One of the challenges in material science has been to prepare macro- or mesoporous zeolite. Although examples of their synthesis exist, there is a need for a facile yet versatile approach to such hierarchical structures. Here we report a concept for designing a single quaternary ammonium head amphiphilic template with strong ordered self-assembling ability through $\pi-\pi$ stacking in hydrophobic side, which stabilizes the mesostructure to form single-crystalline mesostructured zeolite nanosheets. The concept is demonstrated for the formation of a new type of MFI (zeolite framework code by International Zeolite Association) nanosheets joined with a 90° rotational boundary, which results in a mesoporous zeolite with highly specific surface area even after calcination. Low binding energies for this self-assembling system are supported by a theoretical analysis. A geometrical matching between the arrangement of aromatic groups and the zeolitic framework is speculated for the formation of single-crystalline MFI nanosheets.
The development of macro- or mesoporous zeolitic materials with hierarchical pore architectures is of increasing importance for researchers in porous materials science, because the sole presence of micropores in bulk zeolites can cause diffusion limitations and limit their widespread use as industrial catalysts. There are several methods to prepare hierarchical zeolites such as top-down desilication by alkali post-synthetic modification, bottom-up directed assembly by self-assembly of various zeolite seeds and by templates. Much attention has been focused on the synthesis of zeolites with desired pore structure using soft and hard templates, such as surfactants, cationic polymer, polystyrene beads, mesoporous silica and carbon materials. Although much considerable progress has been made in developing strategies to direct the formation of porous zeolites, designing a templating strategy for obtaining ordered hierarchical pore structures with crystallographically ordered zeolite remains an unsolved challenge.

Quaternary ammonium species are well known as zeolite templates because of their strong interactions with the inorganic framework. Long-chain alkyl–quaternary ammonium molecules are universally used to synthesize mesoporous silica materials through the self-assembled liquid crystal templating route. Recently, Ryoo and coworkers succeeded in synthesizing polycrystalline mesostructured MFI (zeolite framework code by International Zeolite Association) zeolite using designed bifunctional surfactants, in which the connection of the head groups of the multiple quaternary ammoniums to hydrophobic alkyl chains is the indispensable factor for the effective structure-directing agent to simultaneously form MFI zeolite and a mesoscale micellar structure. However, directing the structure of zeolite using longer alkyl chain lengths and simple one-head quaternary molecules is generally an energetically unfavourable event compared with the use of multiple quaternary ammonium head groups. The high synthetic energy in one-head quaternary groups would disrupt the formation of their lamellar structure.

An approach to designing feasible templates for the synthesis of hierarchical zeolites is to stabilize the micelle structure by introducing highly rigid segments that have strong interactions with each other in the hydrophobic chain to block crystal growth by forming an extremely stable hydrophobic layer and that form an ordered orientation to provide a geometric match with the MFI zeolite framework. Aromatic–aromatic or π–π stacking interactions are well known as effective noncovalent intermolecular forces, which are normally employed for H-type or J-type stacking of aromatic groups with ring centroid–centroid distances of ~3.3–3.8 Å. In particular, they can facilitate self-assembly or molecular recognition processes while involving extended structures that are constructed from building blocks with aromatic moieties to matching MFI nanosheet. The presence of at least two benzene rings is known to be necessary for the formation of stable bilayer assemblies of amphiphiles. Therefore, energetically stable micellar structures and their ordered orientation would make the single-head amphiphilic template for directing the formation of mesostructured zeolite nanosheets possible.

In this study, first, we introduce biphenyl and naphthyl into the alkyl tail of an amphiphilic template with a single quaternary ammonium head group to form C(H2)n–C8H18–N+(CH3)2–C9H17(Br−) (denoted as C8Ph–n-16.6). Second, MFI nanosheets joining with a 90° rotational boundary SCZN-2 are templated using bolaform amphiphilic molecules with bi-quaternary ammonium head groups and biphenyl groups C10H22–N+(CH3)2–C6H12–N+(CH3)2–(CH2)12–O–C8H4–C8H14–O–(CH3)2–C9H17–N+(CH3)2–C12H18–N+(CH3)2–C8H17–(4Br−) (BChPh–n-6.6). Supplementary Figs 5–10).

Results

Synthesis and characterization of SCZN-1. Figure 1a shows the low-angle X-ray diffraction (XRD) pattern (transmission mode) of the as-made sample synthesized with C8Ph–n-10.6 as a template. Two well-resolved peaks at 20 = 1.84° and 3.65° were indexed as the first- and second-order reflections of layered MFI nanosheets with new unit cell constant B = 4.8 nm (A and C are same as MFI unit), indicating a periodic interlamellar structural order. The electron charge distribution curve (Supplementary Fig. 11, Supplementary Note 1) revealed different scattering powers between the MFI and micelle layers. The thickness of the MFI layer was estimated to be ~2.7 nm, corresponding to the observation from TEM (vide post). Most of the sharp peaks in the high-angle range (Fig. 1b) were associated with the 0kl reflections of the MFI framework, suggesting good crystallinity in the a-c plane. However, the limited information and considerable peak overlapping caused difficulties in distinguishing between the h0l and 0kl reflections in the powder XRD pattern and determining the super mesostructure.

The scanning electron microscopy (SEM) images (Fig. 1c and Supplementary Fig. 12) revealed that the sample was composed of uniform flower-like morphology with a petal thickness of ~30 nm. Recently developed three-dimensional electron diffraction tomography (three-dimensional (3D) EDT) data provided single crystal information not only on the atomic structure of the nanosheets but also on the relative positions of successive sheets. Strong and sharp diffractions from the h0l plane revealed the high structural coherence of the MFI sheets. The super lattice resulting from registered MFI layers was determined to be rhomic with cell parameters of a = 20.5 Å, b = 40.3 Å and c = 13.9 Å. The spatial correlation of layers along the b axis was indicated by spots along the b* axis, the diffusion of which might come from the existence of amphiphilic molecules as well as deviation from the superstructure. The single-crystalline mesostructure could be directly observed in high-resolution transmission electron microscopy images (Fig. 1d,e), where MFI layers were organized along the b direction to form a super mesostructure. In particular, crystallographically ordered MFI layers could connect with each other to MFI single crystals by forming new Si-O-Si bonds after calcination (Fig. 1f,i), with maintaining morphology. Therefore, it can be concluded that SCZN has been synthesized by C8Ph–n-10.6 (we denoted it as SCZN-1).

The N2 desorption–desorption isotherms of calcined SCZN-1 shows a similar profile with conventional bulk MFI zeolite due to the similar single-crystalline structure with conventional ZSM-5. It shows the uptake steps below P/P0 = 0.02 due to micropore filling or capillary condensation (Fig. 1k and Supplementary Fig. S4), which is present in all conventional zeolite samples, as compared with ZSM-5 (ref. 31). The hysteresis loop of SCZN-1 at a relative pressure range of 0.5–1.0 shows a few amount and random distribution of mesopores due to the interconnected single-crystalline pore system and some polycrystalline pores formed by random aggregation of the thin petals. The Brunauer–Emmett–Teller (BET) surface area, micro- and mesopore volumes of SCZN-1 were measured to be 395 m² g⁻¹, 0.12 cm³ g⁻¹ and 0.30 cm³ g⁻¹, respectively, similar to those of conventional ZSM-5 (Supplementary Fig. 13). The relatively low BET surface area also confirmed the formation of a MFI single crystal after calcination, while polycrystalline MFI zeolite with a high surface area was obtained after calcination due to the large
amount exposure of ac plane as reported by Ryoo. Similarly, the template $C_{Nh-10-6}$ can also produce SCZN-1 (Supplementary Fig. 14). Our strategy was also successfully extended to the bolaform amphiphilic molecules with the single quaternary ammonium head (Supplementary Fig. 15).

**Synthesis and characterization of SCZN-2.** It is well known that rotational boundaries are commonly found in MFI zeolite with an overgrown relationship between the $(h00)$ and $(0k0)$ faces, which increases the possibility of the construction of a hierarchical structure with a large surface area and pore volume. The approximate cell parameters of $a$ and $b$ in MFI and the similar 10-ring pores provide a fundamental possibility for the occurrence of the phenomena of intergrowth on itself, which is inherent to the MFI structure. Several small molecules, in particular, the dimers of the tetrapropyl ammonium bromide cation can generate structural constraints or stresses and can easily form the boundaries of MFI crystals. However, the mesoscopic porosity in these materials cannot be controlled with small structural-directing agents (SDAs) alone, which always resulted in the mesoporous structure with broad pore size distributions. Here, we rationally designed a series of bolaform amphiphilic molecules with bi-quaternary ammonium head groups and biphenyl groups (BCPh-n-6-6), which could act as particular cationic dimers, to direct a new type of hierarchical SCZN with uniform mesopore size due to the presence of their hydrophobic parts (we denoted these samples as SCZN-2).

Figure 2 shows the XRD patterns of the as-made SCZNs synthesized with BCPh-n-6-6 ($n = 4, 6, 8, 10, 12$). All samples show ordered lamellar structures. The first-order reflections were gradually shifted to a smaller 2$\theta$ value as the carbon chain increased from 4 to 12 with a distinct interlamellar spacing ($d_{11}$)

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**Figure 1 | Structural characterization of SCZN-1 templated by CPh–Ph-10-6**. (a) and (b) XRD patterns of the as-made SCZN indicating the highly ordered lamellar structure. The peaks of the calcined material in the low-angle XRD pattern disappeared due to the removal of the template. (c) SEM image revealing that the as-made sample possessed a petal-like morphology. (d,e) high-resolution transmission electron microscopy (HRTEM) image taken along the [010] and [100] axis of the as-made SCZN. (f-h) 3D EDT projections with multiple unit cell meshes along different directions illustrating the structural details in 3D reciprocal space. (i) HRTEM image taken along the [100] axis of the calcined sample that reveals the formation of MFI single crystal. (j) Structural model of SCZN before and after calcination. (k) The N$_2$ adsorption-desorption isotherms of calcined SCZN-1 and conventional ZSM-5. The synthesis molar composition was 1 CPh–Ph-10-6: 20 SiO$_2$: 2.5 Na$_2$O: 0.2 Al$_2$O$_3$: 800 H$_2$O. The scale bars in c,d,e and i represent 2µm, 20 nm, 5 nm and 5 nm, respectively.
in the samples templated by BC Ph-6-6-6 and BC Ph-8-6-6, compared
the number of 90 /C176 /C176 of these SCZNs have an extraordinary boundary structure with reflections. As shown in Fig. 3, the SEM images revealed that all the crystal structure of layered MFI, which includes only the

5.52 nm (2
n
¼
12), 4.93 nm (2
n
¼
8), 5.29 nm (2
n
¼
10) and 5.52 nm (2
n
¼
12). The high-angle XRD patterns reveal the crystal structure of layered MFI, which includes only the h0l reflections. As shown in Fig. 3, the SEM images revealed that all of these SCZNs have an extraordinary boundary structure with the 90° rotation of adjacent faces. However, it was found that the number of 90° rotational crystals appears at a significant level and dominant house-of-cards-like morphologies were observed only in the samples templated by BCPh6-6-6 and BCPh8-6-6 compared with the other three samples. The others synthesized by BCPhn-6-6 (n = 4, 10, 12) show only limited amounts of intergrowth without house-of-cards-like structure. This result suggests that only proper chain lengths (for example n = 6 and 8 of BCPhn-6-6) are favourable for the formation of house-of-cards-like joining with 90° rotational crystals.

To analyse the internal boundary structure, the TEM images of thin sections of the as-made samples were observed. Taking the sample templated by BCPh6-6-6 as an example (Fig. 4a,b; Supplementary Fig. 16), the perpendicular crystal plates with a boundary relationship shared a common c axis, in which the (100) faces are overgrown on the (010) faces; a schematic representation of a structural model of the boundary is illustrated clearly in Supplementary Fig. 17. Two independent layers join through chemical bonding on the ac plane and zig-zag channels of one layer are interconnected with straight channels of the other layer. The connectivity at the joints could arise through the formation of a new set of Si-O-Si bonds (Supplementary Fig. 18), which would sustain the lamellar structure and improve its stability. From some ultrathin crossed nanosheets as shown in Fig. 3c (although not so many), it can be found that they penetrate into each other. Therefore, the connection with MFI/MEL twins is also possible in these intergrowth domains, which is the similar to Tsapatsis’s report34. After the template molecule was removed by calcination in air, the MFI layers in the main plates collapsed to form single crystals, whereas the majority of the boundary layers did not completely collapse to produce clear mesopores because of the framework connectivity (Fig. 4c,d; Supplementary Fig. 19). In addition, the readily apparent house-of-cards-like morphology could construct a new macroporous system (~100 nm) due to the mutual pillaring between ultrathin plates (Supplementary Fig. 20). Therefore, this type of SCZN-2 possesses well-defined micro–meso–macroporous architecture, even after calcination.

The representative TEM images (Supplementary Fig. 21) of the other samples by BCPhn-6-6-6 show different degrees of intergrowth, once more confirming that only the templates with proper chain lengths are favourable for the formation of 90° rotational crystals. The cause of this result can be explained in terms of the geometric matching between the intergrowth crystal structure and the hydrophobic chain length of the bolaform templates. Based on the inherent characters of the MFI intergrowth structure (crystallographically correlative connectivity and uniform thickness of each MFI sheet, Supplementary Figs 17,18), three kinds of possible models with the narrowest distance range (corresponding to the molecular size used here) for the connectivity can be considered, exhibiting different distances ~4.0, 4.9 and 5.9 nm (Supplementary Fig. 22). The as-made samples templated by BCPh6-6-6 all exhibit lamellar structure with the same MFI layer thickness of ~2.7 nm and interlamellar distance range from 4.37 to 5.52 nm, as confirmed from XRD patterns (Fig. 2a) and TEM observations (Supplementary Fig. 23). The interlamellar spacing by BCPh6-6-6 and BCPh8-6-6 are found to be 4.83 and 4.93 nm, respectively, very close to 4.9 nm, while that by BCPh4-6-6, BCPh10-6-6 and BCPh12-6-6 are 4.37, 5.29 and 5.52 nm, respectively, far away from the three model sizes. Therefore, it is reasonable to be considered that a high degree of matching between the molecular size and space distance between

Figure 2 | XRD Patterns. Low- (a) and high-angle (b) XRD patterns of as-made samples. They are synthesized by bolaform templates with different hydrophobic carbon chain, BCPhn-6-6 (n = 4, 6, 8, 10, 12), all indicating the

Figure 3 | SEM images of as-made samples shown in Fig. 2. BCPh4-6-6 (a), BCPh6-6-6 (b,c), BCPh8-6-6 (d), BCPh10-6-6 (e), BCPh12-6-6 (f), all showing the formation of SCZNs with 90° rotational boundary. The scale bars in a,b,c,d,e,f represent 1 µm, 500 nm, 100 nm, 500 nm, 1 µm and 1 µm, respectively.

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two adjacent MFI sheets would encourage successive rotational intergrowth.

The XRD patterns (Supplementary Fig. 24) of the calcined samples show that a broad Bragg peak existed in the samples templated by BCPh-6-6-6 and BCPh-8-6-6, indicating the presence of abundant mesopores. Figure 5 shows the N\textsubscript{2} desorption-desorption isotherms of calcined samples by BC\textsubscript{Ph-n-6-6}. All samples show the uptake steps below \( P/P_0 = 0.02 \) due to the microporous MFI structure\textsuperscript{31}, while only the samples templated by BC\textsubscript{Ph-6-6-6} and BC\textsubscript{Ph-8-6-6} exhibit a higher uptake at a relative pressure range of 0.2–0.8 due to the presence of abundant and uniform mesopores after calcination. The capillary condensation loop at \( P/P_0 = 0.1–0.3 \) reveals the presence of small mesopores formed by the collapse of the lamellar structure near the joints (Fig. 4d), and the hysteresis loop at \( P/P_0 = 0.5–0.7 \) indicates the presence of interconnected pores formed by the aggregation of card-like sheets. The BET surface area, micro-, and mesopore volumes of SCZN-2 were 658 m\textsuperscript{2} g\textsuperscript{–1}, 0.11 and 0.51 cm\textsuperscript{3} g\textsuperscript{–1}, respectively. The sharp peaks at 2.4 nm (approximately equal to the scale of one lamellar micelle) were clearly caused by the 90° rotational boundary relationship. However, the other three samples prepared from BC\textsubscript{Ph-n-6-6} (\( n = 4, 10, 12 \)) exhibited no obvious uptake at a relative pressure range of 0.2–0.8, no peaks in the pore size distribution curve and low BET surface areas (Supplementary Table 1) owing to the presence of a reduced boundary structure, indicating the little amount of mesopores in these samples as has been shown in their SEM and TEM images.

In addition, it was found that the intergrowth structure produced by BC\textsubscript{Ph-6-6-6} was formed as the result of an \textit{in situ} phase transformation process, specifically from amorphous to crystalline; this observation varies significantly from previous reports, that is, where a solution-mediated seed crystal growth mechanism was indicated in the small SDAs system\textsuperscript{37}. As shown in the supporting information, the amorphous solid (Supplementary Figs 25,26a) then gradually yielded intermittent lattice fringes (Supplementary Fig. 26b,c), which were wide along the \( a \) axis and \( c \) axis; this observation provided sufficient evidence to justify the initial nucleation of MFI nanosheets and the structural units for subsequent 90° rotational growth. Along with further crystallization growth, SCZN with sufficient 90° rotational boundaries was gradually constructed (Supplementary Fig. 26d,e).

The intergrowth crystals that reside perpendicular to each other grow through the process of \textit{in situ} transformation, which involves an amorphous-to-crystalline evolution (or solid-state
Experimental results. Using C_{22-6} as the template, we obtained data. The layered models were represented by a slab model with rules. The bulk models were constructed using experimental XRD work based on the common (Lorentz–Berthelot) combination fields have been tested for relevant molecules and applied in this study. Molecules and atomic model for the zeolites were tested. These force martini coarse-grained (CG) models for the amphiphilic molecules and the zeolite frameworks were saturated with OH groups. The 3D periodic boundary condition was applied. The interlayer space was filled with the side groups of SDAs and filled with water molecules so that the density is 1.0 g cm^{-3}. The average binding energies between the amphiphilic molecules and the zeolite frameworks were calculated to evaluate the stabilities. The relative stabilities were calculated by subtracting the binding energies of the bulk model from that of the nanosheet model. The results are summarized in Table 1, and the details of the calculations are given in Supplementary Figs 27, 28, Supplementary Table 2. The calculation result indicates that the bulk model (-104.5 kJ mol^{-1}) is more stable than the layered one (-93.6 kJ mol^{-1}) for C_{22-6}, which is consistent with our experimental results. Using C_{22-6} as the template, we obtained only bulk ZSM-5 crystals (Supplementary Fig. 29), which is similar to those obtained using CTAB as SDA in the hydrothermal synthesis. We could not obtain MFI nanosheets by C_{22-6} with numerous setting of the synthesis conditions. For C_{22-6-6}, the layered structure (-114.0 kJ mol^{-1}) is more stable than the bulk one (-152.2 kJ mol^{-1}). As a matter of fact, Ryoo and co-workers have reported that the layered structures can be easily made by using C_{22-6-6} as SDA. As the aromatic groups are introduced into the hydrophobic tail in C_{Ph-Ph-10-6}, our data shows that the layered structure (-439.6 kJ mol^{-1}) is also more stable than the bulk one (-487.1 kJ mol^{-1}). After combining the experimental data for the mesostructured MFI nanosheets synthesized by both C_{22-6-6} and C_{Ph-Ph-10-6}, the calculation results indicate that the presence of both the second quaternary ammonium head and biphenyl groups in an amphiphilic molecule would significantly reduce the binding energies of the mesostructured zeolite synthesis system.

Although both C_{Ph-Ph-10-6} and C_{22-6} direct the formation of lamellar-structured nanosheets, close analysis of the calculated energies reveal that the stabilities are due to quite different mechanisms. For C_{22-6-6}, the electrostatic interactions between the quaternary ammonium groups outside of the slabs and the slab surface that otherwise do not exist in the bulk structure contribute the most to the binding energy. From the optimized configuration of C_{Ph-Ph-10-6} nanosheet model (Supplementary Fig. 28), the distances between two phenyl rings are about 3 Å, indicating the π–π interactions among the biphenyl groups play an important role to stabilize the nanosheet model. In addition, the steric repulsions between the bulky aromatic groups and the MFI channels reduce the stability of the bulk structure.

Table 1 | Calculated binding energies.

<table>
<thead>
<tr>
<th>Templates</th>
<th>E_a (kJ mol^{-1})</th>
<th>ΔE_b (nanosheet-bulk) kJ mol^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>nanosheet</td>
<td></td>
</tr>
<tr>
<td>C_{22-6}</td>
<td>-104.5</td>
<td>-93.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.9</td>
</tr>
<tr>
<td>C_{22-6-6}</td>
<td>-114.0</td>
<td>-152.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-38.2</td>
</tr>
<tr>
<td>C_{Ph-Ph-10-6}</td>
<td>-439.6</td>
<td>-487.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-47.5</td>
</tr>
</tbody>
</table>

Different calculated binding energy in the three amphiphilic molecules-NFI systems.

Speculation of the arrangement manner of templates in SCZN. To investigate the role of the template, the stereoregularity of C_{Ph-Ph-10-6} was studied using UV–visible absorption spectroscopy (Fig. 6a). In a dilute water solution, C_{Ph-Ph-10-6} molecules were isolated from each other, resulting in absorption bands from the molecule itself at 199 nm (benzene ring) and 260 nm (biphenyl group). In the crystalline solid state, the packing of the template molecules was very close and regular and the interactions of biphenyl groups result in clear π–π interactions. The energy for the transition from the π highest occupied molecular orbital to the π* lowest unoccupied molecular orbital decreased due to π–π molecular orbital overlap from the aromatic groups, which led to a red shift of the absorption bands of ~37 nm (at 297 nm). Identical absorption bands were also obtained from the as-made SCZN, which demonstrated the formation of similar π–π stacking interactions.

As mentioned above, the position of aromatic rings in the centre of micelles was confirmed by electron charge distributions based on the low-angle XRD data (Supplementary Fig. 11). The intact configuration of C_{Ph-Ph-10-6} template without decomposition in SCZN was confirmed by 13C nuclear magnetic resonance (NMR) spectra (Supplementary Fig. 30). The thermogravimetric analysis combined with elemental analysis data (ratio of N/Si = 0.035) indicate that not only that all micropores were directed by the quaternary ammonium groups, but also that one template corresponds to one micropore (Supplementary Fig. 31). Therefore, it can be speculated that the single ammonium groups...
of the template molecules are located in the straight channel of the MFI framework to direct the formation of MFI micropores and the aromatic groups in the hydrophobic tails to form stable network with strong π-π stacking (Fig. 6b). From the top view of the biphenyl groups along the b direction, the arrangement of biphenyl groups from adjacent MFI layers along the a–c plane can also generate strong π-π stacking with the adjacent ones (red dotted lines, Fig. 6c, see Supplementary Figs 32,33, Supplementary Note 2 for more detailed description). In this way, all of the biphenyl groups possess a favourable T-shaped configuration with a well-defined network, which geometrically matches the MFI frameworks and produce the crystallographically related single-crystalline MFI layers. This is also the reason why C_{22,6-6} and C_{Ph–Ph-10-6} directly polycrystalline and single-crystalline MFI nanosheets, respectively. The arrangement of the biphenyl groups in BC_{Ph-6-6-6} was similar to that of C_{Ph–Ph-10-6} (Supplementary Figs 34–36, Supplementary Note 3,4).

However, such an arrangement remains speculative. Generally, the interaction distance and the stacking conformation of the aromatic rings can be effectively determined via X-ray crystallography. However, a suitable single crystal is required to obtain these data in conjunction with an X-ray single-crystal diffractometer. Unfortunately, the aromatic arrangement in the structures of our MFI nanosheets are limited to several layers (Fig. 1e, Supplementary Fig. 12) and are separated by a layer-type zeolitic framework, which cannot be discerned using X-ray crystallography; therefore, the corresponding diffraction pattern cannot be detected.

Discussion

We aimed to design self-assembling, single-SCZN by introducing aromatic groups (such as biphenyl and naphthyl) into the hydrophobic tail of the amphiphilic molecule. The strong self-assembling ability and highly ordered orientation of aromatic groups through π-π stacking stabilize the lamellar micelle structure to make the amphiphilic molecules with single quaternary ammonium head group for directing SCZN possible. This was confirmed by single-crystal analysis with 3D EDT, powder XRD and EM. The low binding energies of this self-assembling system, obtained by computer simulation using molecular mechanics calculations, provided a theoretical evidence for the feasibility of our strategy. Furthermore, when the aromatic groups connected to the bolaform amphiphilic molecules in the hydrophobic region, a new type of hierarchical zeolite, in which the SCZN join with 90° rotational boundary, was obtained due to the special branch configuration of the bolaform molecule and the stronger π-π stacking around the boundary joints. Because of the chemically bonded connection at the crossed joints, the lamellar structures did not completely collapse, even after calcination, and they exhibited a highly specific surface area. The formation of SCZN with crystallographically correlated mesostructure from crystallized MFI units is probably the result of a geometrical match between aromatic groups and MFI zeolitic framework. We expect that our findings will provide new insight into the molecular factors governing the formation of the inorganic–organic mesophase and microporous materials, which would open up new possibilities for elaborately fabricating mesoporous zeolites.

Methods

Synthesis of amphiphilic molecules C_{n,Ph-10-6} (1). The synthesis procedure was illustrated in Supplementary Fig. 1. 4-Phenylphenol (3.4 g, 20 mmol) and 1,10-dibromodecane (30.0 g, 100 mmol) were mixed in 250 ml of ethanol containing 1.2 g of KOH and refluxed under an N₂ atmosphere for 1 day. The product was filtered and washed repeatedly with C₂H₅OH several times to obtain the intermediate 9. Then, 7.8 g (20 mmol) of 9 and 3.9 g (22 mmol) of N,N-dimethylhexylamine were mixed in 150 ml of acetonitrile and refluxed at 95 °C for 24 h. After cooling to room temperature, the product 1 was filtered, washed with diethyl ether and dried in a vacuum oven overnight (9.6 g, 93%). The detailed characterization of these novel organic compounds was shown in Supplementary Methods.

Synthesis of C_{N,N-10-6} (2). The synthesis of C_{N,N-10-6} followed the similar procedures for the preparation of 1 instead of the use of 2-naphthol.

Synthesis of BC_{Ph-10-6} (3). 4,4′-Biphenyl (4.7 g, 25 mmol, TCI) and 1,10-dibromodecane (37.3 g, 125 mmol) were mixed in 300 ml of ethanol containing 3.0 g of KOH and refluxed under an N₂ atmosphere. The product was filtered and washed repeatedly with hot C₂H₅OH and water to obtain 11. Then, 11 (3.8 g, 10 mmol) and N,N-dimethylethylamine (3.9 g, 22 mmol) were refluxed in 150 ml of acetonitrile for 3 days. Solid product 3 was obtained after the crude product was filtered and washed with diethyl ether several times (8.3 g, 94%).

Synthesis of BC^{N,N,12-6} (4-9). The detailed synthetic procedures were illustrated in Supplementary Fig. 5. Take the preparation of BC_{Ph,10-6-6} (7) for an example, 12.5 g of 11 (20 mmol) and 43.0 g (0.25 mol) of N,N,N’-tetrathylethyl-1,6-diaminohexane were mixed in 300 ml of acetonitrile/toluene (1:1) and stirred at 65 °C for 20 h. The intermediate 18 was filtered and washed with cold diethyl ether three times. The final product 7 was obtained by adding 4.8 g (5 mmol) of 18 and 4.2 g (23 mmol) of 1-bromohexane, followed by refluxing in 200 ml of acetonitrile for 1 days. After cooling to room temperature, the product was filtered, washed with diethyl ether and dried in a vacuum oven overnight (5.8 g, 90%). The amphiphilic molecules with different alkyl chain length (BC_{Ph,4-6-6}, BC_{Ph,6-6-6}, BC_{Ph,10-6-6} and BC_{Ph,12-6-6}) were also obtained following the similar procedures. The intermediates 12-19 were synthesized through the similar methods for the preparation of 11 and 18 by substituting 1,10-dibromodecane with 1,4-dibromobutane, 1,6-dibromohexane, 1,8-dibromoaclane and 1,12-dibromododecane,

Figure 6 | Schematic representation of the formation of SCZN. (a) Ultraviolet-visible absorption spectra of template molecules (C_{n,Ph-10-6}) in a dilute water solution (the black line) showing absorption bands of the isolated molecule. A red shift to 297 nm in the crystalline solid (the red line) and in the as-made SCZN (the blue line) revealing the similar formation of π-π stacking between biphenyl groups due to π-π molecular orbital overlaps. (b) Single quaternary ammoniums in the template molecules are located in the straight channel and serve as a template to direct the formation of SCZN. (c) The arrangement of biphenyl groups from adjacent MFI layers along the a–c plane orientation matching the MFI frameworks.
respectively, see Supplementary Methods for all of the characterization for these organic compounds.

**Synthesis of single-crystalline MFI nanosheets.** In a typical synthesis of MFI nanosheets, 0.518 g C22-6, 0.10 g template, 0.2 g NaOH, 0.0328 g sodium oleate and 14.4 g distilled water were mixed together and stirred for ~0.5 h. Then, 0.146 g tetraethoxysilane (98%) was added to yield a nominal molar composition of 1 C22-6: 10 C176: 20 SiO2: 2.5 Na2O: 0.2 Al2O3: 800 H2O. The mixtures were stirred for an additional 2 h. Crystallization was conducted in Teflon-lined stainless steel autoclaves (25 ml) at 150 °C, with the autoclaves tumbling at 40 r.p.m. The products were filtered, washed with distilled water and dried at 105 °C overnight, and then they were calcined in air at 550 °C. The other zeolite materials were synthesized following similar procedures only with different templates.

**Characterization.** Powder XRD patterns were recorded on a Rigaku X-ray diffractometer D/Max-IIIA equipped with a Cu Kα radiation source (40 kV, 30 mA) and transmission mode measurements were made on a PANalytical XPert with a Cr Kα radiation source. 3D HRTEM data were collected on a JEOL JEM-7401F electron microscope operating at 1kV. Zeolite thin section preparation was carried out after the mixing of epoxy resin and zeolite material with further solidifying. For visualization of 50–60 nm thin sections were then loaded on a TEM grid (400 mesh Cu). High-resolution transmission electron microscopy was performed using a JEOL JEM-3010 microscope operating at 300 kV (Cs = 0.6 mm, resolution of 1.7 nm). Images were recorded with Kevex film 900-163 using low-energy electron-diffraction conditions. 3D HRTEM data were collected on a JEOL JEM-2100 (LaB6 filament) with Cs = 1.4 mm operated at 200 kV. Herein, the total range of angles covered is 80° with 0.1° step. The nitrogen adsorption/desorption isotherms were measured at 77 K using an ASAP 2010 M + C analyser. The surface area was calculated by the BET method, and the pore size was determined from the pore size distribution curve calculated by the Barrett-Joyner-Halenda method using the adsorption branch of the isotherm. Ultra violet/visible diffuse reflectance spectra were recorded on a Perkin-Elmer Lambda 20 UV/Vis spectrophotometer, whereas the UV/Vis absorption spectrum of the filter was measured with a Shimadzu UV-2450 spectrophotometer. The absorbance spectra were recorded in opposite orientations in the channel. The channel allows coexistence of two alkyl chains so that two alkyl chains from different SDAs are tangled in the channel, but one benzene ring of CPh–Ph-10-6 is in the channel. In the layered structures, parts of the SDA molecules are in the interlayers. Due to hydrophobic effect, water molecules are separated from the clusters of hydrocarbons. In addition, the interlayer space was filled with the side groups of SDAs and filled with water molecules so that the density is 1.0 g cm−3. The configurations of C22-6 were optimized using the L-BFGS algorithm48 with an energy tolerance of 10.0 kJ mol−1 nm−1. A cutoff value of 1.0 nm was used for non-bond interactions. The calculations were conducted using GROMACS 4.55 (ref. 41). The optimized structures of the simulated models are shown in Supplementary Fig. 28.

The average binding energy (ESE) between one SDA molecule and the MFI framework in either bulk or layered structure is defined as:

$$E_S = \frac{E[\text{MFI} + \text{SDAs}] - E[\text{MFI}] - nE[\text{SDA}]}{n}$$

where $E[\text{MFI} + \text{SDAs}]$ is the total energy of MFI and SDAs, $E[\text{MFI}]$ is the energy of MFI only and $E[\text{SDA}]$ is the energy of SDA in isolation and $n$ is the number of SDAs.

The absolute binding energies between bulk and nanosheet zeolite structures are ~ −104.5 kJ mol−1 and ~ −93.6 kJ mol−1 for C22-6 and −115.2 kJ mol−1 for C22-6-6. −43.9 kJ mol−1 and ~ −48.7 kJ mol−1 for CPh–Ph-10-6, respectively. The absolute values for different template molecules cannot be directly compared, however, because different models are adopted for phenyl and alkyl groups, and the standard states do not correspond to solution syntheses.

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Author contributions
S.C. designed the experiment and led the project. D.X. synthesized MFI zeolite nanosheets and carried out SEM, HRTEM and UV measurements. D.X., Y.M., L.H., P.O. and O.T. worked on structural characterization through powder XRD, SEM and HRTEM. Z.X., F.C. and H.S. worked on theoretical analysis. B.S., J.F. and X.S. took part in the discussions.

Additional information
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