) A. Corma, M. J. Diaz-Cabanas, J. Martinez-Triguero, F. Rey and J. Rius, *Nature* 2002, *418*, 514-517; (b) T. Blasco, A. Corma, M. J. Diaz-Cabanas, F. Rey, J. Rius, G. Sastre and J. A. Vidal-Moya, *J. Am. Chem. Soc.* 2004, *126*, 13414-13423.
- S17 J. Liang, J. Su, Y. Wang, Y. Chen, X. Zou, F. Liao, J. Lin and J. Sun, Chem. Euro. J. 2014, 20, 16097-16101.
- S18 (a) C. V. A. Duke, J. M. Miller, J. H. Clark and A. P. Kybett, *Spectrochim. Acta A*, 1990, 46, 1381-1389;
 (b) E. Klock, L. Delmottte, M. Soulard and J.L. Guth, F⁻: A Multifunctional Tool for Microporous Solids
 b 19F of As-Synthesized and Post-Syngthesis Treated Materials, *Proc. 9th International Zeolirte Conference, Montreal*, 1992, Eds.: von Ballmoos et al., Butterworth-Heinemann, 1993, 611-618.
- S19 J. H. Kang, D. Xie, S. I. Zones, and M. E. Davis, Chem. Mater., 2020, 32, 2014-2024.