

Ionic clusters as high-connectivity secondary building units for crystalline porous organic salts

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1. Materials and methods

Materials

All reagents and solvents were obtained from Sigma-Aldrich, Fisher Scientific, Manchester Organics, and Alfa Aesar and used as received. 3,3',5,5'-tetraiodo-2,2',4,4',6,6'-hexamethyl-1,1'-biphenyl was obtained from Yanshen Technology Co., Ltd., and 2,3,6,7,12,13-hexabromotriptycene was obtained from BLD Pharm. TAHP was obtained from Fluorochem Limited. All gases for sorption analysis were supplied by BOC at a purity of $\geq 99.9\%$.

Powder X-ray diffraction (PXRD)

Ambient PXRD analysis were performed on Panalytical Empyrean diffractometer in transmission mode with a high throughput screening XYZ stage, an X-ray focusing mirror, and a PIXcel detector, utilizing Cu-K α radiation ($\lambda = 1.541 \text{ \AA}$). The samples were placed on thin Mylar film in aluminium well plates for PXRD measurement.

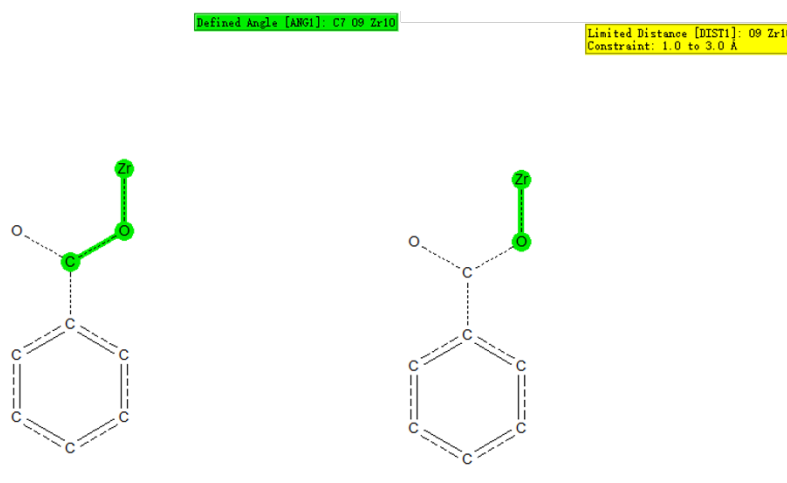
Single crystal X-ray diffraction (SC-XRD)

All the crystals data were collected on Rigaku XtaLAB Synergy (Dualflex, HyPix, CuK α radiation, $\lambda = 1.54184 \text{ \AA}$). To minimize the deterioration of diffraction quality caused by crystal weathering, all crystals were coated with NVH oil or polyisobutene prior to mounting.

Bond length and angle index in CSD

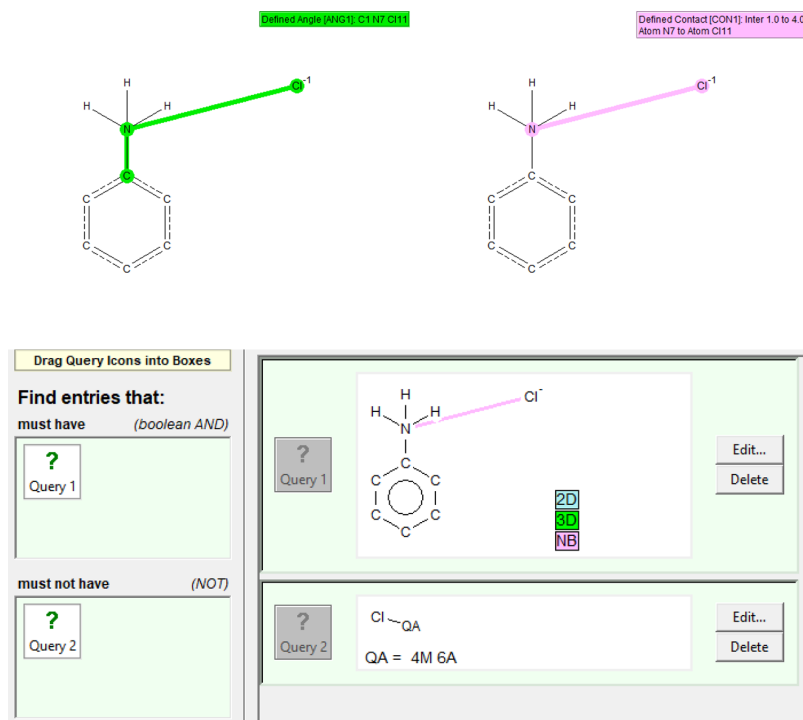
The bond length and angle statistics were obtained using ConQuest based on the CSD version 6.01 (Update Nov 2025) database, applying a filter of R factor ≤ 0.1 .

The query for the carboxylate Zr coordination bond was constructed as illustrated in Supplementary Fig. 1, with both the carboxylate group and the coordination bonds defined as any. The 3D geometric parameters of the Zr–O bond length and the C–Zr–O bond angle were set for analysis, with the Zr–O bond length restricted to the range of 1.0–3.0 $\text{\AA}$.



Supplementary Fig. 1. Structure setting and the 3D geometric parameters setting of carboxylate Zr in ConQuest search.

The query for the anilinium chloride ionic pair was constructed as illustrated in Supplementary Fig. 2. The 3D geometric parameters of the $\text{Cl}\cdots\text{N}$ distance and the $\text{Cl}\cdots\text{N}-\text{C}$ angle were set for analysis, with the $\text{Cl}\cdots\text{N}$ distance restricted to the range of 1.0–4.0 Å. Structures of Cl bonded to any metal and chalcogen elements were excluded from the dataset to avoid the inclusion of other Cl bonded anions.



Supplementary Fig. 2. Structure setting and the 3D geometric parameters setting of anilinium chloride ionic pair in ConQuest search.

Pore analysis

The pore limiting diameter and maximum pore diameter were calculated using Zeo++ with default settings.¹ The solvent-accessible void was calculated using the Void module in Mercury 2025.3.0 with a probe radius of 1.2 Å and visualized using CrystalMaker 11.

NMR

¹H NMR spectra were recorded at 400 MHz on a Bruker Avance 400 NMR spectrometer. Chemical shifts are reported in ppm with reference to internal residual protonated species of the deuterated solvents used for ¹H analysis.

Mass spectrometry

ESI-TOF MS spectra were measured on Bruker maXis 4G ESI-Q-TOF and MALDI-TOF MS spectra were measured on Bruker ultraflexTOF with trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile matrix.

Crystal stability test

The stability of the crystals exhibiting solvent-accessible voids was evaluated by single-crystal X-ray diffraction (SCXRD). Crystals obtained from the high-throughput experiments were immersed in the corresponding antisolvent for solvent exchange. After the exchange was completed, the samples were dried under vacuum, or dried using supercritical CO₂, followed by SCXRD measurements. Crystals that retained diffraction signals after these drying treatments were considered structurally stable and potentially capable of activation.

Among all the porous materials obtained, TAHP·Cl- β , TAHPMe·N₁₂Cl₇, and TPA·N₁₂Cl₉ retained their crystallinity after solvent removal. Therefore, these three materials were further synthesized on a larger scale for stability and gas-adsorption tests.

Guest exchange of TAHPMe·N₁₂Cl₁₂

Although TAHPMe·N₁₂Cl₁₂ was confirmed to be unstable after the loss of antisolvent, the structure became stable when the solvent was replaced with hydrocarbons such as *n*-pentane, *n*-heptane, or cyclohexane. The single-crystal or powder samples were first exchanged with fresh dichloromethane every 24 h for three cycles. The samples were then further exchanged with the corresponding solvent every 24 h for three cycles and dried under vacuum at room temperature for 12 h before other analysis.

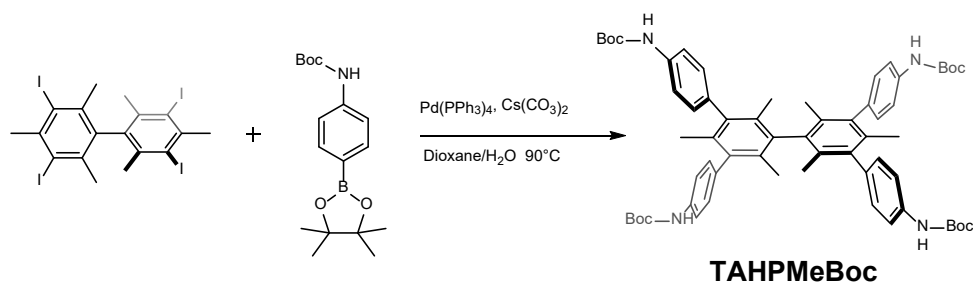
Gas sorption analysis

H₂ adsorption isotherms at 67, 77, 87 and 100 K for determining the isosteric heats of adsorption (Q_{st}) of TAHPMe·N₁₂Cl₇ and 195 K CO₂ for TAHP·Cl- β were measured on a Micromeritics 3Flex volumetric adsorption analyser. The other adsorption isotherms were collected on Micromeritics ASAP 2020 volumetric adsorption analyser. All the data were processed using MicroActive software (version 7.00).

Topology Analysis

Topological analysis was performed using ToposPro 5.5.4.1.² The connectivity models were simplified by treating the geometric centres of the organic linkers and ionic clusters as nodes. Systre V1.2.0 beta 2³ was then used to identify the higher-symmetry embeddings of the resulting periodic nets.

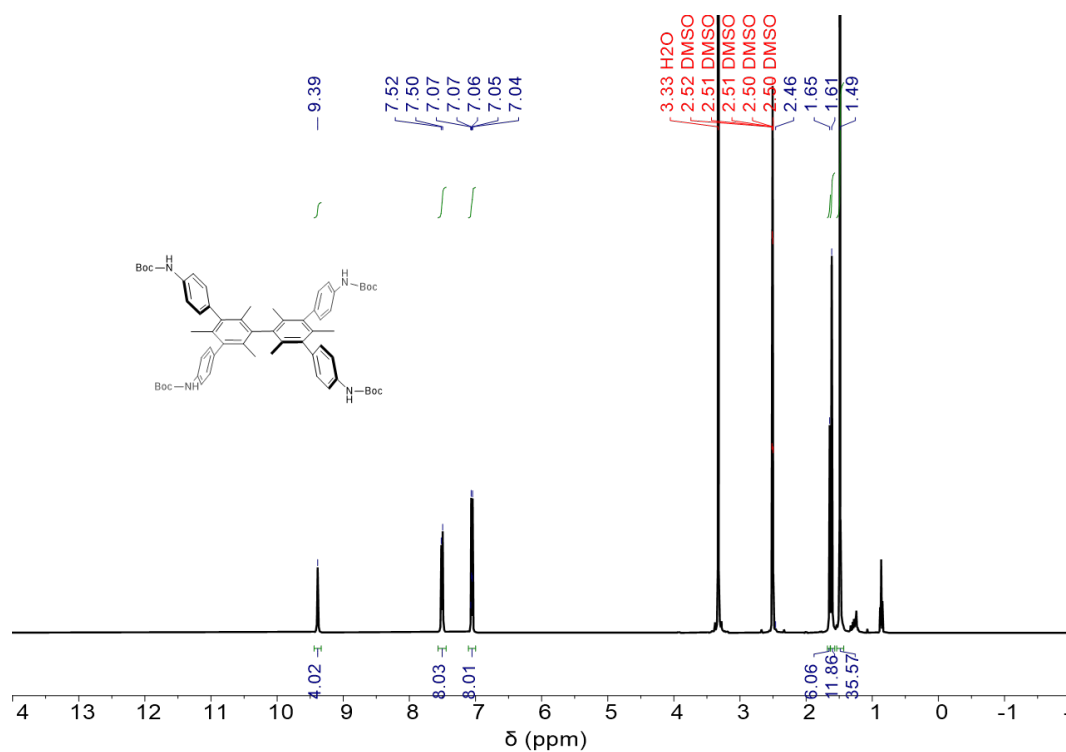
2. Synthetic procedure



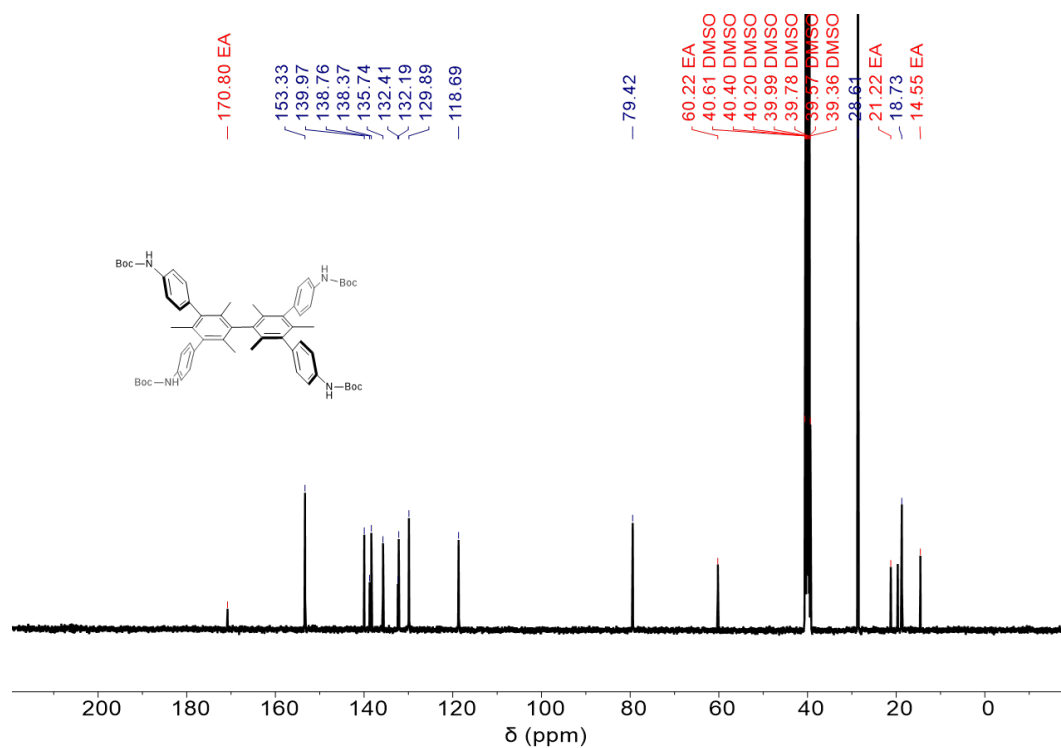
Synthesis of TAHPMeBoc

A 250 mL round-bottom flask was charged with 3,3',5,5'-tetraiodo-2,2',4,4',6,6'-hexamethyl-1,1'-biphenyl (2.8 g, 3.8 mmol), 4-(N-Boc-amino)phenylboronic acid pinacol ester (8 g, 25.1 mmol), palladium tetrakis(triphenylphosphine) (0.3 g, 0.26 mmol), and caesium carbonate (Cs_2CO_3 , 8 g, 24.6 mmol). Subsequently, 100 mL of dioxane and 10 mL of deionized water were added. The reaction mixture was then heated under a nitrogen atmosphere at 90°C for 7 days. After cooling to room temperature, the mixture was extracted with ethyl acetate. The organic phase was dried over anhydrous sodium sulfate and concentrated under reduced pressure. 30 mL of ethyl acetate was added to the oily crude product. After standing at room temperature overnight, a white precipitate formed, which was washed with ethyl acetate twice and dried under vacuum to give the white TAHPMeBoc product (2.9 g, 76%).

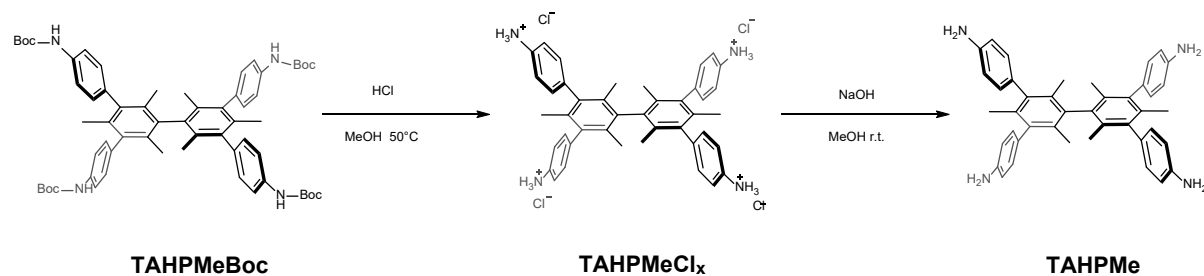
^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 9.39 (s, 4H), 7.51 (d, $J = 8.3$ Hz, 8H), 7.05 (m, 8H), 1.65 (s, 6H), 1.61 (s, 12H), 1.49 (s, 36H). ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 153.33, 139.97, 138.76, 138.37, 135.74, 132.41, 132.19, 129.89, 118.69, 79.42, 28.61, 18.73. MALDI-TOF MS: m/z calc. for $\text{C}_{62}\text{H}_{74}\text{N}_4\text{O}_8 + \text{Na}^+$: 1025.54, found: 1025.72.



Supplementary Fig. 3 ¹H NMR of TAHPMeBoc (400 MHz, DMSO-*d*₆).



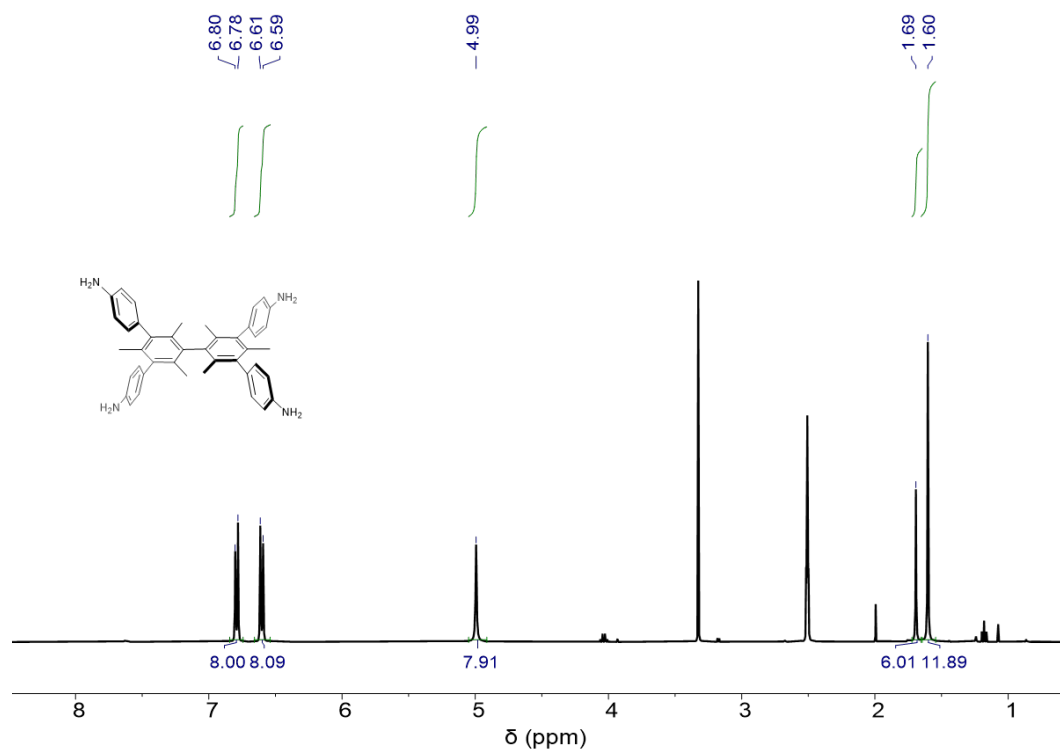
Supplementary Fig. 4 ¹³C NMR of TAHPMeBoc (101 MHz, DMSO-*d*₆).



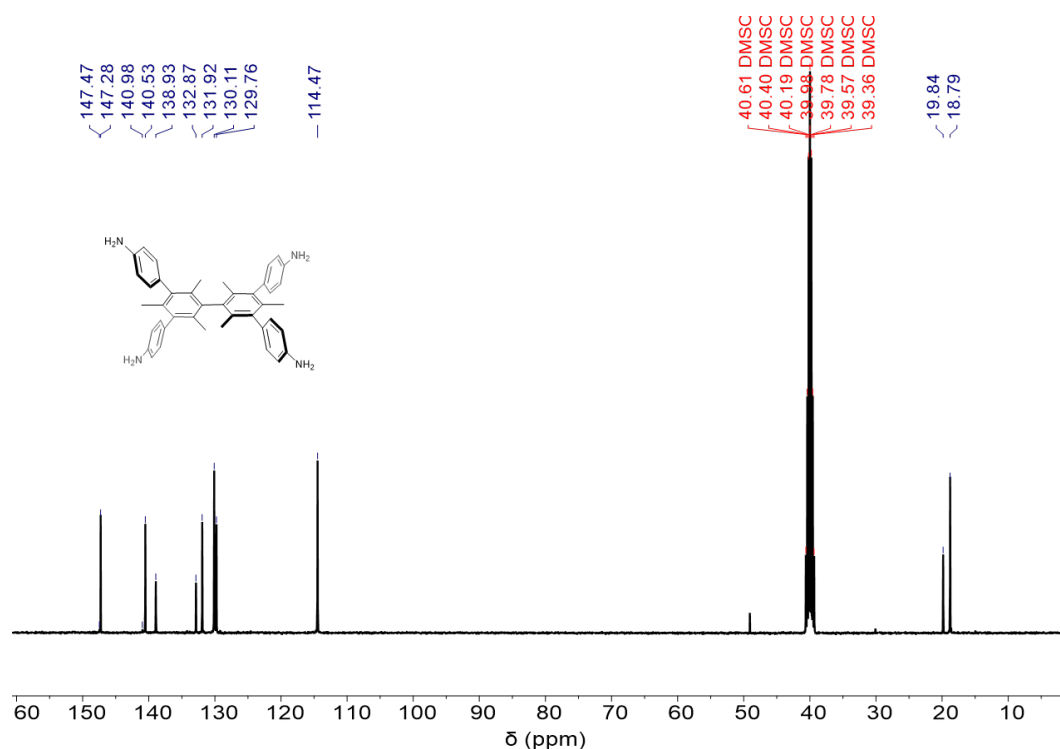
Synthesis of TAHPMe

A 250 mL round-bottom flask was charged with TAHPMeBoc (1.0 g, 1.0 mmol), followed by the addition of 4 mL of methanol and 4 mL of HCl solution (3 M in MeOH). The mixture was heated at 50 °C for 24 h, during which the white solid completely dissolved. After cooling to room temperature, 100 mL of dichloromethane was added to precipitate TAHPMe·Cl_x, which was collected by filtration and washed with dichloromethane twice to give a white TAHPMe·Cl_x solid. To obtain the deprotonated form, the obtained TAHPMe·Cl_x was suspended in 1 mL of methanol. Then, 5 mL of aqueous NaOH solution (1 M) was added, resulting in the formation of a white precipitate. The mixture was stirred for 1 h, and the solid was collected then washed with water twice and dried under vacuum to afford TAHPMe as a white solid (560 mg, 93%).

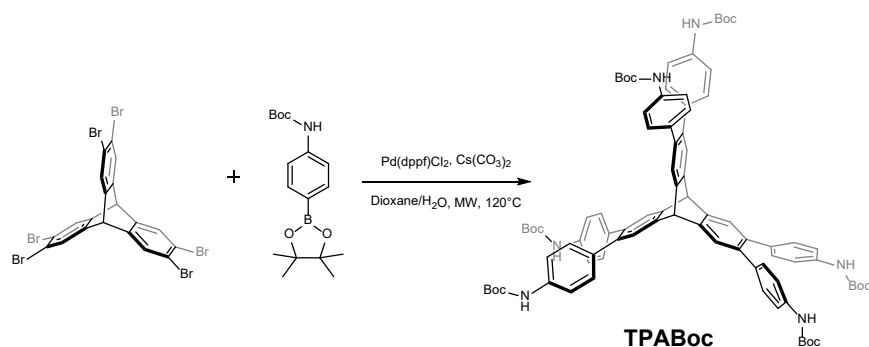
¹H NMR (400 MHz, DMSO-*d*₆) δ 6.79 (d, *J* = 8.5 Hz, 8H), 6.60 (d, *J* = 8.5 Hz, 8H), 4.99 (s, 8H), 1.69 (s, 6H), 1.60 (s, 12H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 147.28, 140.53, 138.93, 132.87, 131.92, 130.11, 129.76, 114.47, 19.84, 18.79. ESI-TOF MS: *m/z* calc. for C₄₂H₄₂N₄ + H⁺: 603.348, found: 603.357.



Supplementary Fig. 5. ¹H NMR of TAHPMe (400 MHz, DMSO-*d*₆).



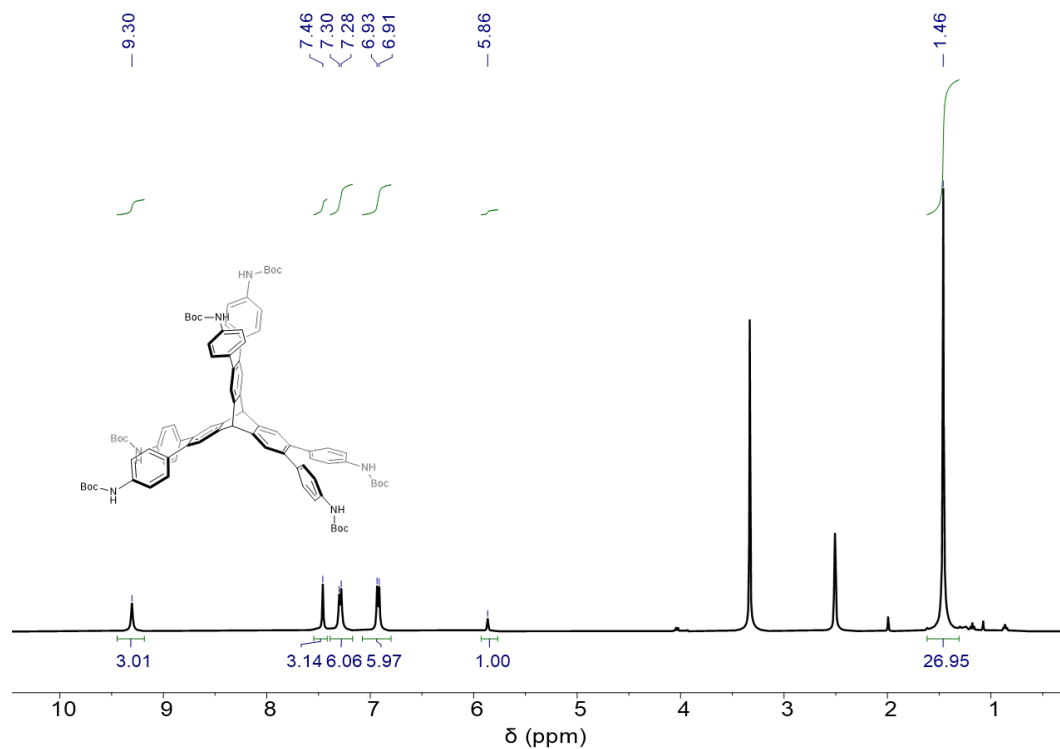
Supplementary Fig. 6. ^{13}C NMR of TAPHPMe (101 MHz, $\text{DMSO}-d_6$).



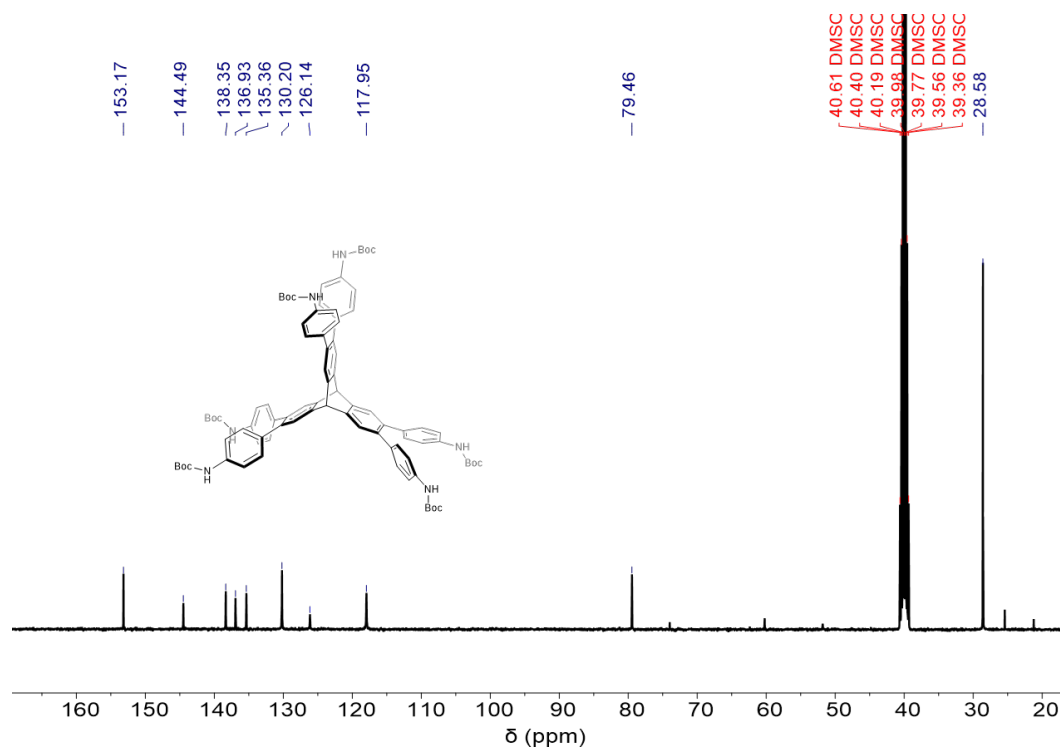
Synthesis of TPABoc

In a 20 mL microwave reaction vial were placed 4-(N-Boc-amino)phenylboronic acid pinacol ester (2.0 g, 6.27 mmol), 2,3,6,7,12,13-hexabromotriptycene (0.32 g, 0.44 mmol), $\text{Pd}(\text{dppf})\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$ (0.09 g, 0.11 mmol), and Cs_2CO_3 (1.50 g, 4.60 mmol). Dioxane (13 mL) and H_2O (1 mL) were then added. The reaction mixture was deoxygenated by bubbling with N_2 for 30 min, sealed, and heated under microwave at 120°C for 2 h. After cooling to room temperature, the reaction progress was monitored by TLC. The solvent was removed under reduced pressure, and the residue was extracted with ethyl acetate. The combined organic extracts were dried over anhydrous Na_2SO_4 , filtered, and concentrated. Purification by column chromatography (PE/EA, gradient elution) afforded the desired product as a white solid (0.49 g, 80%).

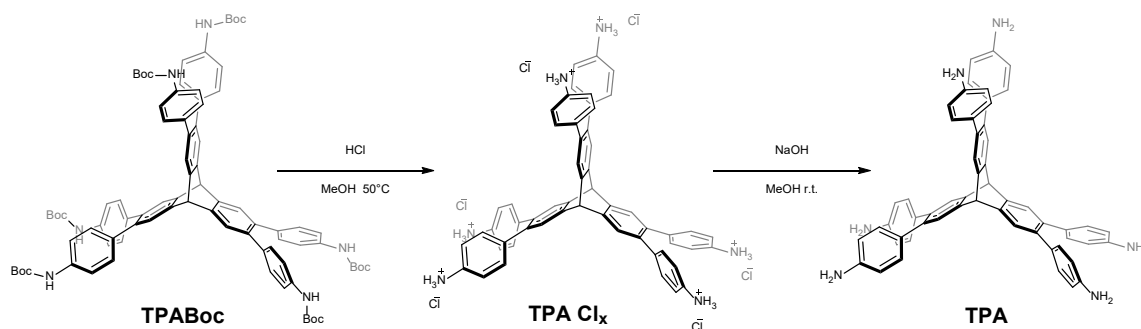
^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 9.30 (s, 3H), 7.46 (s, 3H), 7.29 (d, $J = 8.3$ Hz, 6H), 6.92 (d, $J = 8.3$ Hz, 6H), 5.86 (s, 1H), 1.46 (s, 27H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 153.17, 144.49, 138.35, 136.93, 135.36, 130.20, 126.14, 117.95, 79.46, 28.58. MALDI-TOF MS: m/z calc. for $\text{C}_{86}\text{H}_{92}\text{N}_6\text{O}_{12} + \text{Na}^+$: 1423.67, found: 1423.89.



Supplementary Fig. 7. ^1H NMR of TPABoc (400 MHz, $\text{DMSO-}d_6$).



Supplementary Fig. 8. ^{13}C NMR of TPABoc (101 MHz, $\text{DMSO-}d_6$).

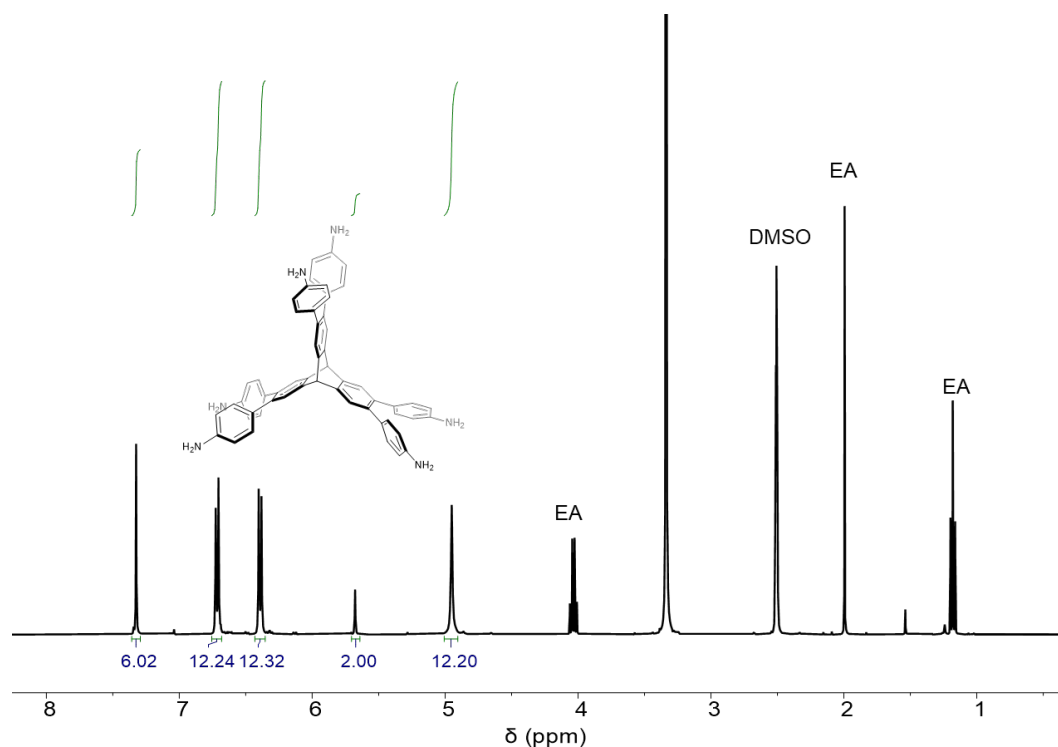


Synthesis of TPA

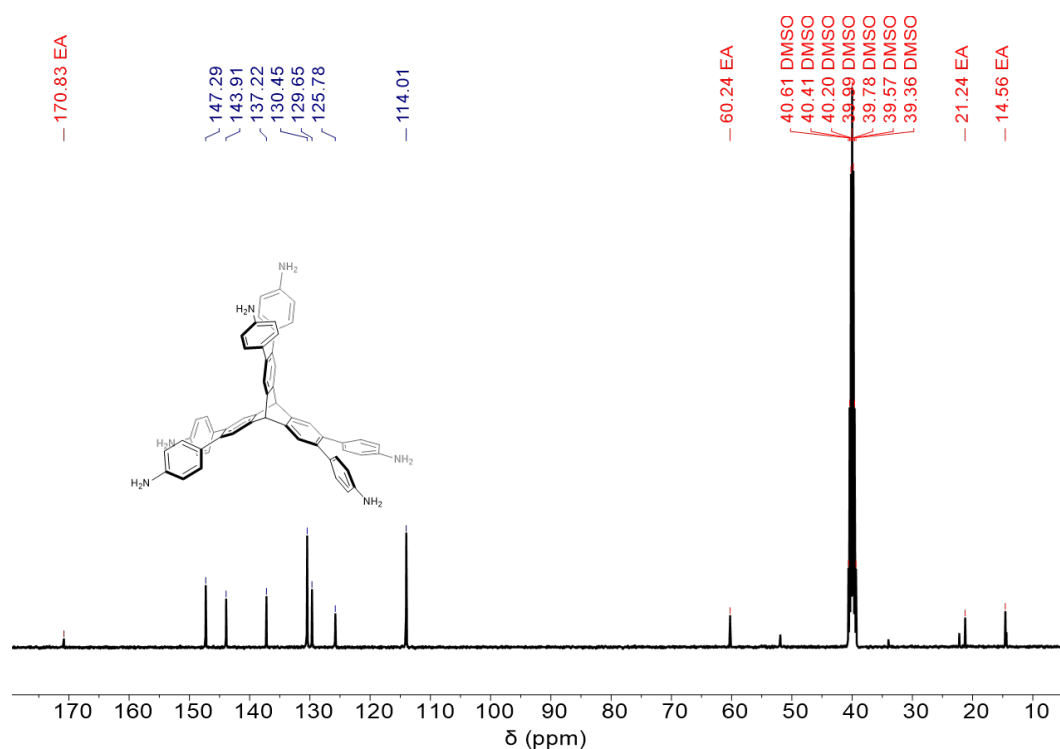
A 25 mL round-bottom flask was charged with TPABoc (300 mg, 0.21 mmol), followed by the addition of 2 mL of methanol and 2 mL of HCl solution (3 M in MeOH). The mixture was heated at 50 °C for 10 h. After cooling to room temperature, 50 mL of ACN was added to precipitate $\text{TPA}\cdot\text{Cl}_x$, which was collected by filtration and washed with ACN twice to give a white $\text{TPA}\cdot\text{Cl}_x$ solid.

To obtain the deprotonated form, the obtained $\text{TPA}\cdot\text{Cl}_x$ was suspended in 2 mL of methanol. Then, 2 mL of ammonium hydroxide solution (30%) was added, resulting in the formation of a white precipitate. The mixture was stirred for 1 h, and the solid was collected then washed with water twice, and extracted with EA. The solvent was removed under reduced pressure, affording a light brown TPA solid (140 mg, 83%).

^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.32 (s, 6H), 6.76 – 6.68 (m, 12H), 6.43 – 6.35 (m, 12H), 5.68 (s, 2H), 4.95 (s, 12H). ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 147.29, 143.91, 137.22, 130.45, 129.65, 125.78, 114.01. ESI-TOF MS: m/z calc. for $\text{C}_{56}\text{H}_{44}\text{N}_6 + \text{H}^+$: 801.370, found: 801.384.



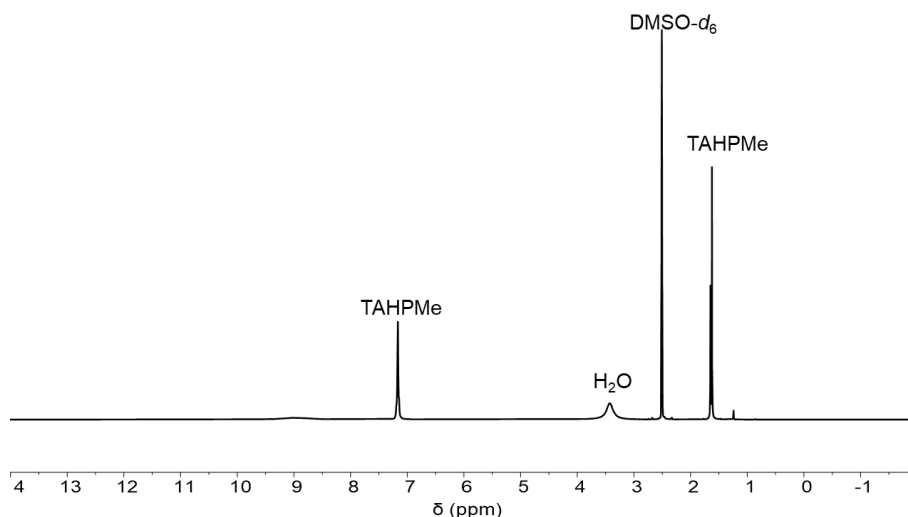
Supplementary Fig. 9. ^1H NMR of TPA (400 MHz, $\text{DMSO}-d_6$).



Supplementary Fig. 10. ¹³C NMR of TPA (101 MHz, DMSO-*d*₆).

Synthesis and activation of TAHPMe·N₁₂Cl₇

TAHPMe·Cl_x (200 mg) was dissolved in MeOH (4 mL), and acetonitrile (10 mL) was added dropwise under gentle stirring. After the addition was complete, the vial was sealed and heated at 80 °C for 10 h, followed by slow cooling to room temperature to afford the TAHPMe·N₁₂Cl₇ powder. The solid was isolated by centrifugation, washed with acetonitrile three times, and subsequently exchanged with fresh acetonitrile every 24 h for three cycles. The wet material was then exchanged with liquid CO₂ for five times in an E3100 critical-point dryer (Quorum Technologies Ltd.). The chamber was heated to 35 °C to bring CO₂ into its supercritical state and maintained for 48 h, after which the pressure was released gradually over 12 h. The activated samples were transferred into adsorption tubes and further degassed at 35 °C for 6 h before gas-adsorption measurements.



Supplementary Fig. 11. ^1H NMR of $\text{TAHPMe}\cdot\text{N}_{12}\text{Cl}_7$ after activation (400 MHz, $\text{DMSO-}d_6$).

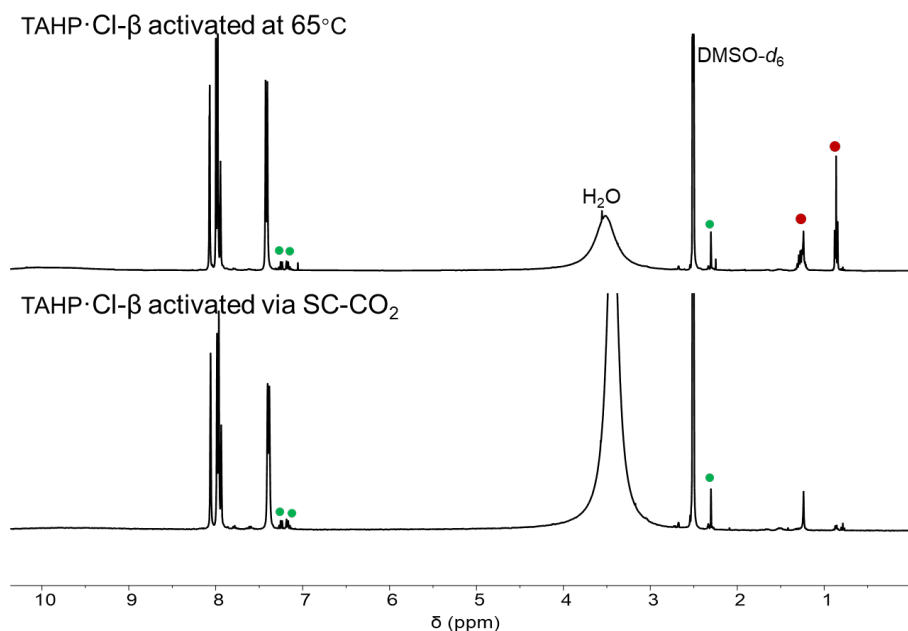
Synthesis of $\text{guest@TAHPMe}\cdot\text{N}_{12}\text{Cl}_{12}$

TAHPMe (200 mg, 0.33 mmol) was suspended in MeOH (4 mL), followed by the addition of HCl (1 mL, 3 M in MeOH). Dichloromethane (100 mL) was then slowly added dropwise to the TAHPMe solution under gentle stirring. After the addition was complete, the resulting solid was collected by filtration, washed with acetonitrile for three times, and then exchanged with fresh dichloromethane every 24 h for three times. The sample was then exchanged with guests (i.e. *n*-pentane, *n*-heptane, cyclohexane) every 24 h for three times. The solid was collected and dried under vacuum for 12 h to give $\text{guest@TAHPMe}\cdot\text{N}_{12}\text{Cl}_{12}$.

Synthesis and activation of $\text{TAHP}\cdot\text{Cl-}\beta$

Despite multiple attempts, $\text{TAHP}\cdot\text{Cl-}\beta$ crystals were difficult to obtain in larger vials. Therefore, crystallization of $\text{TAHP}\cdot\text{Cl-}\beta$ was carried out under solvothermal conditions in 24 4 mL vials using an OT-2 liquid-handling robot. TAHP (200 μL , 40 mM in DMF) and HCl (400 μL , 100 mM in MeOH) stock solutions were sequentially transferred into each 4 mL glass vial, followed by the addition of toluene (1.6 mL) as the antisolvent. The resulting mixtures were allowed to stand at room temperature for 1 h, sealed, and heated at 80 $^{\circ}\text{C}$ for 10 h, then cooled slowly to room temperature. The obtained solids were collected and washed with toluene three times and then exchanged with fresh toluene every 24 h for three times and followed by *n*-pentane every 24 h for three times. The exchanged samples were dried under vacuum at 65 $^{\circ}\text{C}$. $\text{TAHP}\cdot\text{Cl-}\beta$ exhibits strong binding interactions with guest molecules, and NMR analysis indicates that a substantial amount of *n*-pentane remains within the framework after conventional activation. Therefore, supercritical CO_2 was employed for further activation of the sample. The sample then exchanged with liquid CO_2 for five times in the critical-point dryer. The chamber was heated to 35 $^{\circ}\text{C}$ to bring CO_2 into its supercritical state and maintained for 48 h, after which the pressure

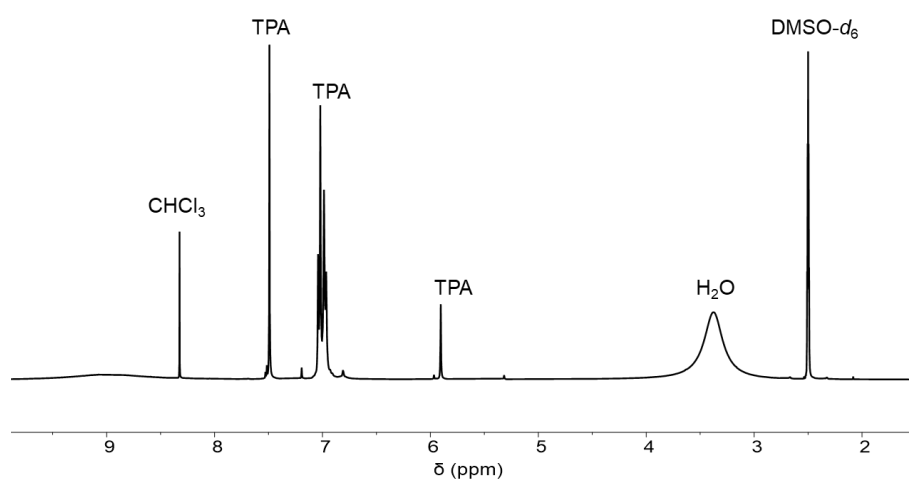
was released gradually over 12 h. The sample was transferred into adsorption tubes and further degassed at 35 °C for 6 h before gas-adsorption measurements.



Supplementary Fig. 12. ^1H NMR of $\text{TAHP}\cdot\text{Cl}\cdot\beta$ after activation at 65 °C under vacuum for 12 h and supercritical CO_2 drying (400MHz, $\text{DMSO}-d_6$). Residual toluene and n -pentane peaks are marked with green and red dots respectively. $\text{TAHP}\cdot\text{Cl}\cdot\beta$ exhibits a strong binding affinity toward n -pentane and toluene, such that conventional activation methods are insufficient to fully remove them. Although supercritical CO_2 treatment effectively removes the bound n -pentane, a small amount of toluene remains difficult to remove.

Synthesis and activation of $\text{TPA}\cdot\text{N}_{12}\text{Cl}_9$:

A 30 mL glass vial containing $\text{TPA}\cdot\text{Cl}_x$ (700 mg) dissolved in methanol (15 mL) was placed inside a container containing chloroform. After several days, hexagonal prismatic crystals of $\text{TPA}\cdot\text{N}_6\text{Cl}_7$ gradually formed. The crystals were isolated and then exchanged with fresh chloroform every 6 h for three times and dried under vacuum at 100 °C for 24 h to afford the partially protonated $\text{TPA}\cdot\text{Cl}_y$ (480 mg). A portion of this material (180 mg) was redissolved with methanol (8 mL) in a vial and placed again in a chloroform container. Rod shape crystals of $\text{TPA}\cdot\text{N}_{12}\text{Cl}_9$ formed over several days. The crystals were collected, then exchanged with fresh chloroform every 6 h for three times. The dry $\text{TPA}\cdot\text{N}_{12}\text{Cl}_9$ crystals were found to be sensitive to humid air, so the wet solid was directly loaded into the adsorption tube and evacuated under an oil pump for 24 h before being backfilled with N_2 . The tube was subsequently transferred to the ASAP 2020 instrument and further degassed at room temperature for 2 h prior to gas-adsorption measurements.



Supplementary Fig. 13. ^1H NMR of $\text{TPA}\cdot\text{N}_{12}\text{Cl}_9$ after adsorption (400 MHz, $\text{DMSO-}d_6$).

3. Crystal structure analysis

To avoid the redissolution of crystals caused by the evaporation of the antisolvent, all samples were washed with the corresponding antisolvent prior to further SCXRD characterization. However, the crystals of $\text{TPA} \cdot \text{N}_6\text{Cl}_7$ were found to be very unstable and the originally hexagonal prismatic crystals broken into pieces when washed with the antisolvent chloroform. The $\text{TPA} \cdot \text{N}_{12}\text{Cl}_9$ crystals containing chloroform showed noticeable sensitivity to strong X-ray irradiation. To minimise radiation damage, the crystals were first dried under vacuum and the data were subsequently collected using intensity reduced X-ray.

All of the structures were solved with the SHELXT⁴ structure solution program using Intrinsic Phasing and refined with the SHELXL⁵ refinement package using Least Squares minimisation in OLEX2⁶ program package. The detailed crystal parameters are listed in the Supplementary Table 1-4 and the supporting CIFs. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions using the riding model and refined isotropically. The protonation state of the amino group was identified based on the C–N bond length. The C–N > 1.45 Å was determined as R–NH₃⁺ and the C–N < 1.45 Å was determined as R–NH₂. Solvent mask was employed to remove the contribution of the diffuse electron density arising from highly disordered solvent molecules that could not be modelled reliably.

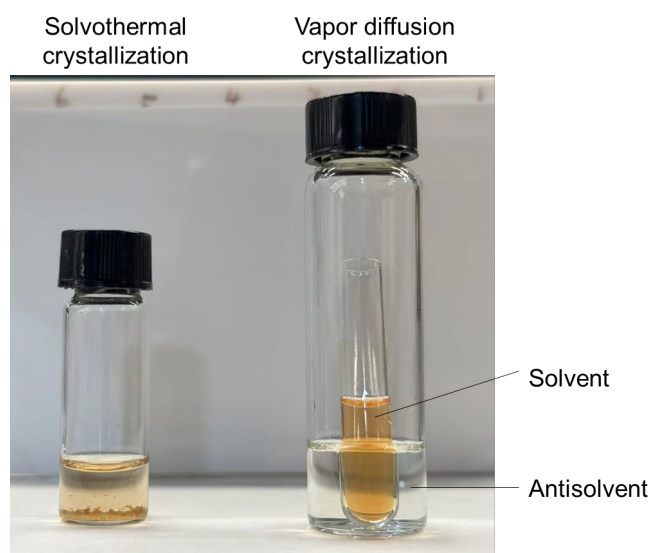
After completion of the crystal structure refinement, the CheckCIF report for TAHP·Cl-β generated a B level alert.

PLAT094_ALERT_2_B Ratio of Maximum / Minimum Residual Density 4.53

Author Response: The relatively elevated residual density ratio is attributed to electron density associated with partially occupied guest species located within the small channels, which could not be completely removed by the solvent mask procedure.

For the guest inclusion structure of TAHPMe·N₁₂Cl₁₂. We also investigated *n*-pentane, methylcyclohexane and carvone, in addition to the *n*-heptane and cyclohexane guests discussed in the main text. However, owing to the high symmetry of the host framework, low-symmetry guests such as methylcyclohexane and carvone could not be resolved unambiguously. Smaller linear guests such as *n*-pentane are less well matched to the cavity, resulting in more disordered electron density. In addition, the guest molecules confined within the highly symmetric cavity-2 and cavity-3 sites could not be unambiguously resolved. By contrast, guest binding could only be clearly identified at the lower-symmetry cavity-1 sites for *n*-heptane and cyclohexane.

The central chloride in the TAHPMe·N₁₂Cl₇ and TPA·N₆Cl₇ clusters refine as unprotonated. However, the chloride is expected as protonated for charge balance, the corresponding protons are expected to be present within the framework and the positions cannot be reliably located.



Supplementary Fig. 14. Vials used for solvothermal crystallization and vapor diffusion crystallization.

Supplementary Table 1. Crystallographic data of TAHP·Cl- α and TAHP·Cl- β

Identification code	TAHP·Cl- α	TAHP·Cl- β
Empirical formula	C ₃₇ H ₃₈ Cl ₄ N ₄ O	C ₃₆ H ₃₄ Cl ₄ N ₄
CCDC	2515978	2515979
Formula weight	696.51	664.47
Temperature/K	100.00(10)	150.00(10)
Crystal system	orthorhombic	orthorhombic
Space group	Cmcm	Cmme
a/Å	29.1734(17)	32.1420(7)
b/Å	7.6247(4)	32.5559(6)
c/Å	7.8363(4)	8.0737(2)
$\alpha/^\circ$	90	90
$\beta/^\circ$	90	90
$\gamma/^\circ$	90	90
Volume/Å ³	1743.09(16)	8448.4(3)
Z	2	8
$\rho_{\text{calc}}/\text{cm}^3$	1.327	1.045
μ/mm^{-1}	3.363	2.738
F(000)	728	2768
Crystal size/mm ³	0.04 × 0.01 × 0.01	0.07 × 0.01 × 0.01
Radiation	Cu K α (λ = 1.54184)	Cu K α (λ = 1.54184)
2 Θ range for data collection/ $^\circ$	6.06 to 155.286	5.43 to 136.49
Index ranges	-34 ≤ h ≤ 35, -3 ≤ k ≤ 9, -9 ≤ l ≤ 9	-36 ≤ h ≤ 38, -38 ≤ k ≤ 39, -9 ≤ l ≤ 7
Reflections collected	3051	24584
Independent reflections	946 [R _{int} = 0.0279, R _{sigma} = 0.0293]	3992 [R _{int} = 0.0424, R _{sigma} = 0.0294]
Data/restraints/parameters	946/15/110	3992/0/207
Goodness-of-fit on F ²	1.067	1.075
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.1059, wR ₂ = 0.2223	R ₁ = 0.0467, wR ₂ = 0.1352
Final R indexes [all data]	R ₁ = 0.1095, wR ₂ = 0.2239	R ₁ = 0.0608, wR ₂ = 0.1421
Largest diff. peak/hole / e Å ⁻³	0.47/-0.58	1.10/-0.24

Supplementary Table 2. Crystallographic data of TAHPMe·N₄Cl₄, TAHPMe·N₁₂Cl₇-A and TAHPMe·N₁₂Cl₇-C.

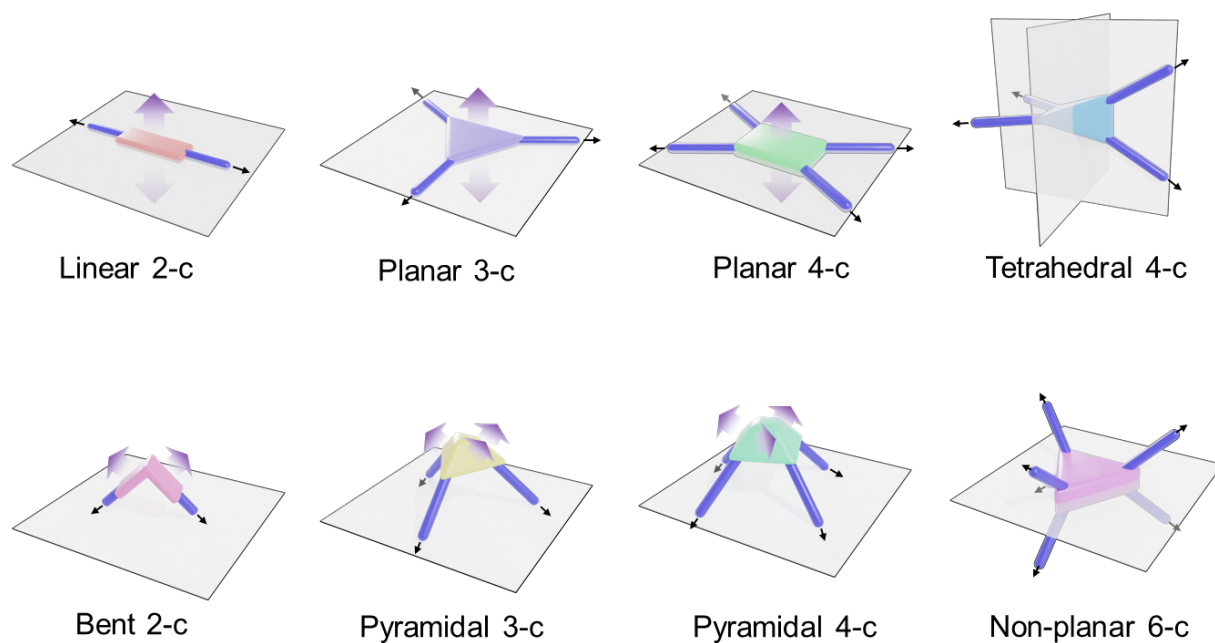
Identification code	TAHPMe·N ₄ Cl ₄	TAHPMe·N ₁₂ Cl ₇ -A	TAHPMe·N ₁₂ Cl ₇ -C
Empirical formula	C ₆₆ H ₉₄ Cl ₄ N ₄ O ₁₂	C ₁₂₆ H ₁₃₂ Cl ₇ N ₁₂	C ₁₂₆ H ₁₃₂ Cl ₇ N ₁₂
CCDC	2515981	2515982	2515983
Formula weight	1277.25	2062.58	2062.58
Temperature/K	100	100	100
Crystal system	monoclinic	trigonal	trigonal
Space group	I2/a	R32	R32
a/Å	18.6790(6)	24.5036(3)	24.4950(5)
b/Å	18.9209(5)	24.5036(3)	24.4950(5)
c/Å	19.9372(6)	21.0117(3)	20.4478(8)
α/°	90	90	90
β/°	96.043(3)	90	90
γ/°	90	120	120
Volume/Å ³	7007.1(4)	10925.8(3)	10625.1(6)
Z	4	3	3
ρ _{calc} /cm ³	1.211	0.94	0.967
μ/mm ⁻¹	2.015	1.57	1.614
F(000)	2728	3273	3273
Crystal size/mm ³	0.08 × 0.08 × 0.08	0.1 × 0.1 × 0.1	0.05 × 0.05 × 0.05
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.458 to 156.266	5.92 to 157.072	6.004 to 155.66
Index ranges	-22 ≤ h ≤ 23, -23 ≤ k ≤ 18, -23 ≤ l ≤ 25	-29 ≤ h ≤ 25, -15 ≤ k ≤ 31, -26 ≤ l ≤ 25	-29 ≤ h ≤ 19, -27 ≤ k ≤ 30, -24 ≤ l ≤ 25
Reflections collected	25136	20027	24372
Independent reflections	6917 [R _{int} = 0.0401, R _{sigma} = 0.0384]	4870 [R _{int} = 0.0210, R _{sigma} = 0.0134]	4647 [R _{int} = 0.0303, R _{sigma} = 0.0232]
Data/restraints/parameters	6917/8/411	4870/0/224	4647/0/224
Goodness-of-fit on F ²	1.041	1.061	1.054
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0651, wR ₂ = 0.1892	R ₁ = 0.0362, wR ₂ = 0.1039	R ₁ = 0.0548, wR ₂ = 0.1597
Final R indexes [all data]	R ₁ = 0.0794, wR ₂ = 0.2034	R ₁ = 0.0373, wR ₂ = 0.1048	R ₁ = 0.0604, wR ₂ = 0.1644
Largest diff. peak/hole / e Å ⁻³	0.73/-1.05	0.19/-0.28	0.34/-0.21
Flack parameter		0.029(4)	0.062(7)

**Supplementary Table 3. Crystallographic data of Cyclohexane@TAHPMe·N₁₂Cl₁₂
Heptane@TAHPMe·N₁₂Cl₁₂.**

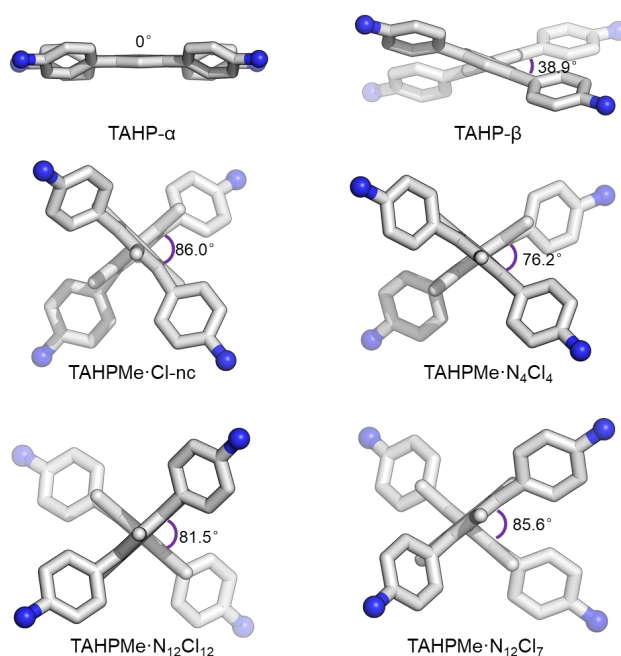
Identification code	Cyclohexane@TAHPMe· N ₁₂ Cl ₁₂	Heptane@TAHPMe· N ₁₂ Cl ₁₂	TAHPMe·Cl-nc
Empirical formula	C ₁₂₆ H ₁₇₆ Cl ₈ N ₈	C ₄₉ H ₆₂ Cl ₄ N ₄	C ₄₂ H ₄₆ Cl ₄ N ₄
CCDC	2515984	2515985	2515980
Formula weight	2086.34	848.82	748.63
Temperature/K	120.00(10)	100.01(10)	100.00(10)
Crystal system	trigonal	trigonal	monoclinic
Space group	R-3c	R-3c	I2/a
a/Å	32.0272(4)	32.3220(8)	10.1838(4)
b/Å	32.0272(4)	32.3220(8)	16.3023(7)
c/Å	44.6176(7)	43.4361(10)	29.9501(11)
$\alpha/^\circ$	90	90	90
$\beta/^\circ$	90	90	99.728(3)
$\gamma/^\circ$	120	120	90
Volume/Å ³	39634.6(12)	39299(2)	4900.8(3)
Z	9	18	4
$\rho_{\text{calc}}/\text{cm}^3$	0.787	0.646	1.015
μ/mm^{-1}	1.425	1.379	2.479
F(000)	10116	8136	1696
Crystal size/mm ³	0.2 × 0.2 × 0.2	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.1
Radiation	Cu K α (λ = 1.54184)	Cu K α (λ = 1.54184)	Cu K α (λ = 1.54184)
2 θ range for data collection/ $^\circ$	5.084 to 157.266	5.15 to 155.17	5.988 to 156.044
Index ranges	-39 ≤ h ≤ 38, -25 ≤ k ≤ 39, -53 ≤ l ≤ 55	-39 ≤ h ≤ 27, -35 ≤ k ≤ 38, -53 ≤ l ≤ 48	-12 ≤ h ≤ 12, -16 ≤ k ≤ 20, -35 ≤ l ≤ 38
Reflections collected	43266	40783	18076
Independent reflections	8839 [R _{int} = 0.0196, R _{sigma} = 0.0129]	8647 [R _{int} = 0.0579, R _{sigma} = 0.0404]	4776 [R _{int} = 0.0388, R _{sigma} = 0.0330]
Data/restraints/parameters	8839/339/447	8647/105/296	4776/95/290
Goodness-of-fit on F ²	1.064	1.053	1.057
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0859, wR ₂ = 0.2636	R ₁ = 0.0859, wR ₂ = 0.2775	R ₁ = 0.1296, wR ₂ = 0.3427
Final R indexes [all data]	R ₁ = 0.0928, wR ₂ = 0.2723	R ₁ = 0.1195, wR ₂ = 0.3089	R ₁ = 0.1370, wR ₂ = 0.3473
Largest diff. peak/hole / e Å ⁻³	0.81/-0.32	0.58/-0.39	0.67/-0.39

Supplementary Table 4. Crystallographic data of TPA, TPA·N₆Cl₇, TPA·N₁₂Cl₉.

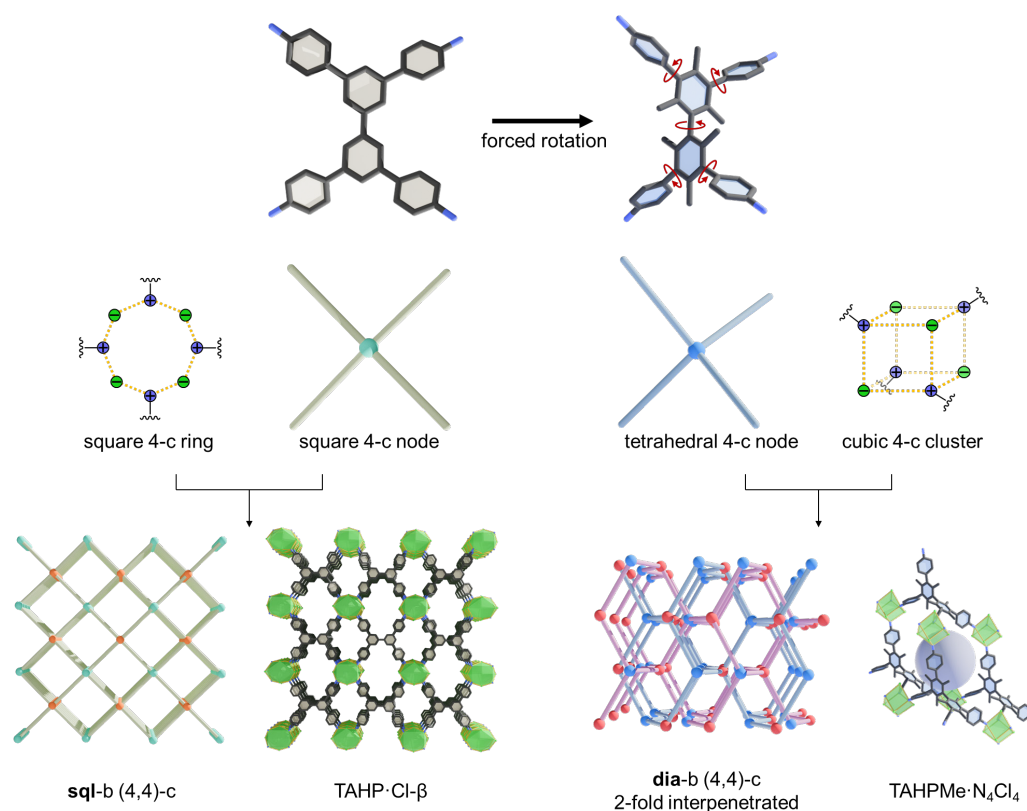
Identification code	TPA	TPA·N ₆ Cl ₇	TPA·N ₁₂ Cl ₉
Empirical formula	C ₅₆ H ₄₄ N ₆	C ₅₆ H ₅₀ Cl ₇ N ₆	C ₁₁₂ H ₉₇ Cl ₉ N ₁₂
CCDC	2515986	2515987	2515988
Formula weight	800.97	1055.17	1930.06
Temperature/K	130.00(10)	150.00(10)	99.94(13)
Crystal system	triclinic	hexagonal	monoclinic
Space group	P-1	P6 ₃ /mmc	P2 ₁
a/Å	9.21740(10)	19.7415(4)	13.6154(2)
b/Å	16.5382(2)	19.7415(4)	31.8704(3)
c/Å	19.4184(3)	20.3575(4)	19.5183(2)
α/°	110.5460(10)	90	90
β/°	95.6960(10)	90	93.3090(10)
γ/°	99.4190(10)	120	90
Volume/Å ³	2694.84(6)	6870.9(3)	8455.42(17)
Z	2	2	2
ρ _{calc} /cm ³	0.987	0.51	0.758
μ/mm ⁻¹	0.453	1.449	1.617
F(000)	844	1094	2012
Crystal size/mm ³	0.05 × 0.05 × 0.05	0.05 × 0.05 × 0.01	0.4 × 0.1 × 0.1
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2θ range for data collection/°	4.932 to 158.302	5.168 to 157.594	4.534 to 133.2
Index ranges	-9 ≤ h ≤ 11, -20 ≤ k ≤ 20, -22 ≤ l ≤ 24	-23 ≤ h ≤ 23, -20 ≤ k ≤ 23, -16 ≤ l ≤ 25	-16 ≤ h ≤ 16, -37 ≤ k ≤ 37, -23 ≤ l ≤ 21
Reflections collected	36525	23904	90884
Independent reflections	10651 [R _{int} = 0.0209, R _{sigma} = 0.0208]	2623 [R _{int} = 0.0263, R _{sigma} = 0.0155]	29441 [R _{int} = 0.0560, R _{sigma} = 0.0589]
Data/restraints/parameters	10651/0/565	2623/1/86	29441/4/1210
Goodness-of-fit on F ²	1.026	1.392	1.044
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0480, wR ₂ = 0.1369	R ₁ = 0.1098, wR ₂ = 0.3053	R ₁ = 0.0833, wR ₂ = 0.2276
Final R indexes [all data]	R ₁ = 0.0548, wR ₂ = 0.1416	R ₁ = 0.1159, wR ₂ = 0.3181	R ₁ = 0.1023, wR ₂ = 0.2482
Largest diff. peak/hole / e Å ⁻³	0.33/-0.29	0.72/-0.53	1.66/-0.44



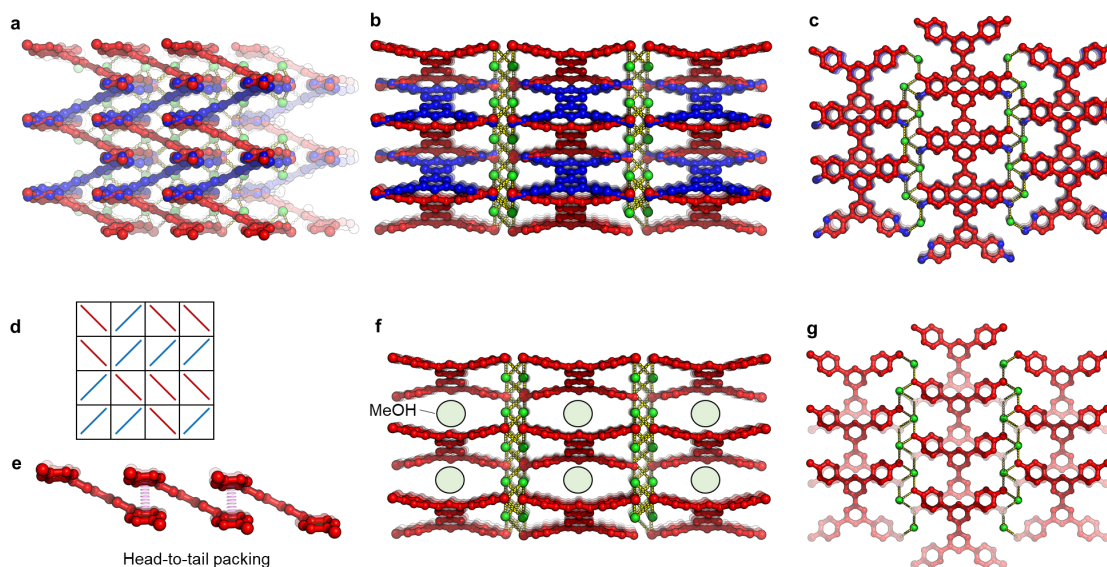
Supplementary Fig. 15. Comparison of geometric configurations between different linkers. Charge-bearing arms of the linkers are shown as dark-blue sticks. Electrostatic and inter-linker dispersion interactions are represented by black and light-purple arrows respectively.



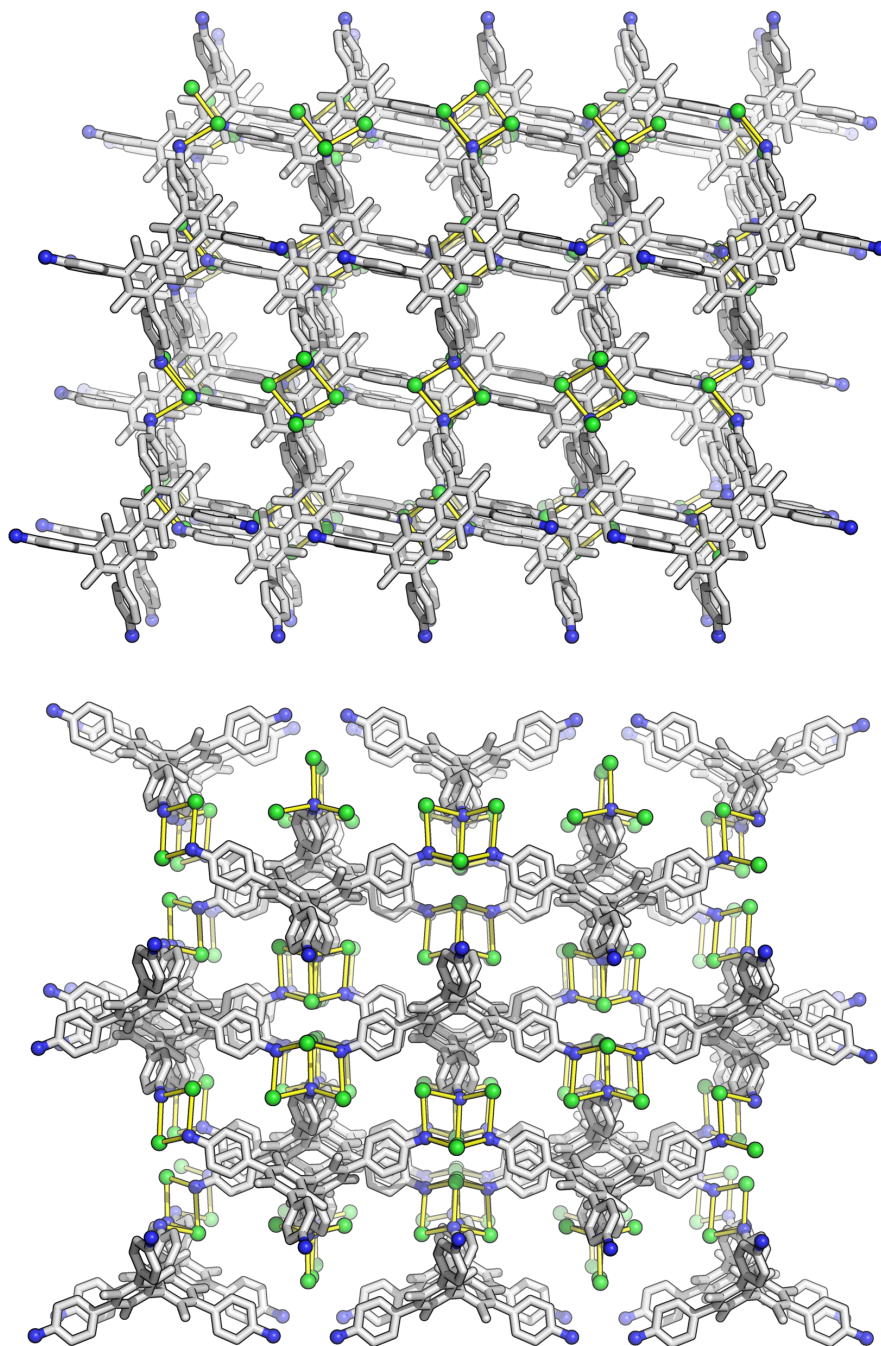
Supplementary Fig. 16. The torsion angles of TAHP and TAHPMe in different crystal structures.



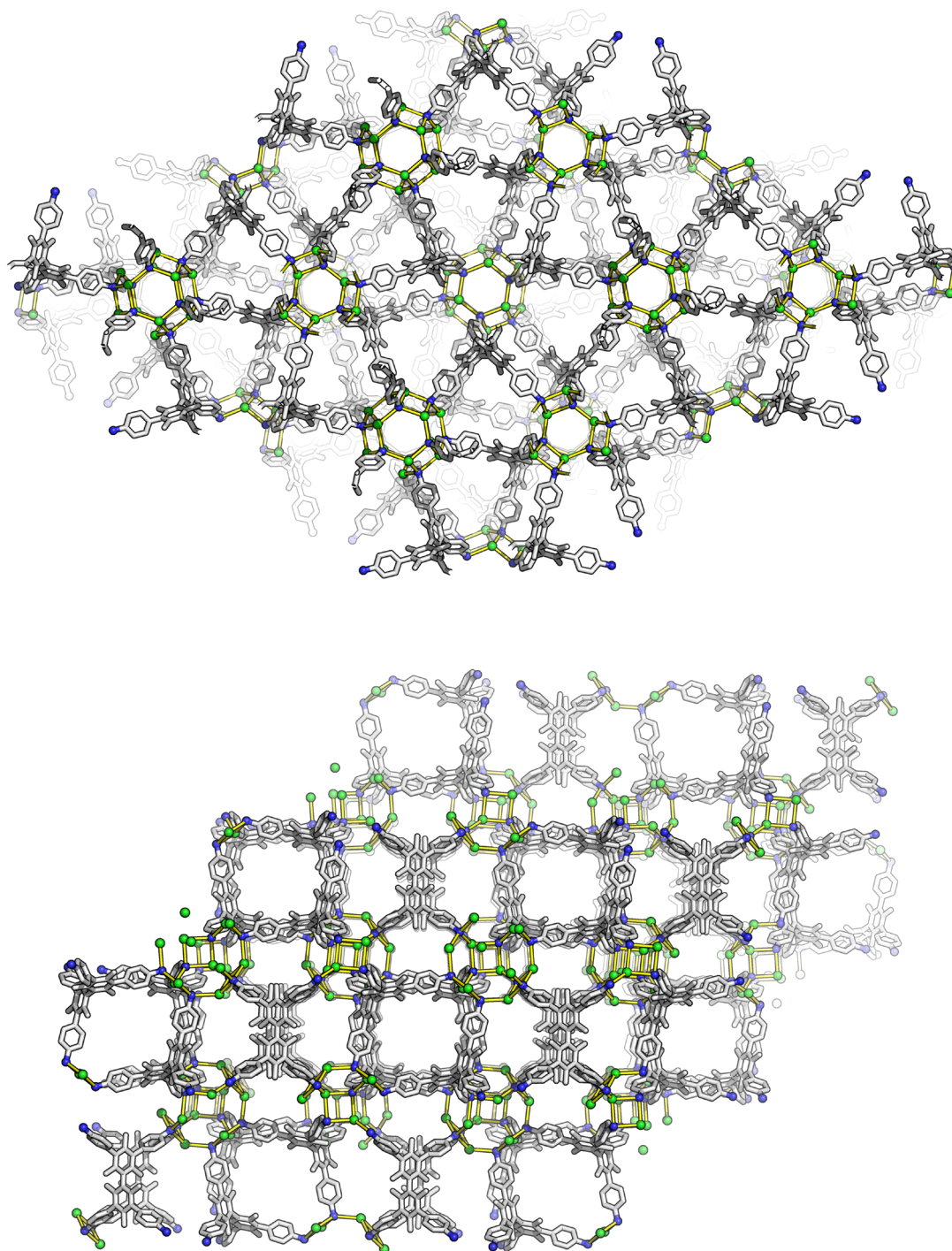
Supplementary Fig. 17. Forced linker rotation changes the linker geometry from square to tetrahedral connectivity. This geometrical mismatch drives the transformation of the cyclic 4+4 ionic centre into cluster-type nodes, giving rise to a **dia-b** net.



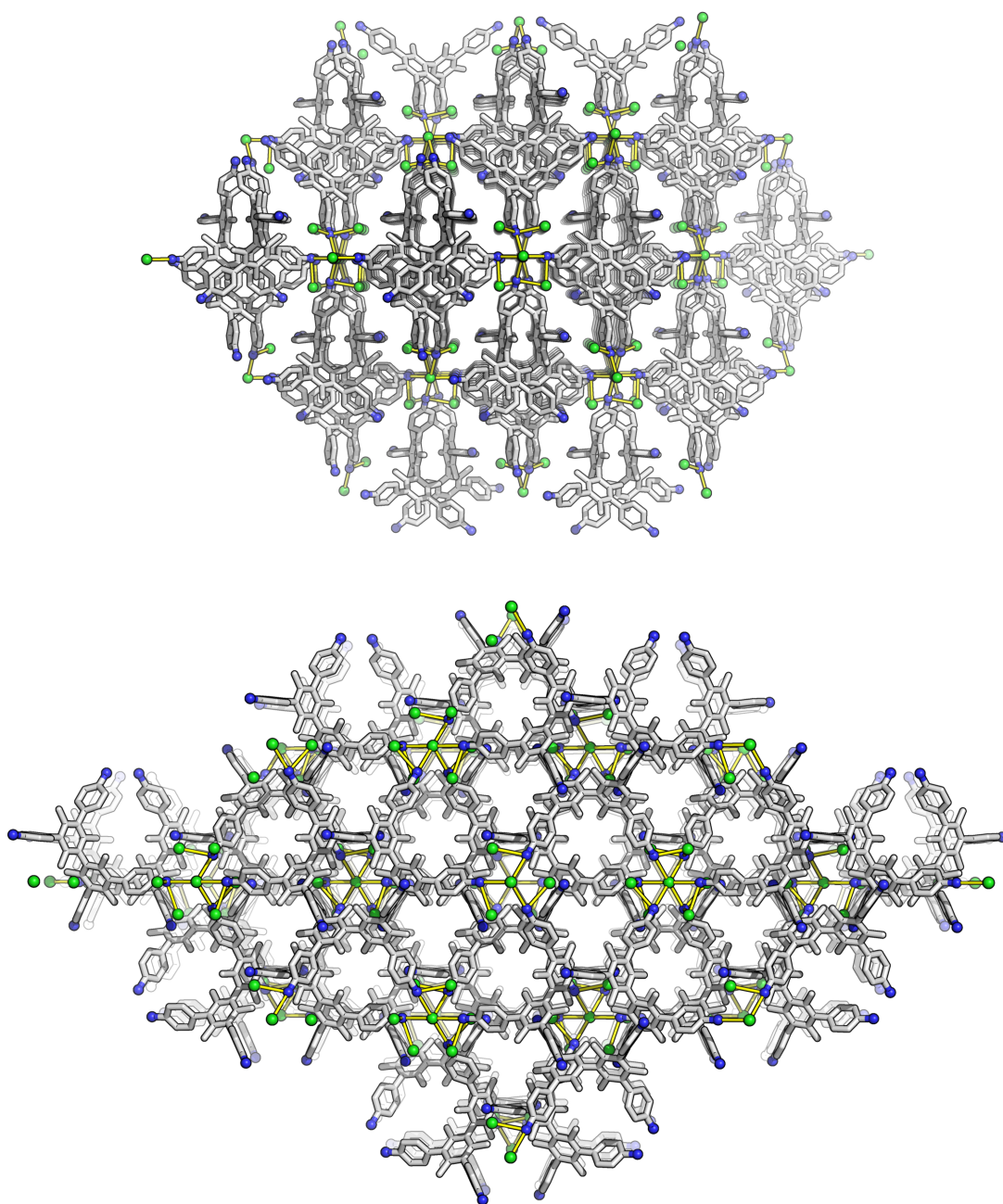
Supplementary Fig. 18. Packing of TAHP·Cl-α. Views along the a, b and c axes showing the two disordered parts of TAHP·Cl-α (**a–c**). Illustration of positional disorder of the TAHP in the structure (**d**). Head-to-tail packing of TAHP (**e**). The packing of one disordered part viewed along the b and c axes. Hydrogen atoms are omitted for clarity.



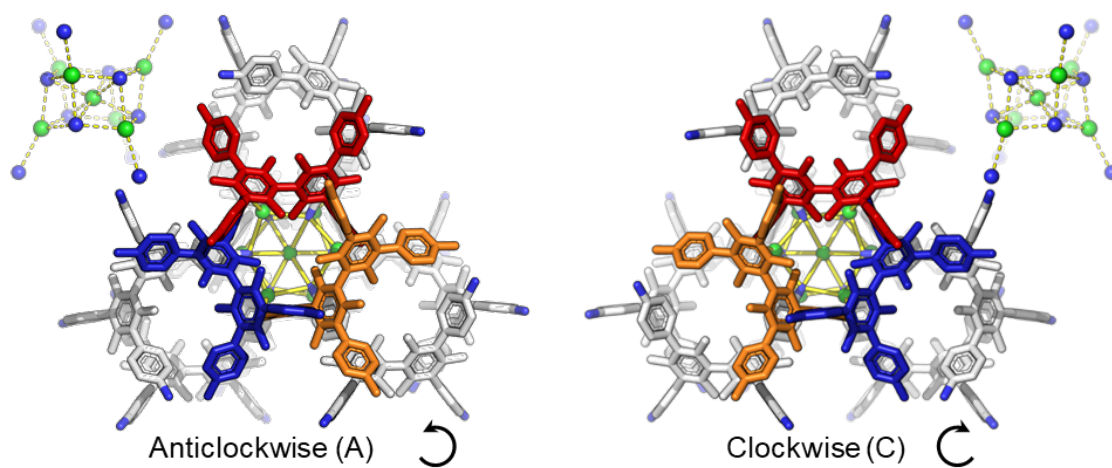
Supplementary Fig. 19. Packing of TAHPMe·N₄Cl₄. Hydrogen atoms are omitted for clarity.



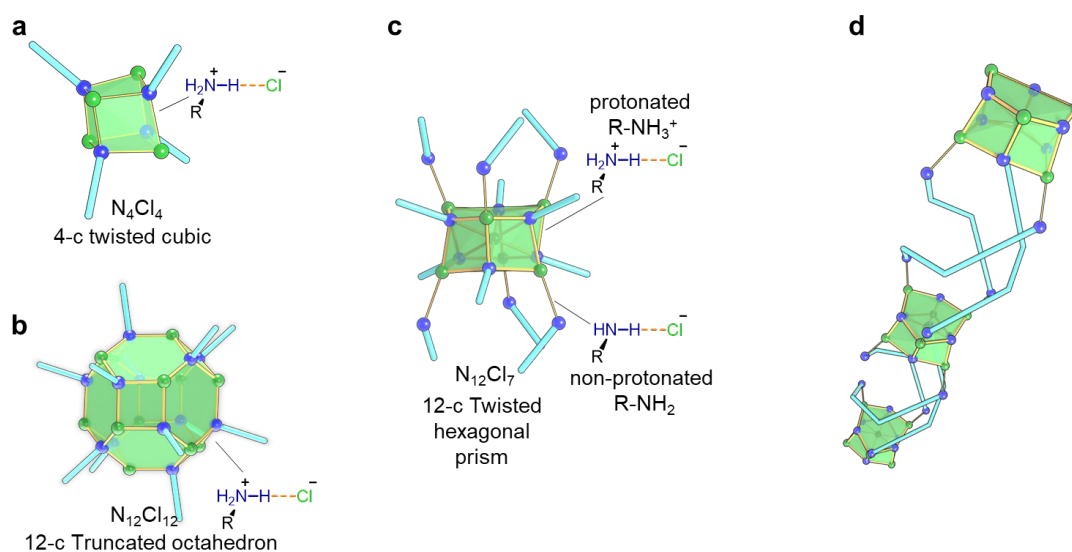
Supplementary Fig. 20. Packing of TAHPMe·N₁₂Cl₁₂. Hydrogen atoms are omitted for clarity.



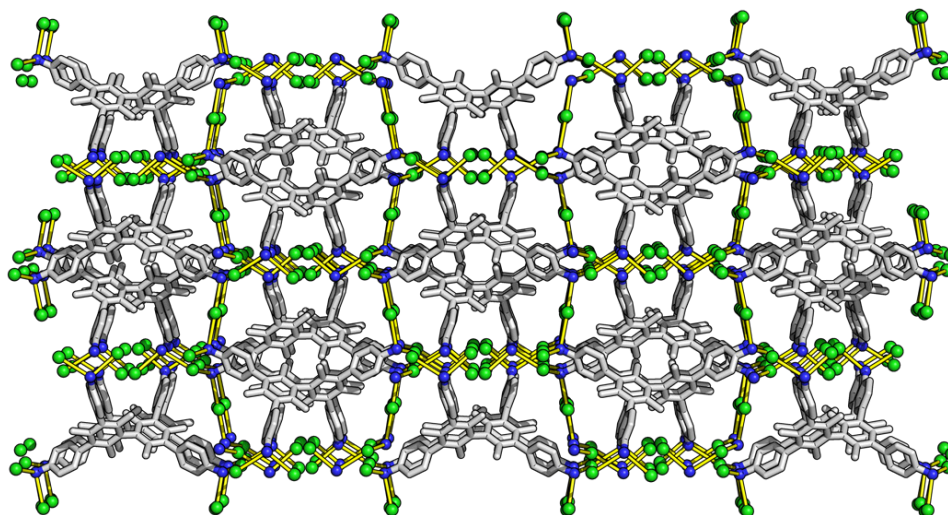
Supplementary Fig. 21. Packing of TAHPMe·N₁₂Cl₇. Hydrogen atoms are omitted for clarity.



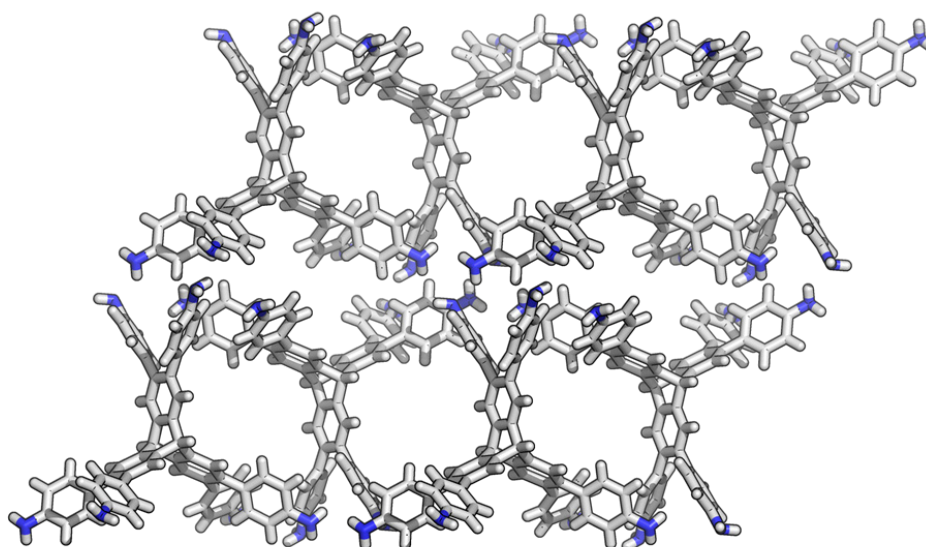
Supplementary Fig. 22. Detailed twisted hexagonal prism $N_{12}Cl_7$ cluster structure and its chiral configuration. Hydrogen atoms are omitted for clarity.



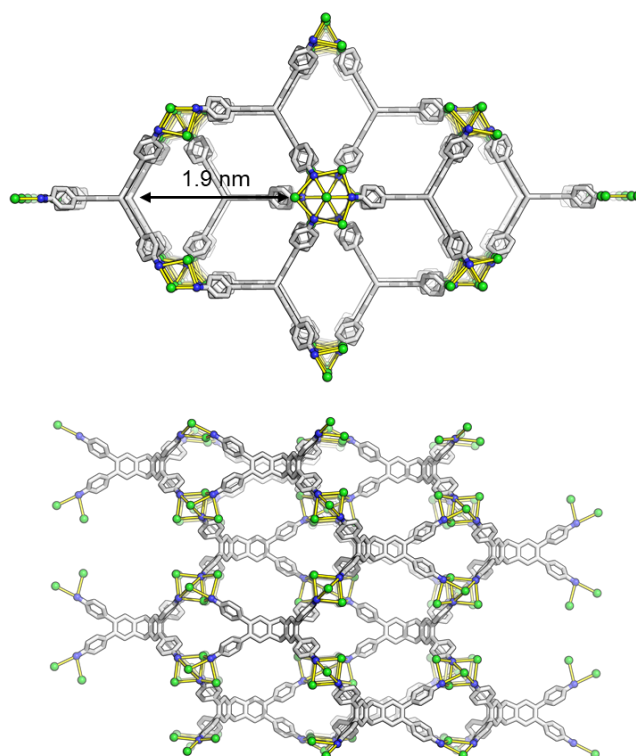
Supplementary Fig. 23. **a–c**, Structures of 4-c N_4Cl_4 twisted cuboid (**a**), 12-c $N_{12}Cl_{12}$ truncated octahedron (**b**), and 12-c $N_{12}Cl_7$ twisted hexagonal prism (**c**). **d**, Chiral helicate formed by the ionic clusters in $TAHPMe \cdot N_{12}Cl_7$.



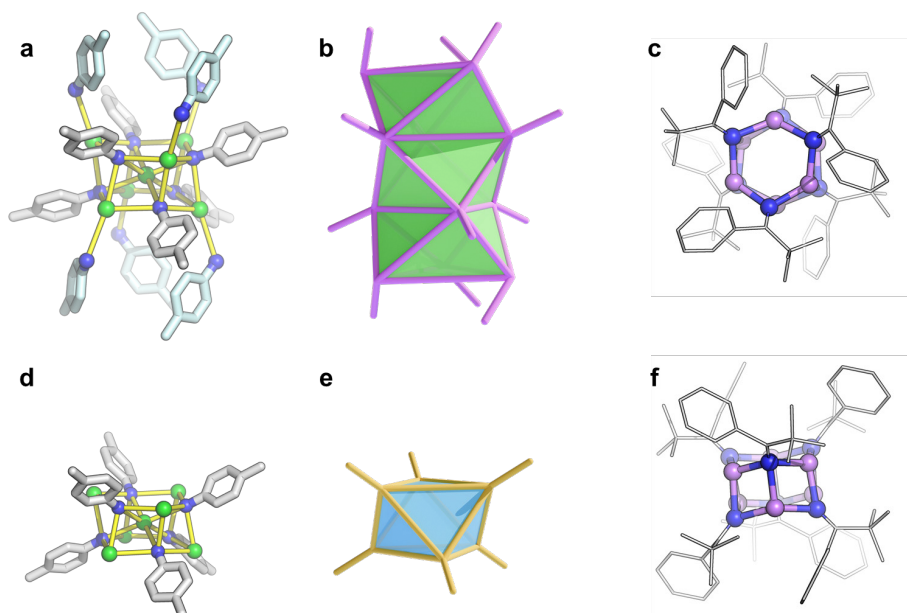
Supplementary Fig. 24. Packing of TAHPMe·Cl-nc. One part of disorder and hydrogen atoms are omitted for clarity.



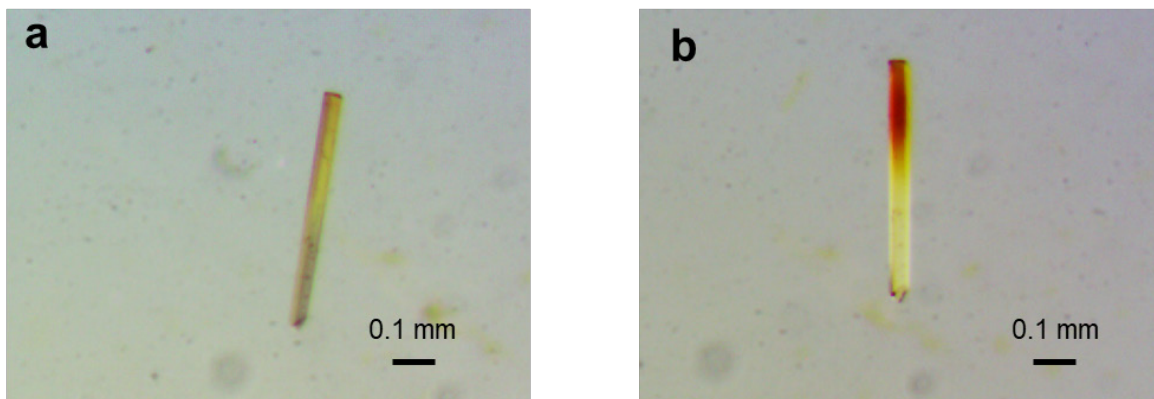
Supplementary Fig. 25. Packing of TPA linker (not protonated). No obvious interactions were observed between the triptycene cores.



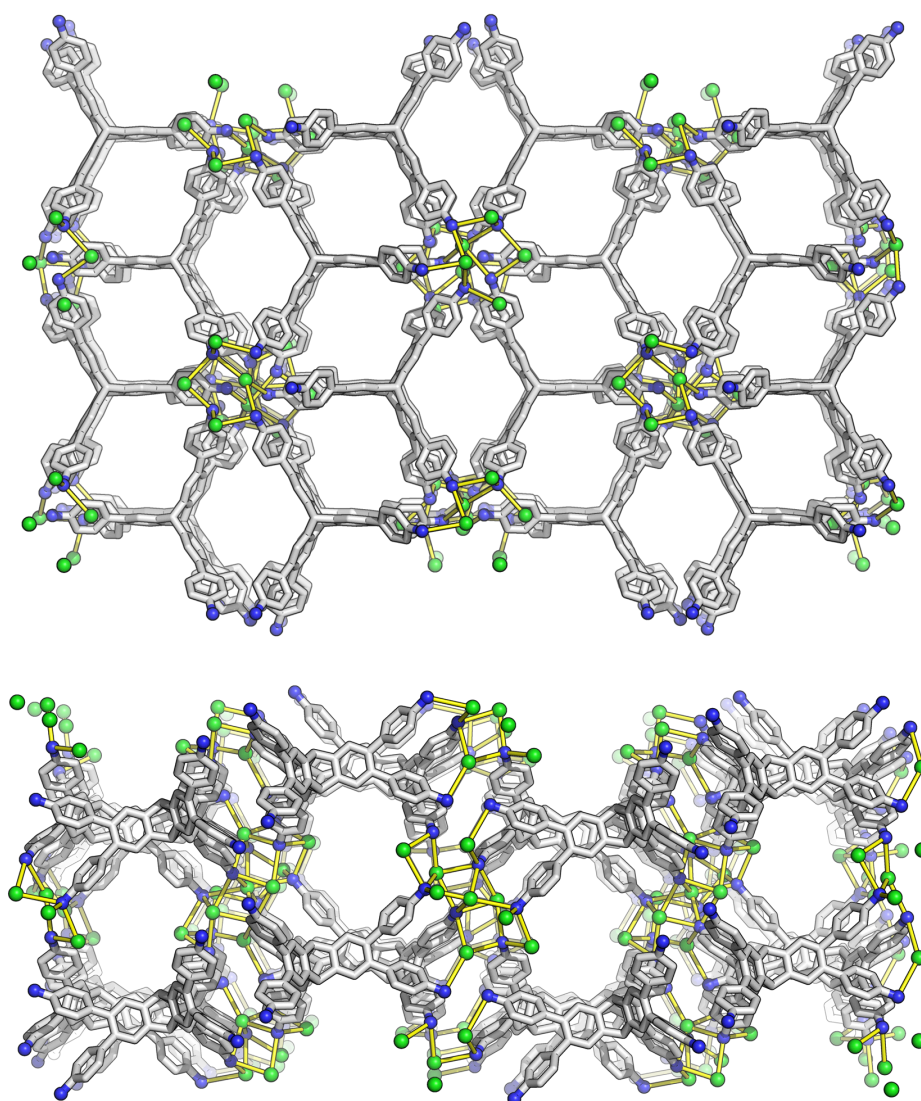
Supplementary Fig. 26. Packing of TPA·N₆Cl₇. One part of disorder and hydrogen atoms are omitted for clarity.



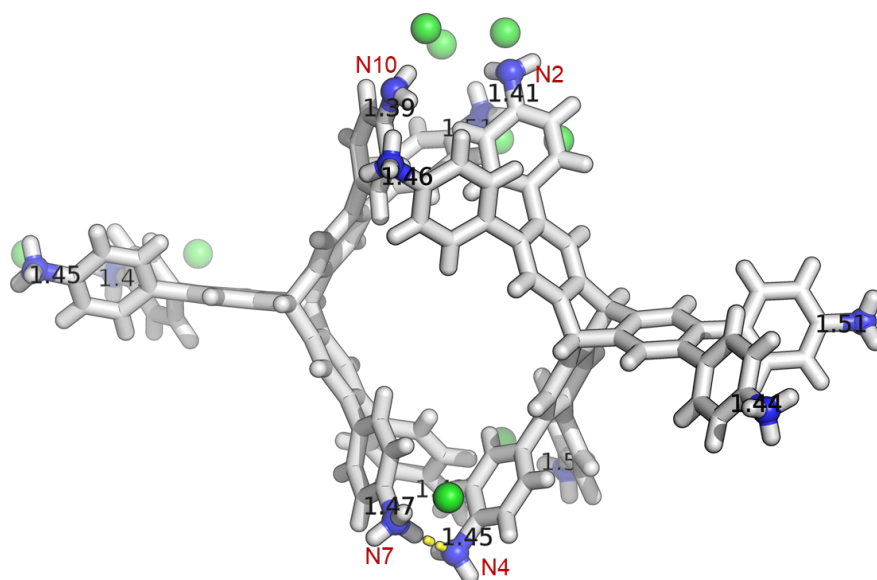
Supplementary Fig. 27. **a**, Detailed view of the twisted hexagonal prism N₁₂Cl₇ cluster, with the non-protonated auxiliary linkers shown in cyan. **b**, Face-sharing trigonal antiprisms SBU with 12-c derived from N₁₂Cl₇ cluster. **c**, Top view of the twisted hexagonal N₆Li₆ prism for comparison. **d**, Detailed view of the twisted hexagonal prism N₆Cl₇ cluster. Both N₁₂Cl₇ and N₆Cl₇ share the same hexagonal prismatic core. **e**, Trigonal antiprisms SBU with 6-c derivate from N₆Cl₇ cluster. **f**, Side view of the twisted hexagonal N₆Li₆ prism for comparison (CCDC 1140461).⁷ Hydrogen atoms are omitted for clarity.



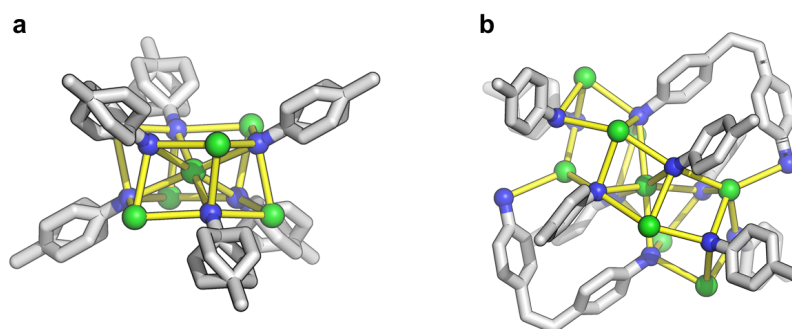
Supplementary Fig. 28. Crystal images of $\text{TPA} \cdot \text{N}_{12}\text{Cl}_9$ before (a) and after (b) exposure to a strong Cu rotating anode X-ray source. Obvious beam damage can be observed. For high-quality diffraction data, the X-ray intensity was reduced to 20% by adjusting the beam slit.



Supplementary Fig. 29. Packing of $\text{TPA} \cdot \text{N}_{12}\text{Cl}_9$. Hydrogen atoms are omitted for clarity.



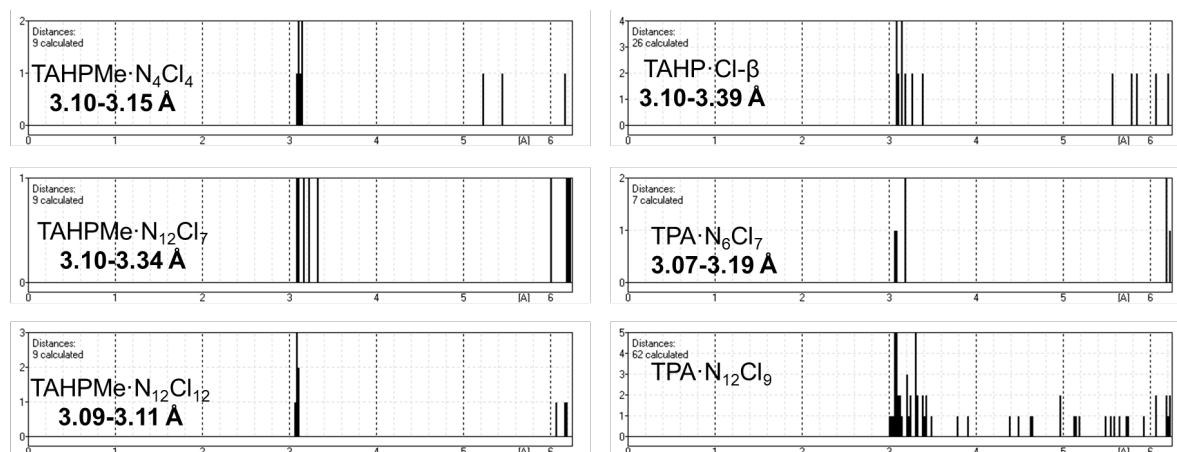
Supplementary Fig. 30. Protonation state and C–N bond length of the asymmetric unit in $\text{TPA} \cdot \text{N}_{12}\text{Cl}_9$. The two N atoms N10 and N2, which exhibit the shortest C–N distances, were assigned as unprotonated amines. N7 and N4 are connected by a hydrogen bond and a shared hydrogen atom lead the elongation of the corresponding C–N bond. N4 is therefore also assigned as unprotonated amine.



Supplementary Fig. 31. Detailed structures of the phenyl segments in $\text{TPA} \cdot \text{N}_6\text{Cl}_7$ (a) and $\text{TPA} \cdot \text{N}_{12}\text{Cl}_9$ (b). $\text{TPA} \cdot \text{N}_6\text{Cl}_7$ exhibits rotational disorder of the phenyl rings, whereas in $\text{TPA} \cdot \text{N}_{12}\text{Cl}_9$ the configurations are locked owing to the interlocking between adjacent phenyl groups. Hydrogen atoms are omitted for clarity.

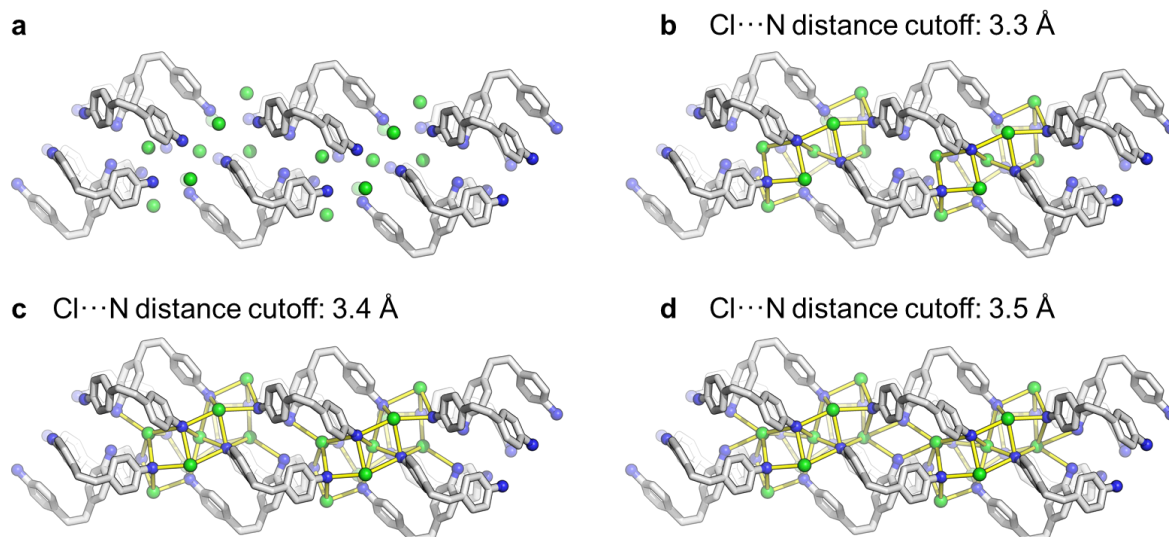
4. Topology analysis

Because the distribution of Cl $\cdots$ N distances is broader than that typically observed for coordination bonds, the choice of cutoff is critical for defining the cluster connectivity. Before carrying out the topological analysis, we therefore examined the Cl $\cdots$ N distance distributions for all obtained structures. For TAHPMe $\cdot$ N₄Cl₄, TAHPMe $\cdot$ N₁₂Cl₇, TAHPMe $\cdot$ N₁₂Cl₁₂, TPA $\cdot$ N₆Cl₇ and TAHP $\cdot$ Cl- β , the relevant Cl $\cdots$ N contacts fall within a relatively narrow range of 3.0–3.4 Å, allowing the connectivity of each cluster node to be assigned unambiguously. In each case, the N/Cl ratio of the resulting cluster model is also consistent with the crystallographic N/Cl stoichiometry, indicating that 3.4 Å is an appropriate cutoff for defining the Cl $\cdots$ N connectivity.



Supplementary Fig. 32. Cl $\cdots$ N distance distributions of the TAHPMe $\cdot$ N₄Cl₄, TAHPMe $\cdot$ N₁₂Cl₇, TAHPMe $\cdot$ N₁₂Cl₁₂, TAHP $\cdot$ Cl- β , TPA $\cdot$ N₆Cl₇ and TPA $\cdot$ N₁₂Cl₉.

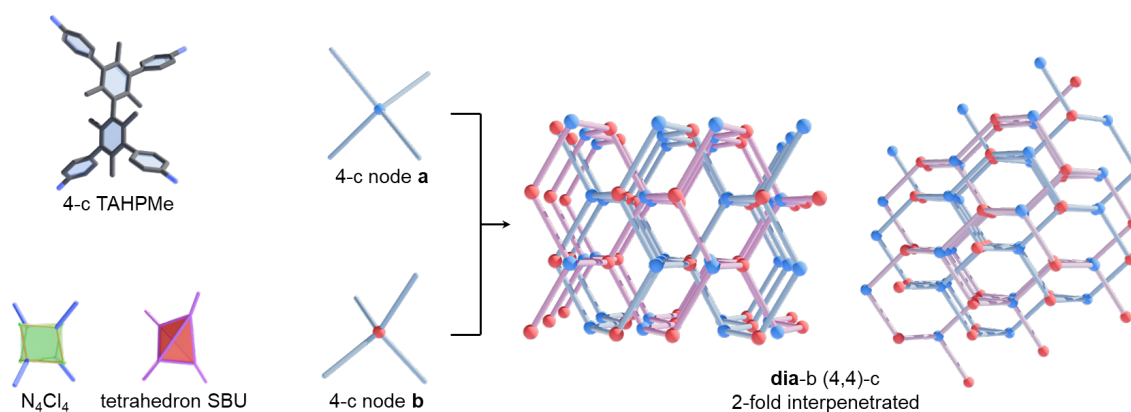
By contrast, TPA $\cdot$ N₁₂Cl₉ has lower symmetry and displays a much broader distribution of Cl $\cdots$ N distances. As a result, the definition of the cluster boundary becomes more subjective, and small changes in the distance threshold can lead to substantial differences in the resulting topological model. We therefore did not include this structure in the formal topological analysis. Without assigning Cl $\cdots$ N connectivity, most of the Cl atoms can nevertheless be seen to be concentrated within a common region (Supplementary Fig. 33a). A shorter cutoff of 3.3 Å gives an incomplete connectivity pattern, whereas a longer cutoff of 3.5 Å introduces shared cluster edges. Using a cutoff of 3.4 Å, the Cl $\cdots$ N connectivity can be described as an N₁₂Cl₉ cluster, which is consistent with the crystallographic stoichiometry and provides a clearer representation of the structure. This cutoff is also consistent with the Cl $\cdots$ N distance range observed for the other cluster models.



Supplementary Fig. 33. Local views of the ionic centre in TPA·N₁₂Cl₉ using different Cl $\cdots$ N distance cutoffs to represent the ionic and hydrogen-bonding interactions.

Topological analysis of TAHPMe·N₄Cl₄

TAHPMe·N₄Cl₄ consists of 4-c TAHPMe linkers connected by 4-c N₄Cl₄ clusters. Topology simplification using ToposPro generated an initial 3-periodic net with *I2/a* symmetry. Subsequent symmetry enhancement in Systre increased the net symmetry to *Fd-3m*, and the point symbol for net was assigned as {6⁶}, allowing the structure to be assigned as a **dia** net. If the two 4-c nodes are retained as distinct node types, the corresponding binodal representation is **dia-b**.

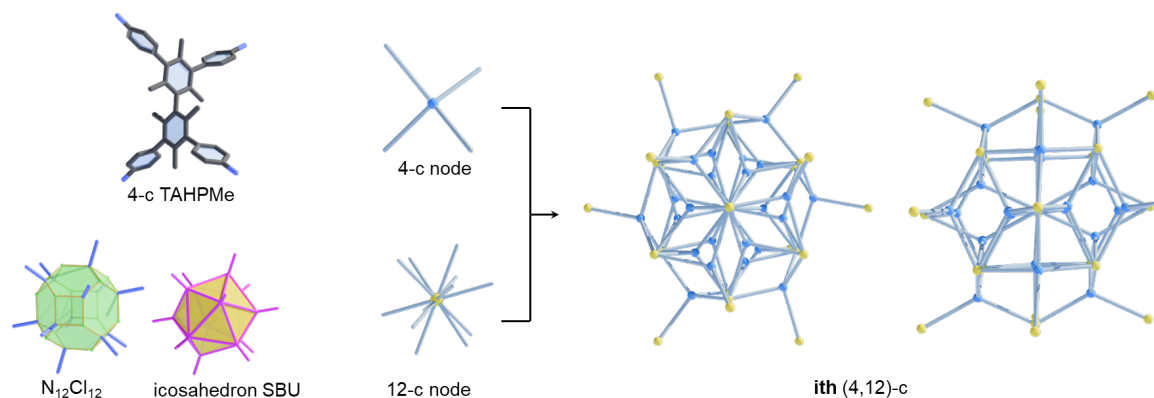


Supplementary Fig. 34. Topological representation of TAHPMe·N₄Cl₄.

Topological analysis of TAHPMe·N₁₂Cl₁₂

TAHPMe·N₁₂Cl₁₂ consists of 4-c TAHPMe linkers connected by 12-c N₁₂Cl₁₂ clusters. Topology simplification using ToposPro generated an initial 3-periodic net with *R-3c* symmetry. Subsequent

symmetry enhancement in Systre increased the net symmetry to $Pm-3n$, and the point symbol for net was assigned as $\{4^{30}.6^{30}.8^6\}\{4^6\}_3$, allowing the structure to be assigned as an **ith** net.



Supplementary Fig. 35. Topological representation of TAHPMe·N₁₂Cl₁₂.

Topological analysis of TAHPMe·N₁₂Cl₇

TAHPMe·N₁₂Cl₇ consists of 4-c TAHPMe linkers connected by 12-c N₁₂Cl₇ clusters. Topology simplification using ToposPro generated an initial 3-periodic net with $R32$ symmetry. Systre showed that the ideal space group remains $R32$. ToposPro analysis identified the net as a previously unreported 4,12-c chiral topology, distinct from known RCSR nets. We refer to this topology as **ahf**, reflecting its discovery in an anilinium halide framework. The details of this **ahf** net are as follows:

Point symbol for net: $\{4^{21}.6^{42}.8^3\}\{4^6\}_3$; 4,12-c net with stoichiometry (4-c)3(12-c); 2-nodal net

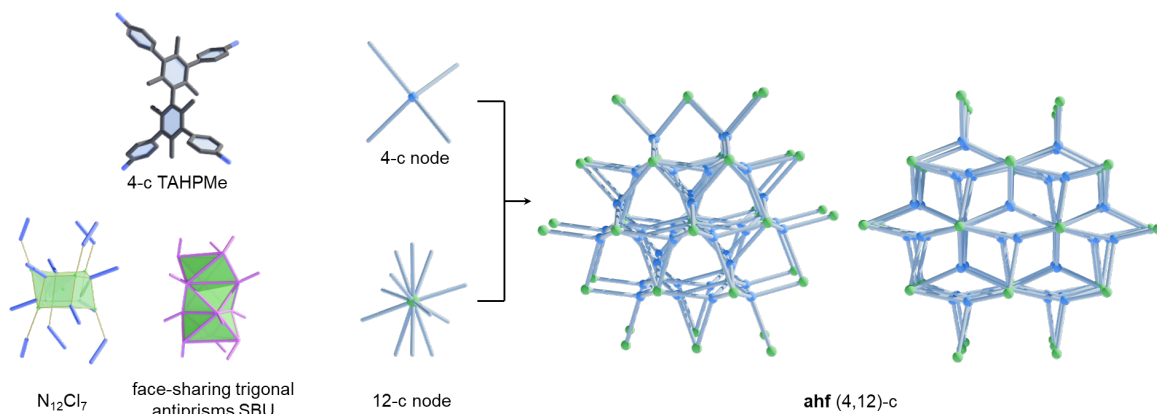
Topological terms for each node:

12-c N₁₂Cl₇ cluster point symbol: $\{4^{21}.6^{42}.8^3\}$; coordination sequence: 12 14 84 50 228 110 444 194 732 302

4-c TAHPMe point symbol: $\{4^6\}$; coordination sequence: 4 36 28 146 76 326 148 578 244 902

TD10=2410

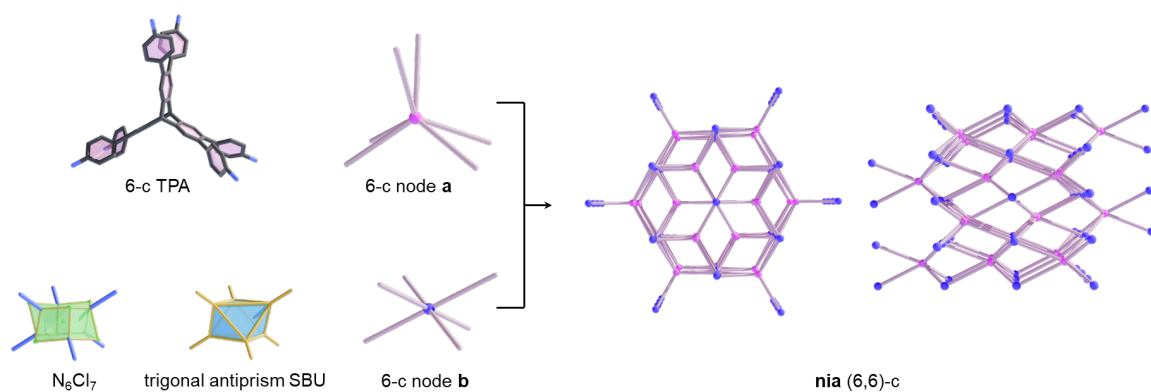
Although three primitive proper tilings were generated, a unique natural tiling could not be constructed because not all candidate faces are shared.



Supplementary Fig. 36. Topological representation of TAHPMe· $N_{12}Cl_7$.

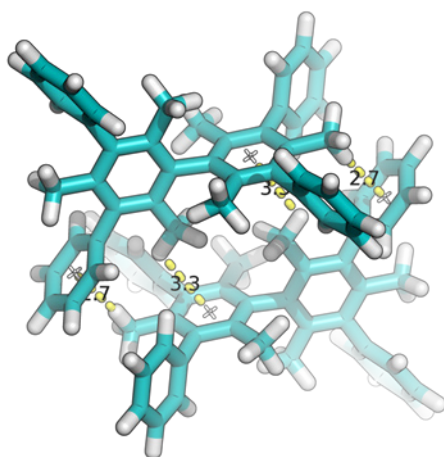
Topological analysis of TPA· N_6Cl_7

TPA· N_6Cl_7 consists of 6-c TPA linkers connected by 6-c N_6Cl_7 clusters. Topology simplification using ToposPro generated an initial 3-periodic net with $P6_3/mmc$ symmetry. Systre showed ideal space group is still $P6_3/mmc$, and the point symbol for net was assigned as $\{4^{12}.6^3\}\{4^9.6^6\}$, allowing the structure to be assigned as an **nia** net.

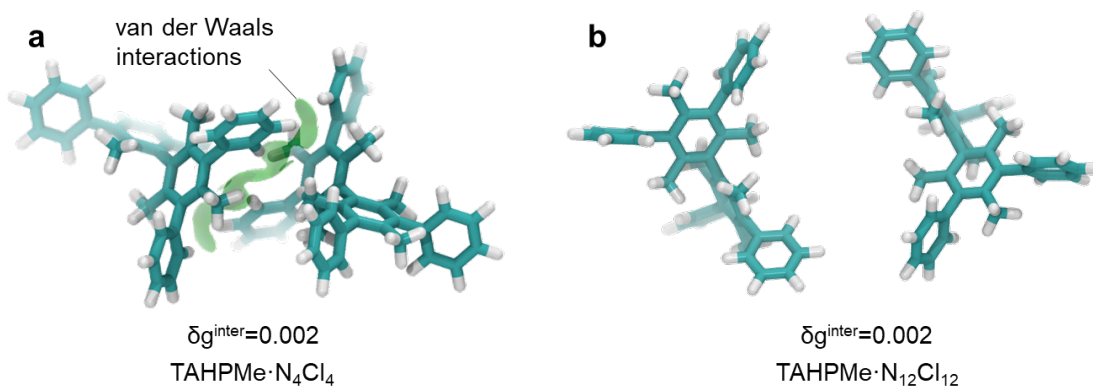


Supplementary Fig. 37. Topological representation of TPA· N_6Cl_7 .

5. Energy decomposition analysis



Supplementary Fig. 38. The packing of the linker fragments in TAHPMe·Cl-nc shows that two non-equivalent methyl groups provide blocking effect that prevents close contact between the aromatic rings.



Supplementary Fig. 39. IGMH isosurfaces ($\delta g^{\text{inter}} = 0.002$ a.u.) of the non-linking parts for TAHPMe·N₄Cl₄ (a) and TAHPMe·N₁₂Cl₁₂ (b).

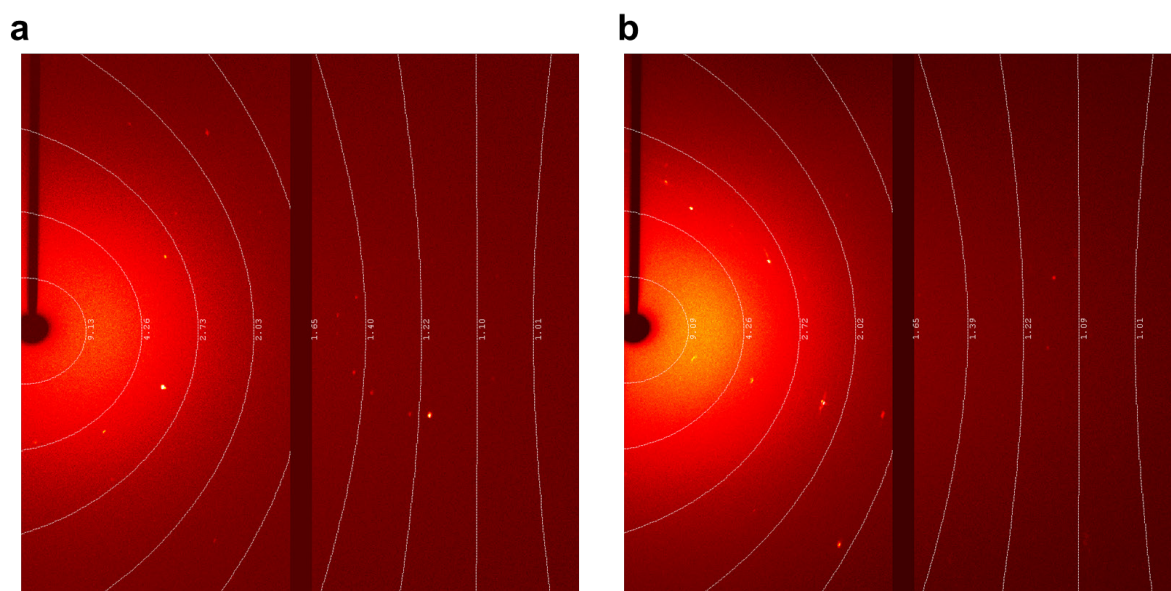
Supplementary Table 5. Interaction energy of non-linking fragment

Structure	Electrostatic (kJ mol ⁻¹)	Exchange- repulsion (kJ mol ⁻¹)	Orbital (kJ mol ⁻¹)	Dispersion (kJ mol ⁻¹)	Total interaction energy (kJ mol ⁻¹)
TAHP·Cl-β	-25.5	133.0	-15.2	-209.4	-117.1
TAHPMe·Cl-nc	-35.1	122.9	-16.7	-146.4	-75.2
TAHPMe·N ₄ Cl ₄	-6.7	30.3	-4.9	-62.1	-43.4
TAHPMe·N ₁₂ Cl ₁₂	-0.2	0.1	0.0	-2.0	-2.1

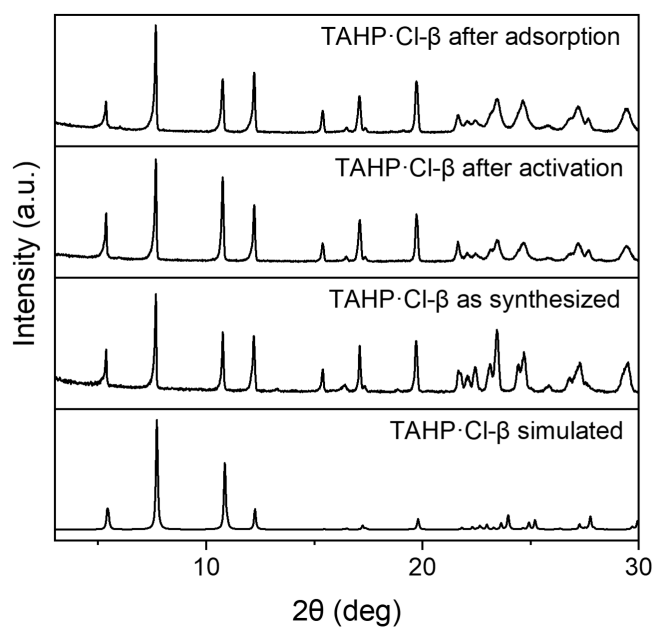
Supplementary Table 6. Average interaction energy of clusters for each $\text{RNH}_3^+\cdots\text{Cl}^-$ ion pair

Cluster	Electrostatic (kJ mol ⁻¹)	Exchange- repulsion (kJ mol ⁻¹)	Orbital (kJ mol ⁻¹)	Dispersion (kJ mol ⁻¹)	Total interaction energy (kJ mol ⁻¹)
N ₄ Cl ₄	-677.6	290.2	-155.0	-79.7	-622.2
N ₁₂ Cl ₁₂	-709.9	309.7	-146.9	-88.5	-635.6

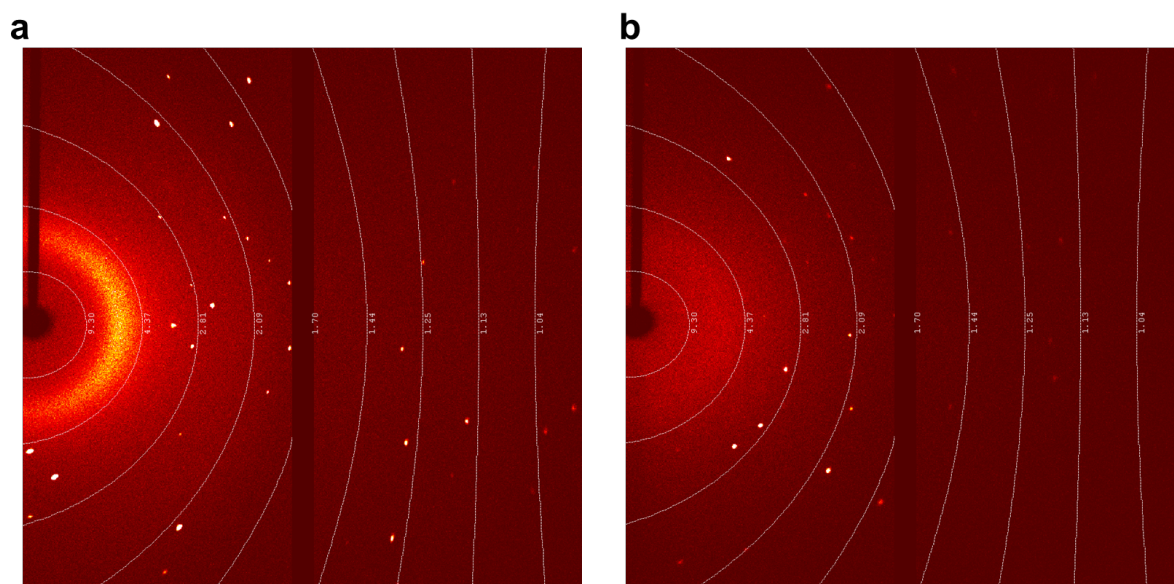
6. Crystal stability



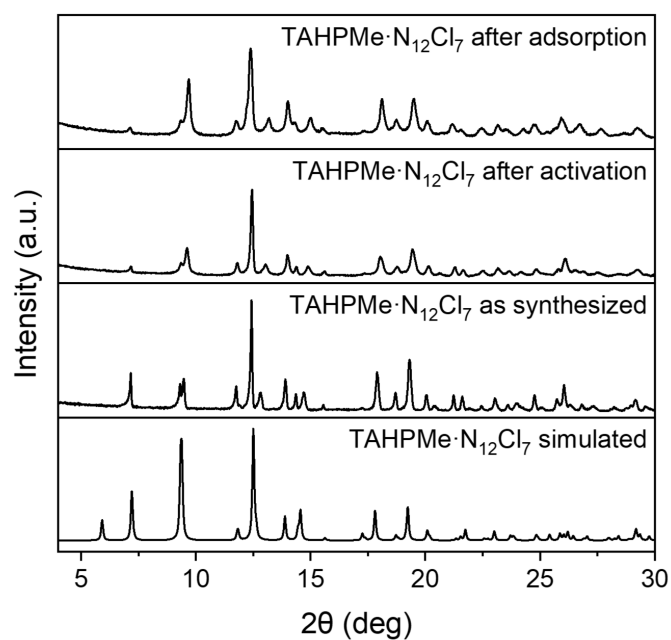
Supplementary Fig. 40. Single crystal diffraction pattern of TAHP·Cl- β before (a) and after (b) vacuum at room temperature for 10 h.



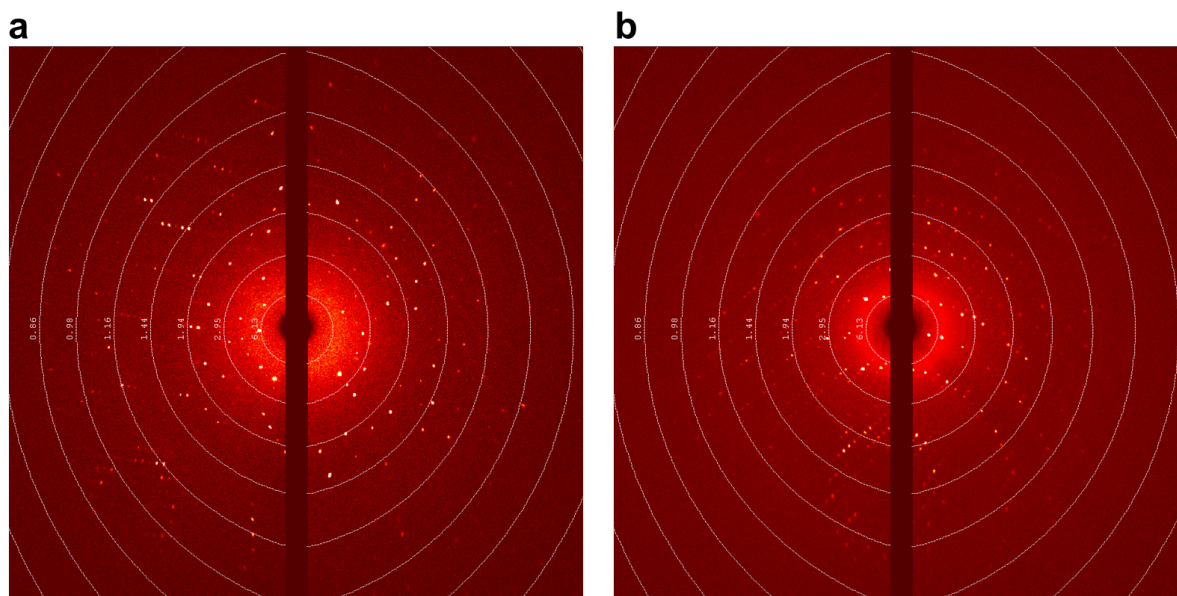
Supplementary Fig. 41. PXRD patterns of TAHP·Cl- β before activation, after scCO_2 activation, and after gas adsorption.



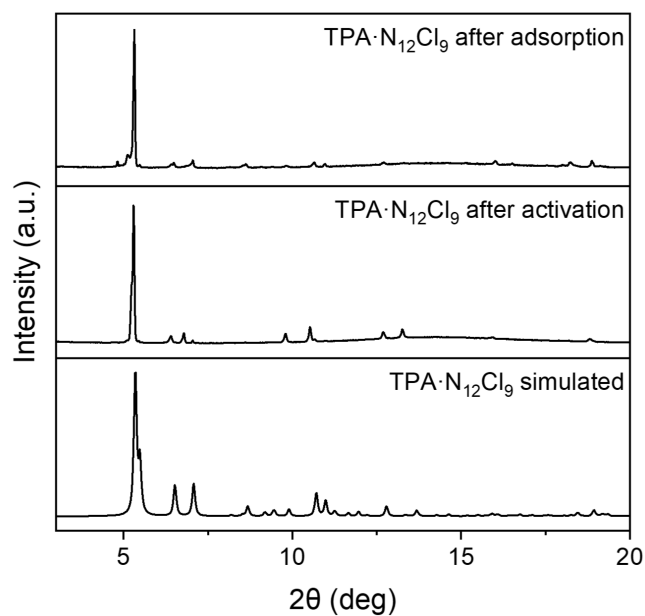
Supplementary Fig. 42. Single crystal diffraction pattern of TAHPMe·N₁₂Cl₇ (a) and after (b) scCO₂ activation.



Supplementary Fig. 43. PXRD patterns of TAHPMe·N₁₂Cl₇ before activation, after scCO₂ activation, and after gas adsorption.

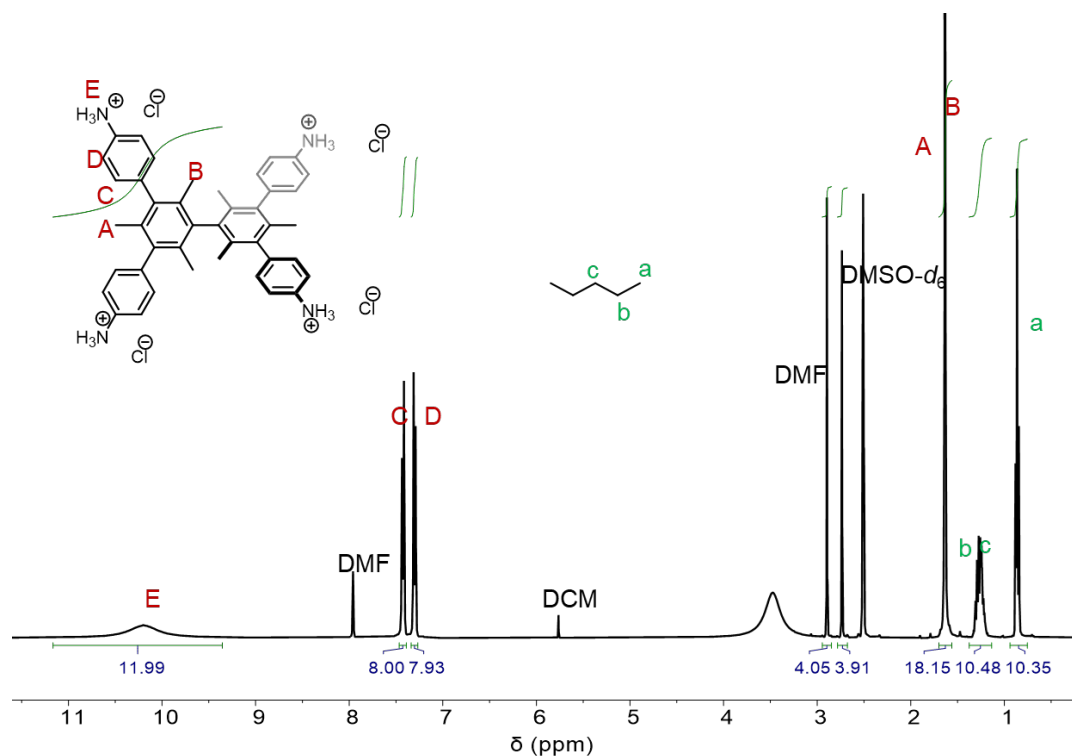


Supplementary Fig. 44. Single crystal diffraction of TPA·N₁₂Cl₉ before (a) and after (b) vacuum activation at room temperature for 10 h.

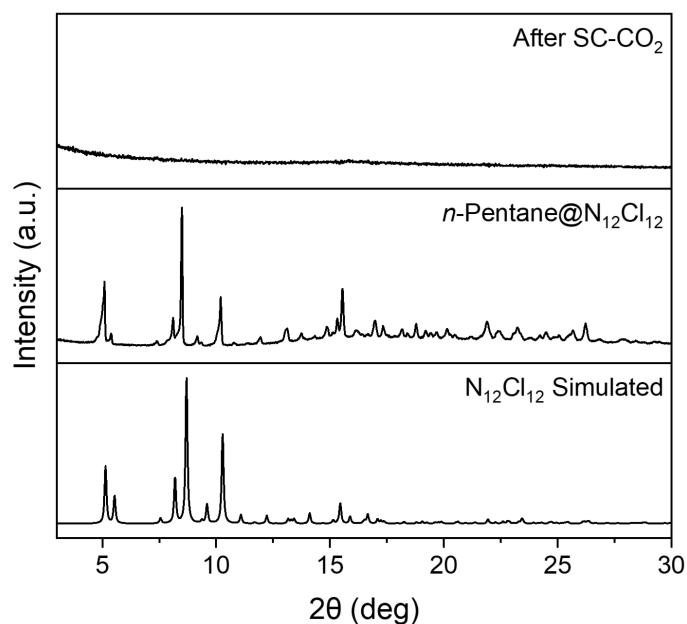


Supplementary Fig. 45. PXRD patterns of TPA·N₁₂Cl₉ after activation, and after gas adsorption. Samples were immediately coated with polyisobutene prior to measurement to minimise moisture-induced degradation of TPA·N₁₂Cl₉.

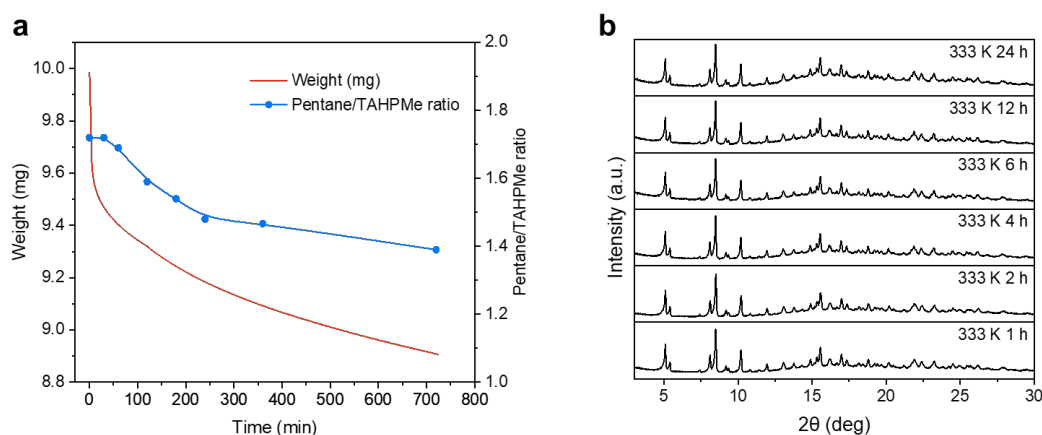
7. Guest inclusion of TAHPMe·N₁₂Cl₁₂



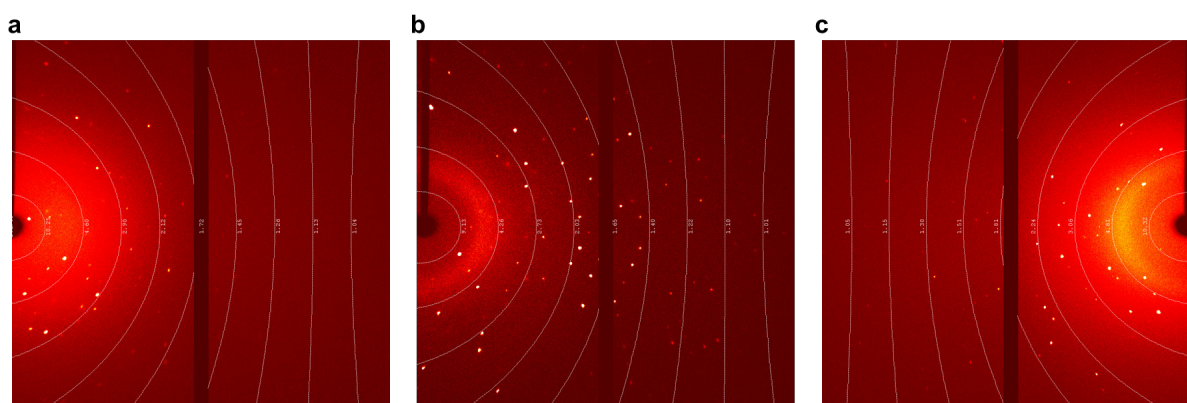
Supplementary Fig. 46. ¹H NMR of dissolved *n*-pentane@TAHPMe·N₁₂Cl₁₂ (4.8 mg), with 0.5 mg of DMF added as an internal standard, indicated an *n*-pentane loading of 14 wt% (400MHz, DMSO-*d*₆). The protons of *n*-pentane are denoted with green letters.



Supplementary Fig. 47. PXRD of *n*-pentane@TAHPMe·N₁₂Cl₁₂ before and after scCO₂ activation. The framework collapsed upon removal of *n*-pentane by supercritical CO₂ treatment, indicating that TAHPMe·N₁₂Cl₁₂ cannot retain its structure after guest removal and cannot achieve permanent porosity.

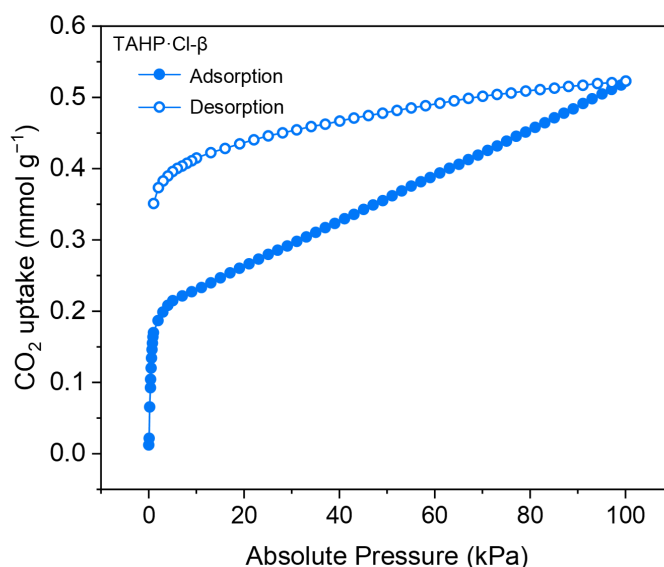


Supplementary Fig. 48. TGA kinetic study of *n*-pentane@TAHPMe·N₁₂Cl₁₂. Approximately 10 mg of the *n*-pentane@TAHPMe·N₁₂Cl₁₂ sample was loaded onto a platinum sample pan and heated at 333 K under N₂ for 0.5, 1, 2, 3, 4, 6, and 12 h, respectively. After each heating the sample was analyzed by PXRD and ¹H NMR to determine the variation in the *n*-pentane/TAHPMe ratio. TGA revealed that *n*-pentane was gradually released upon heating (a), while the majority of the solid remained crystalline (b).

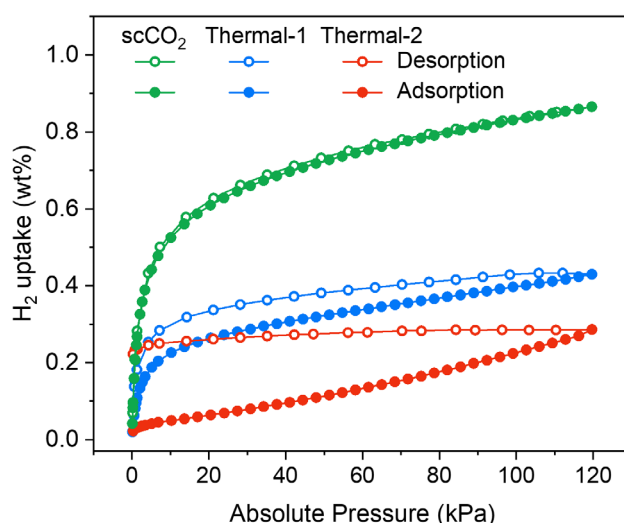


Supplementary Fig. 49. Single crystal diffraction of TAHPMe·N₁₂Cl₁₂ exchanged with DCM (a), cyclohexane (b) and *n*-heptane (c). After solvent exchange with cyclohexane and *n*-heptane, the crystals exhibited improved diffraction patterns, indicating enhanced ordering of both the framework and the encapsulated solvent molecules.

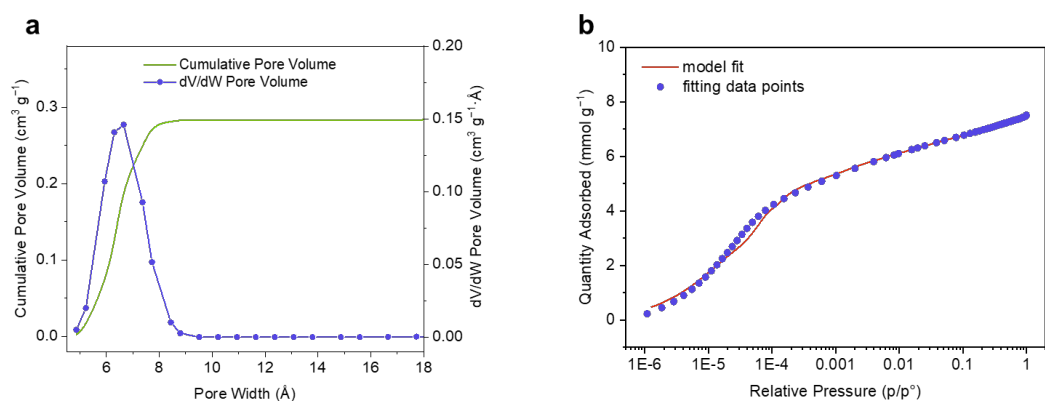
8. Adsorption properties



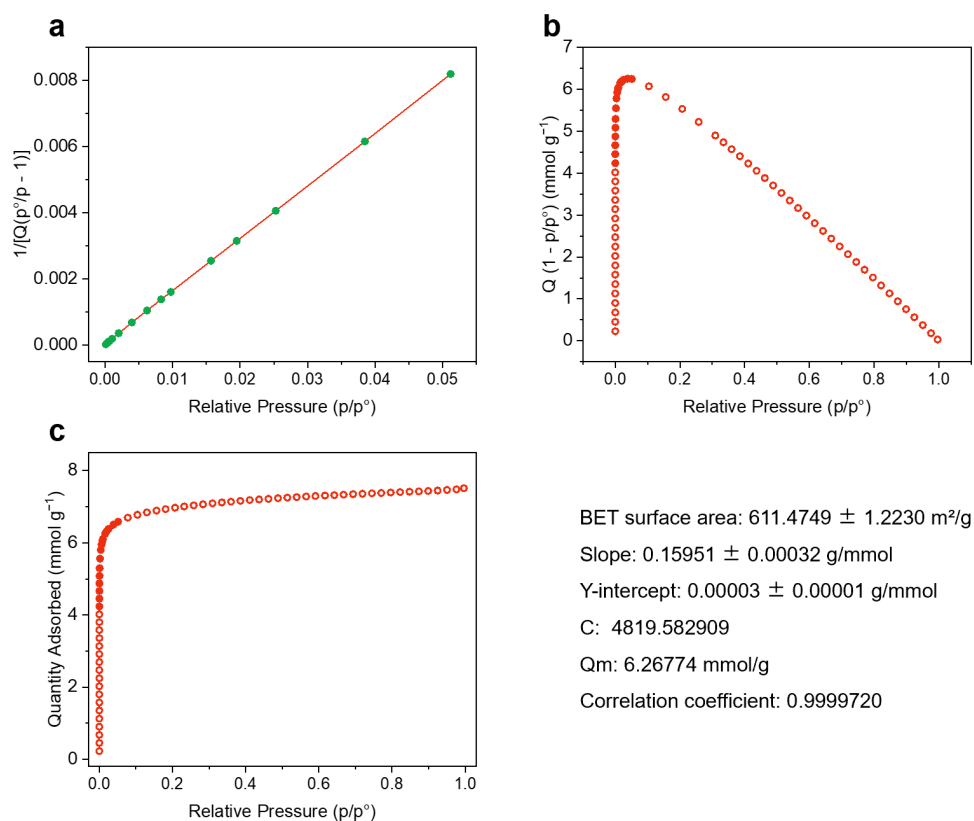
Supplementary Fig. 50. CO₂ adsorption isotherms of TAHP·Cl-β at 195 K. The presence of a small amount of residual solvent within the cavities slows the diffusion of CO₂, giving rise to the pronounced hysteresis observed at 273 K and 298 K. At the lower temperature of 195 K, the reduced mobility further restricts CO₂ access to the pore space, resulting in a lower adsorption uptake than higher temperature.



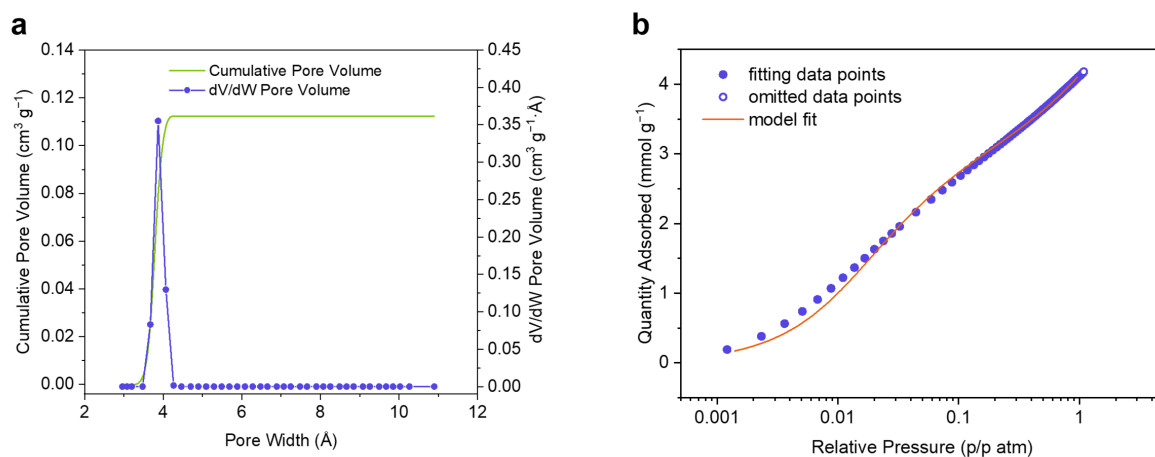
Supplementary Fig. 51. H₂ adsorption isotherms of TAHPMe·N₁₂Cl₇ obtained after different activation methods. For the thermal-1 method, the sample was exchanged with acetonitrile three times and activated directly under dynamic vacuum at 65 °C for 24 h. For the thermal-2 method, the sample was sequentially exchanged with acetonitrile, ethyl acetate and n-pentane, three times for each solvent, and then activated under dynamic vacuum at 45 °C for 24 h. Compared to the scCO₂-activated sample, incompletely activated samples exhibited lower H₂ uptake and marked hysteresis.



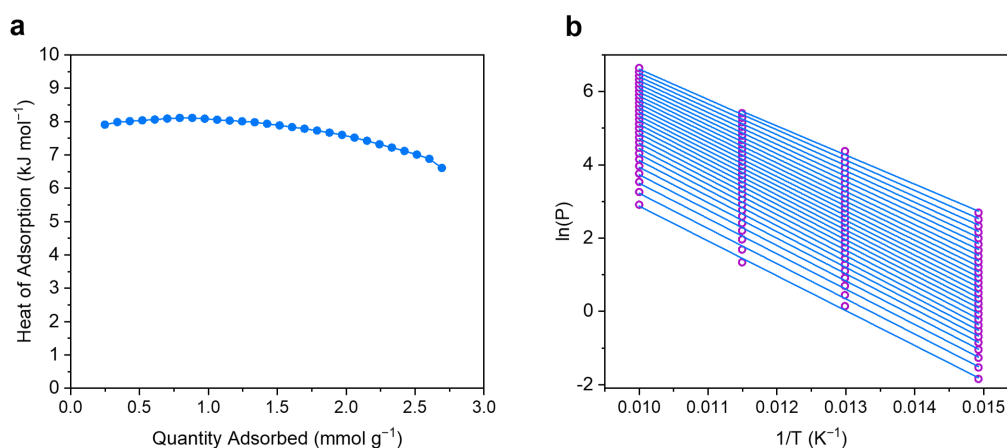
Supplementary Fig. 52. DFT pore size distribution (a) and the data fitting (b) of TPA·N₁₂Cl₉ from the N₂ adsorption isotherm at 77 K.



Supplementary Fig. 53. BET surface area analysis of TPA·N₁₂Cl₉. a, Linear region used for the BET fit. b, Rouquerol plot derived from the 77 K N₂ adsorption isotherm. c, N₂ adsorption isotherm at 77 K. Data included in the BET fit are shown as solid points, the excluded points are shown in circles.



Supplementary Fig. 54. DFT pore size distribution (a) and the data fitting (b) of TAHPMe·N₁₂Cl₇ from the H₂ adsorption isotherm at 77 K.



Supplementary Fig. 55. a, The isosteric heats of adsorption (Q_{st}) of TAHPMe·N₁₂Cl₇ for H₂. b, The Van't Hoff Plot derived from H₂ adsorption isotherms at 67, 77, 87 and 100 K.

Supplementary Table 7. List of pore properties of three N-MOFs

Pore properties	TAHP·Cl-β	TAHPMe·N ₁₂ Cl ₇	TPA·N ₁₂ Cl ₉
Pore limiting diameter (Å) ^a	5.8	3.9	6.2
Largest cavity diameter (Å) ^a	6.5	4.4	8.4
Void (%)	30.1	33.8	50.5
Fitted BET surface area (m ² g ⁻¹)	- ^b	- ^b	616.5
Fitted Pore Size (Å)	- ^b	3.9 ^c	6.5 ^d

a. Calculated from Zeo++ with default setting¹

b. No suitable data for fitting.

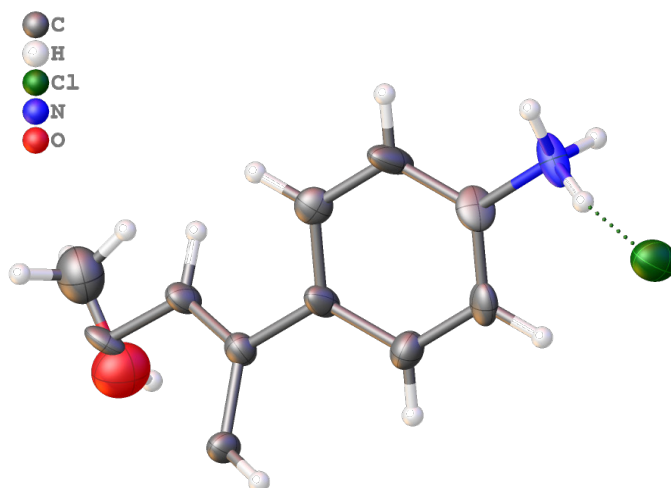
c. Fitted with the NLDFT, Ultramicroporous Zeolites, H₂, 77 Model.

d. Fitted with the N₂-Tarazona NLDFT, Esf = 30.0 K Model.

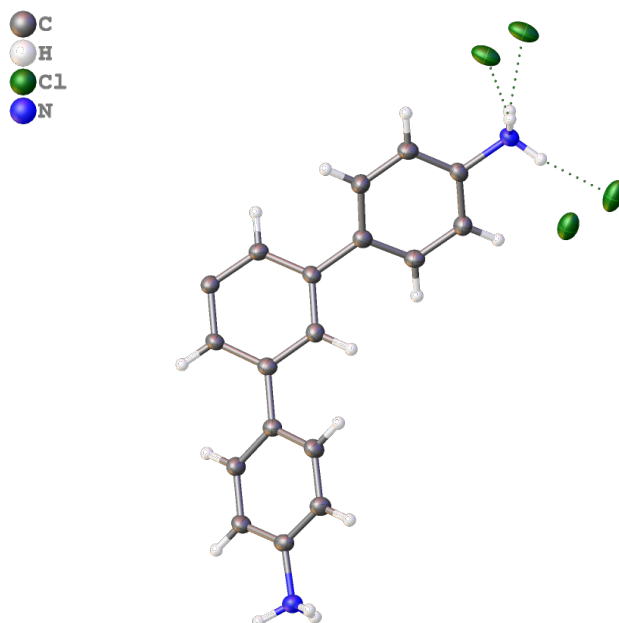
Supplementary Table 8. List of isosteric heat of adsorption (Q_{st}) and pore size of crystalline porous materials.

Materials	Pore size (nm)	Q_{st} (kJ mol ⁻¹)
MOFs		
ZIF-8 ⁸	1.16	4.5
MOF-5 ⁹	1.2	3.8
NU-1000 ¹⁰	3.1	5
NU-1500-Al ¹¹	1.4	4.9
NU-1501-Al ¹¹	1.5-2.5	4
UiO-67 ¹⁰	1.0-2.5	5.8
SIFSIX-2-Cu ¹²	1.3	4.6
SIFSIX-2-Cu-i ¹²	0.5	8.6
Mg ₃ (NDC) ₃ ¹³	0.36	9.5
[Ni ₃ (pzdc) ₂ (ade) ₂] ¹⁴	0.67	9.7
Pb ₂ (C ₁₄ H ₈ O ₆ S) ₂ ¹⁵	0.4	9
COFs		
COF-1 ¹⁶	0.6-1.2	8.8
COF-5 ¹⁶	2.7	4.6
HOFs		
ZJU-HOF-5a ¹⁷	1.5	5.7
RP-H100 ¹⁸	0.8-3.0	6.1
RP-H101 ¹⁸	1.6, 1.9	5
This work TAHPMe·N₁₂Cl₇	0.39	8

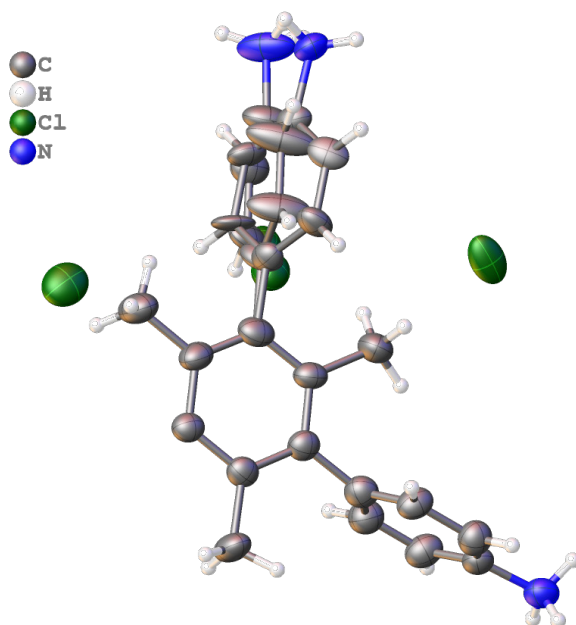
9. ORTEP-style illustration of crystal structures



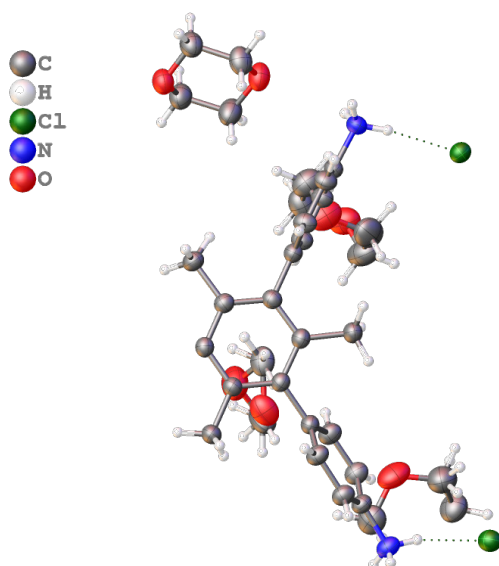
Supplementary Fig. 56. ORTEP representation of the asymmetric unit of TAHP·Cl- α (CCDC 2515978), with displacement ellipsoids drawn at the 50% probability level.



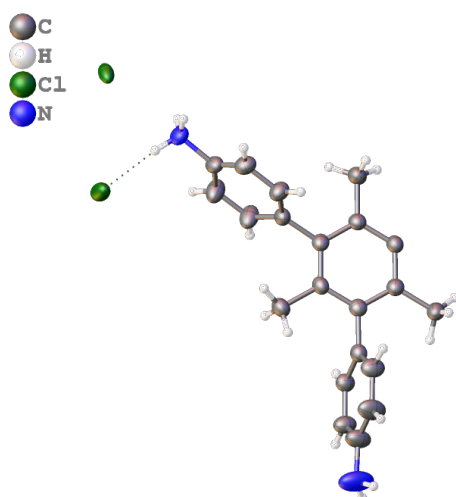
Supplementary Fig. 57. ORTEP representation of the asymmetric unit of TAHP·Cl- β (CCDC 2515979), with displacement ellipsoids drawn at the 50% probability level.



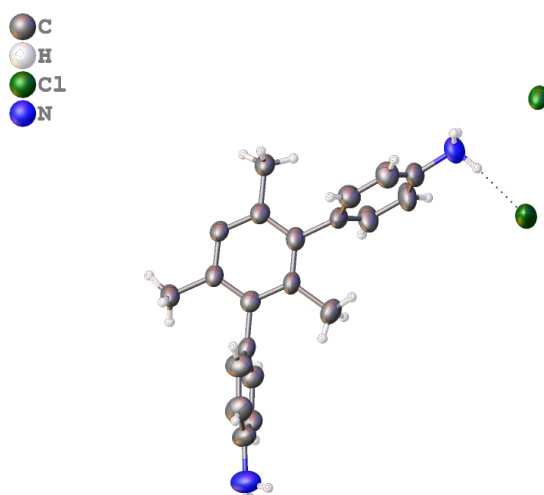
Supplementary Fig. 58. ORTEP representation of the asymmetric unit of TAHPMe·Cl-nc (CCDC 2515980), with displacement ellipsoids drawn at the 50% probability level. Linker disorder is shown in the structure.



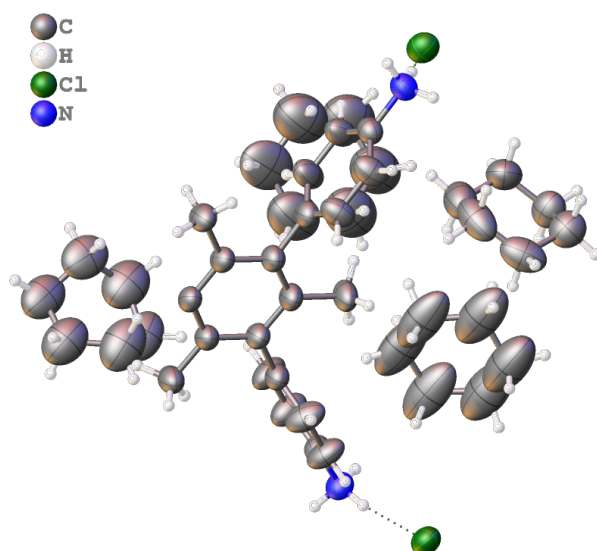
Supplementary Fig. 59. ORTEP representation of the asymmetric unit of TAHPMe·N₄Cl₄ (CCDC 2515981), with displacement ellipsoids drawn at the 50% probability level. Solvent disorder is shown in the structure.



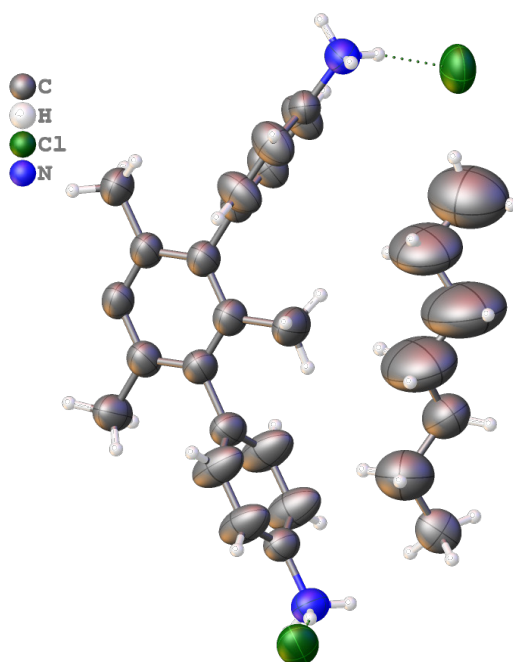
Supplementary Fig. 60. ORTEP representation of the asymmetric unit of TAHPMe·N₁₂Cl₇-A (CCDC 2515982), with displacement ellipsoids drawn at the 50% probability level.



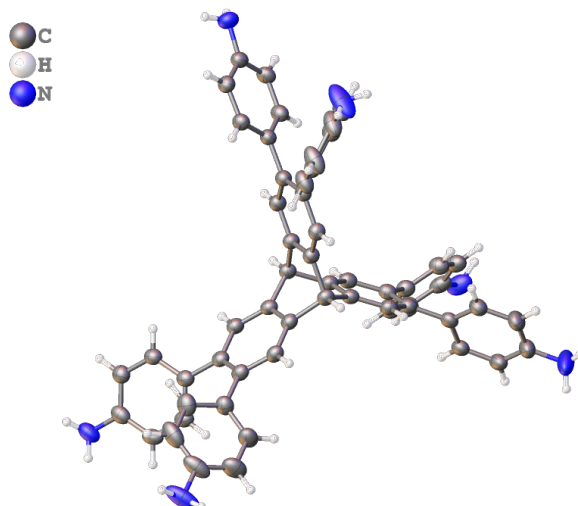
Supplementary Fig. 61. ORTEP representation of the asymmetric unit of TAHPMe·N₁₂Cl₇-C (CCDC 2515983), with displacement ellipsoids drawn at the 50% probability level.



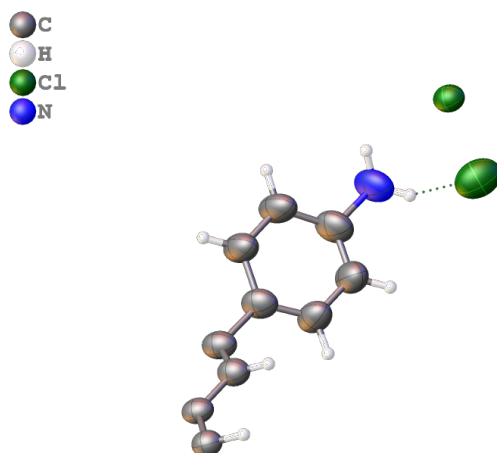
Supplementary Fig. 62. ORTEP representation of the asymmetric unit of Cyclohexane@TAHPMe·N₁₂Cl₁₂ (CCDC 2515984), with displacement ellipsoids drawn at the 50% probability level.



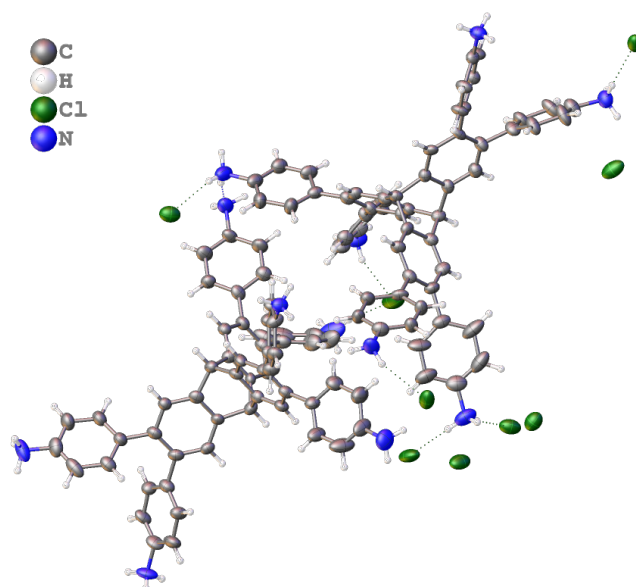
Supplementary Fig. 63. ORTEP representation of the asymmetric unit of *n*-Heptane@TAHPMe·N₁₂Cl₁₂ (CCDC 2515985), with displacement ellipsoids drawn at the 50% probability level.



Supplementary Fig. 64. ORTEP representation of the asymmetric unit of TPA (CCDC 2515986), with displacement ellipsoids drawn at the 50% probability level.



Supplementary Fig. 65. ORTEP representation of the asymmetric unit of TPA·N₆Cl₇ (CCDC 2515987), with displacement ellipsoids drawn at the 50% probability level.



Supplementary Fig. 66. ORTEP representation of the asymmetric unit of TPA·N₁₂Cl₉ (CCDC 2515988), with displacement ellipsoids drawn at the 50% probability level.

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