

Utilization of Evaporation during the Crystallization Process: Self-Templation of Organic Parallelogrammatic Pipes

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Abstract: Analogues of 4-dodecyloxy-2-trifluoromethylbenzamide (**12FH2**) consisting of a hydrophobic alkyl chain, a trifluoromethylated aromatic ring, and a self-complementary hydrogen-bonding amido group were synthesized, and the structural effect of each component on the formation of parallelogrammatic pipes was investigated. Differential scanning calorimetry and powder XRD analyses revealed that all-*trans* **L** and *gauche*-rich **S** polymorphic forms appeared for the analogues with more than eight carbon atoms in the alkyl chain, that is, the polymorphism originates in the conformation of the alkyl groups and hydrogen-bonding patterns of the benzamide group. Also, the trifluoromethyl substituent is crucial in that it provides an

appropriate molecular balance between the benzamide and alkyl groups. Scanning electron microscopy and powder XRD analyses of solids obtained by a drying-mediated assembly process revealed that production of the **L** polymorph by polymorphic transition from the **S** polymorph resulted in evolution of a three-dimensional structure when the alkyl group has more than 12 carbon atoms. Among the series of compounds, **12FH2** and 4-tetradecyloxy-2-trifluoromethylbenzamide (**14FH2**) formed parallelogrammatic pipes with micrometer dimensions. An

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atomic force microscopy study of **12FH2** suggested that a single pipe may be composed of platelike crystallites of **L** polymorph. From a mercury-intrusion porosimetry study, it was determined that macroporous materials with average pore diameters of about 40 μm and porosity of about 80% were obtained. The previously proposed self-templation mechanism by polymorphic transition from **S** to **L** polymorph was further discussed in view of polymorphism and the crystallization rate. An appropriate molecular balance between the benzamide and alkyl groups is necessary to induce a proper polymorphic transition for the development of a three-dimensional hollow structure in the evaporation process.

Introduction

Self-assembly is a powerful tool for fabrication of two- and three-dimensional structures, and spontaneous formation of complex supramolecular structures opens promising possi-

bilities in manufacturing functional nano- and microstructures on a large scale.^[1–4] The structures of self-assembled materials largely depend on their thermodynamic energy levels at equilibrium states. When self-assembly proceeds under nonequilibrium conditions, however, the process strongly influences the structure of self-assembled materials.^[2a,5a] Development of different macroscopic orders and shapes from a homogeneous solution is frequently observed in nonequilibrium self-assembly owing to a different evolution process.^[6,7]

One dramatic example of this can be found in a system in which irreversible evaporation of the solvent leads the system far from the equilibrium.^[8b] A continuous change of concentration and temperature brings about a subsequent change of interactions between the components and generates nonequilibrium phenomena such as Rayleigh–Bénard convection flow and fingering inhomogeneity.^[5] Physical properties of solutes and solvents such as dewetting, surface tension, and intermolecular interaction strongly affect the

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formation of architectures.^[9b] Much effort has concentrated on fabrication of mesoporous materials and arrays of nanoparticles/microspheres by drying-mediated self-assembly,^[8,10,11] but there have been few reports on the use of organic materials in the fabrication of hierarchically structured self-assembled materials.^[9,12]

Recently, we reported on the formation of parallelogrammatic pipes with micrometer dimensions through drying-mediated self-assembly of a small organic compound, namely, 4-dodecyloxy-2-trifluoromethylbenzamide (**12FH2**).^[13] Pipes with a unique shape were readily prepared by evaporation of a hot ethanolic solution of **12FH2** on a silicon wafer within a minute. Observation of the existence of two polymorphs and transition in their population during the evolution process led us to propose self-templated growth of a hollow structure, in which one polymorph serves as a template and the other as a wall. This demonstrates that the utility of drying-mediated assembly can be expanded into the micrometer regime. In addition, it provides a novel route for the generation of unique shapes with lower symmetries in self-assembled structures.

Here we report on the syntheses of structural analogues of **12FH2**, their polymorphic nature, and self-assembly behavior.

Results and Discussion

Synthesis: The benzamide group is a well-known hydrogen-bonding motif in crystal engineering.^[14] Basically, it is a self-complementary motif: in self-association of benzamides, two kinds of supramolecular synthons can be defined and described as $R_2^2(8)$ (face-to-face hydrogen bond involving *syn* hydrogen atoms) and $C(4)$ (side-to-side hydrogen bond involving *anti* hydrogen atoms) according to Etter's rule (Figure 1).^[15] Combination of two synthons yields the two-dimensionally hydrogen bonded network observed in the crystal structure of molecules containing benzamide groups, such as terephthalamide.^[16]

While most studies concerning benzamide compounds have concentrated on cocrystallization with other hydrogen-bonding motifs and subsequent control of hydrogen-bonding patterns,^[17] there have been a surprisingly small number of reports on utilizing them as a structural motifs. A few papers have illustrated the growth of conducting single crystals,^[18] physically cross-linked networks,^[19] and reinforcement of the polymer interface.^[20]

The novel benzamide compound we reported, 4-dodecyloxy-2-trifluoromethylbenzamide (**12FH2**), contains two

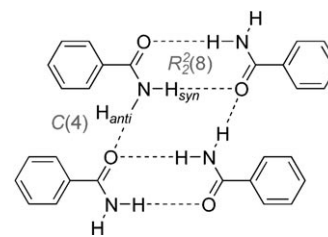
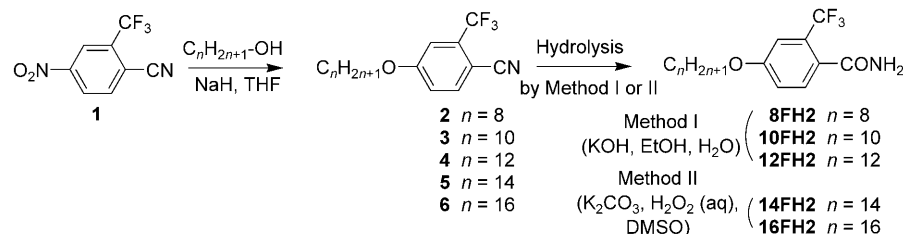


Figure 1. Illustration of two-dimensional hydrogen-bonded network of benzamide groups with $R_2^2(8)$ and $C(4)$ synthons.

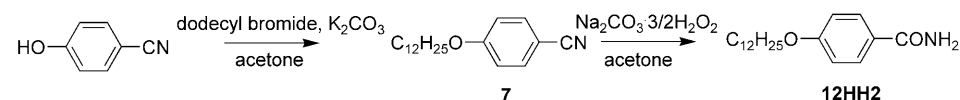
structural components: alkoxy and trifluoromethyl groups. We designed analogues of **12FH2** to examine the structural effect of each component on self-assembly of the benzamide moiety, especially on the ability to form parallelogrammatic pipes. Synthetic routes to the compounds are shown in Scheme 1.

The synthesis was based on a nitrile-activated nucleophilic aromatic substitution (S_NAr) reaction to build an ether linkage between the benzamide and alkyl groups. The nitrile group was transformed into a benzamide group by subsequent hydrolysis. The alkyl group was varied by treating the starting compound 4-nitro-2-trifluoromethylbenzonitrile (**1**) with the corresponding aliphatic alcohols. The trifluoromethyl group also played an important role in the reaction: when potassium hydroxide was used in water/ethanol, hydrolysis of the nitrile group stopped at the amide stage instead of yielding carboxylic acid when the carbon number of the alkyl chain was less than 14 (Method I). Generation of the carboxylic acid from 4-dodecyloxy-2-trifluoromethylbenzonitrile required very severe hydrolytic conditions, reflecting the stability of the corresponding benzamide. It appears that the trifluoromethyl group stabilizes the intermediate benzamide structure during hydrolysis, through an electronic effect and weak hydrogen bonding between fluorine and hydrogen atoms.^[21] Thus, a series of molecules with different lengths of the alkyl groups including 4-octyloxy-2-trifluoromethylbenzamide (**8FH2**), 4-decyloxy-2-trifluoromethylbenzamide (**10FH2**), and **12FH2** were synthesized. When the

4-Alkoxy-2-trifluoromethylbenzamides



4-dodecyloxybenzamide



Scheme 1. Synthetic routes for a series of compounds containing benzamide and alkyl groups.

carbon number was greater than 12, the use of potassium hydroxide was insufficient to complete the hydrolysis. In these cases, hydrogen peroxide in DMSO solution yielded the desired products 4-tetradecyloxy-2-trifluoromethylbenzamide (**14FH2**) and 4-hexadecyloxy-2-trifluoromethylbenzamide (**16FH2**) (Method II).^[22]

Also, 4-dodecyloxybenzamide (**12HH2**) was synthesized to examine the effect of the trifluoromethyl group on self-assembly. 4-Dodecyloxybenzonitrile was obtained by the reaction of 4-cyanophenol with 1-bromododecane, and the nitrile group was hydrolyzed with sodium percarbonate, which is known to selectively generate a primary aromatic amide when there is no substituent at the *ortho* position.^[23]

Investigation of polymorphism: The benzamide group, discovered in 1832 by Wöhler and Liebig,^[24] was the first molecular polymorph to be identified. Recently, the crystal structures of two different polymorphs of benzamide were revealed, 175 years after the discovery of polymorphism.^[25] The different polymorphs show different π - π interaction patterns (i.e., face-to-face versus face-to-edge interaction), although the two-dimensional hydrogen-bonded network is conserved. However, the possibility of face-to-edge interaction was neglected here due to the existence of an alkyl chain along the edge direction that blocks approach of the other aromatic ring.

A previous study revealed that **12FH2** also has two polymorphic forms.^[13] The **L** polymorph, which has a lamellar structure with a longer layer spacing of $d = 2.39$ nm, was observed in a solid crystallized from a melt and from *n*-hexane. X-ray crystallographic analysis revealed that the **L** polymorph has an intercalated head-to-head bilayer structure with all-*trans* conformation of the alkyl groups, induced by a hydrogen-bonded network of benzamide groups with strong side-to-side hydrogen bonds along the layer and face-to-face hydrogen bonds between the layers. The **S** polymorph, another lamellar structure with a shorter layer spacing of $d = 1.48$ nm, was observed in a solid crystallized from polar solvents such as ethanol. Based on FTIR and powder XRD analyses, the structure was interpreted as a different head-to-head bilayer structure with strong face-to-face hydrogen bonds and significantly disordered alkyl groups having a large fraction of *gauche* conformation. The polymorphic transition from **S** to **L** polymorph during the irreversible evaporation of ethanol was suggested to be a key step in the formation of unique macroporous parallelogrammatic pipes. Thus, further investigation of the polymorphism for synthesized analogues of **12FH2** was conducted to obtain more information about the formation of parallelogrammatic pipes.

Figure 2 shows the powder XRD patterns of the analogues, which were obtained from solids crystallized from the melt (Figure 2a) and from ethanol solution (Figure 2b). Both patterns clearly show peaks corresponding to (00*n*) diffractions with remarkably high intensities, that is, all of the analogues have a lamellar structure. The patterns illustrated in Figure 2a showed much longer d spacing for the first

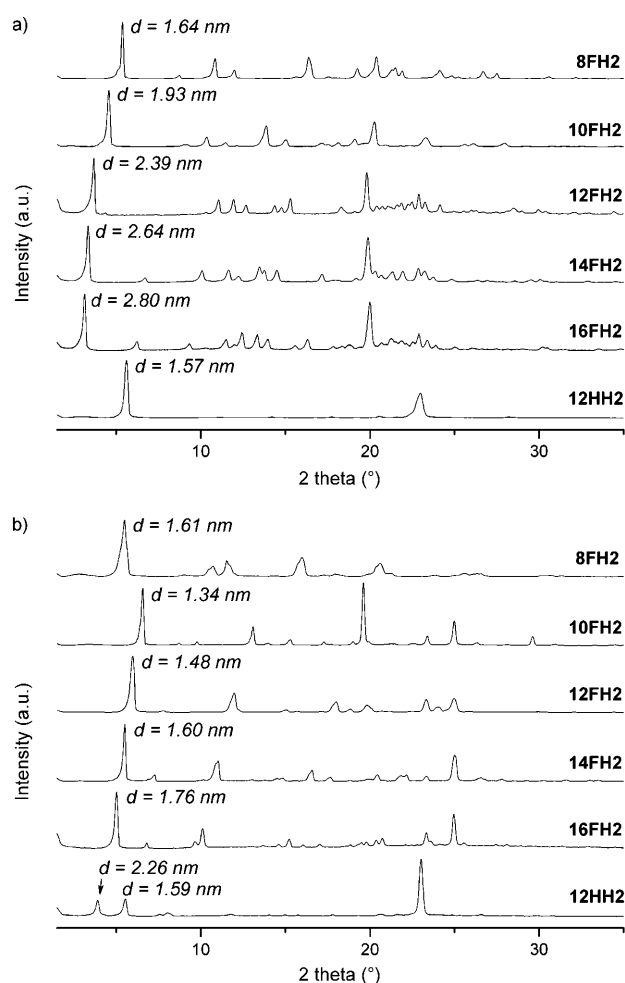


Figure 2. Powder XRD patterns of **8FH2**–**16FH2** and **12HH2**. a) Solids crystallized from the melt. b) Solids crystallized from ethanol. Patterns were normalized by the intensity of the largest peaks.

peaks corresponding to (001) diffraction than the patterns in Figure 2b, with the exception of **8FH2**, which shows identical patterns in both. Also, from **10FH2** to **16FH2**, the d spacing of the (001) diffraction increased with increasing length of the alkyl groups. More importantly, the patterns of analogues **10FH2**, **14FH2**, and **16FH2** were consistent with that of **12FH2**, that is, the **L** and **S** polymorphic forms are preserved throughout the series. It appears that analogues **10FH2**–**16FH2** have the same polymorphism as **12FH2**: **S** polymorphs are obtained by crystallization from ethanol, and **L** polymorphs by crystallization from the melt.

In Figure 2a, the peaks commonly appearing at about 20° were assigned to crystalline oligomethylene.^[26] Growing intensity of the peaks from **8FH2** to **16FH2** indicates that crystalline packing of the alkyl groups is favored for higher numbers of carbon atoms. Also, slight shifts of the peaks for **8FH2** and **10FH2** to wider angles compared to **12FH2**–**16FH2** suggest that the crystalline structure of the alkyl groups is slightly different. In Figure 2b only **10FH2** showed a peak with strong intensity at about 20°, that is, crystalliza-

tion from ethanol produces poorly crystallized alkyl groups. In the case of **10FH2**, the length of the alkyl group may be appropriate to form highly crystalline packing in the predefined geometry of the **S** polymorphic form, which is dominated by the hydrogen bonds of benzamide in ethanol. However, the spacing would not be suitable for the shorter alkyl group in **8FH2** or the longer alkyl groups in **12FH2–16FH2**, and would result in poor crystalline packing.

By taking into consideration previously reported FTIR and ^{13}C solid-state CP-MAS NMR studies,^[13] molecular packings of the **L** and **S** polymorphic forms were suggested (Figure 3). Crystallization from a melt would favor production of the **L** polymorph with a stable packing of alkyl groups and aromatic rings. At the cost of a large fraction of *gauche* conformation in the alkyl group, the **S** polymorph appears to have a more optimal geometry for face-to-face hydrogen bonding between benzamide groups. This is an example of solvent-mediated polymorphism, in which the solvent molecules interact with the solute and preferentially produce a certain polymorph.^[27] In the case of **8FH2**, it appears that face-to-face hydrogen bonds are not preferred, because the alkyl group cannot afford a *gauche*-rich conformation.

The fact that **8FH2** does not exhibit polymorphism provides strong evidence for the origin of the polymorphism: an alkyl group consisting of more than 10 carbon atoms induces polymorphism based on difference in conformation. The octyl group may have only one conformation, because it cannot provide sufficient space for the benzamide groups to form stronger face-to-face hydrogen bonding. Based on the powder XRD analysis, the crystal structure of **8FH2** was assigned as the **L** polymorph, because the *d* spacing was too large for the **S** polymorph.

Compound **12HH2** also follows the aforementioned trend in showing two polymorphs; however, the solid obtained from ethanol consisted of both polymorphs, whereby that with shorter *d* spacing was proven to be the same as the polymorph obtained from the melt. The extremely poor solubility of **12HH2** resulted in rapid crystallization, even from ethanol. However, the occurrence of the other polymorph with longer *d* spacing in ethanol suggests that the lamellar structure of **12HH2** is substantially different from that of **12FH2**. Also, **12HH2** did not show peaks corresponding to crystalline packing of oligomethylene chains in either polymorphic form: instead, a strong peak appeared at about 23° in both polymorphic forms, and it was assigned to π - π stacking of the aromatic rings. This difference indicates that the trifluoromethyl group at the *ortho* position of the benzamide moiety plays an important role in the crystal structure and for the solubility. The role of the trifluoromethyl group may be disruption of π - π stacking of the aromatic ring to provide good solubility in common organic solvents. Also, it may stabilize the face-to-face hydrogen bonds of benzamide moieties via F...H interaction.^[21] This leaves the H_{anti} atom to be solubilized by ethanol molecules and leads to formation of the **S** polymorph.

To gain further insight into the polymorphism and the relevant thermal transitions, a differential scanning calorimetry (DSC) study was conducted. Figure 4 shows DSC thermograms of the solids crystallized from ethanol. In the first heating cycle, the series **8FH2–16FH2** commonly showed a large endothermic peak around 105°C (Figure 4a). This peak was assigned as the melting transition (T_{m}) of the compounds, in which the hydrogen bonds between benzamide groups are cleaved. When the carbon number of the alkyl group was greater than ten, an endothermic premelting transition (T_{pm}) appeared in prior to the melting transition, and

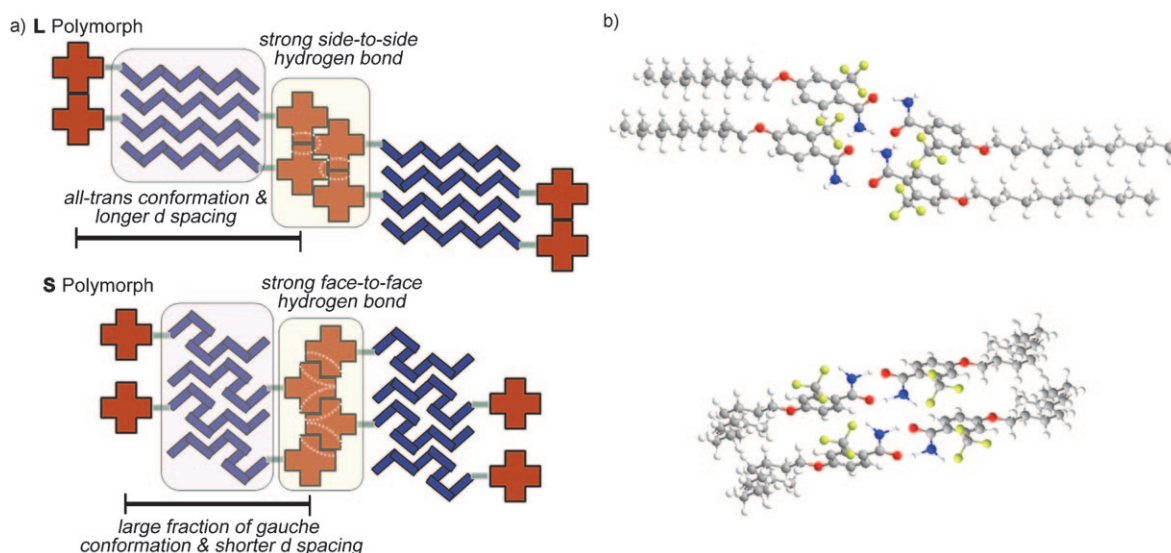


Figure 3. a) Illustration of crystal structures of **L** and **S** polymorphic forms appearing in **8FH2–16FH2**. Red cross: benzamide group. Blue rectangles: alkyl group. Green rectangle: etheral oxygen atom. b) Suggested hydrogen-bonded molecular packing of **L** (top) and **S** (bottom) polymorphic forms of **12FH2**. White H, gray C, red O, blue N, yellow F.

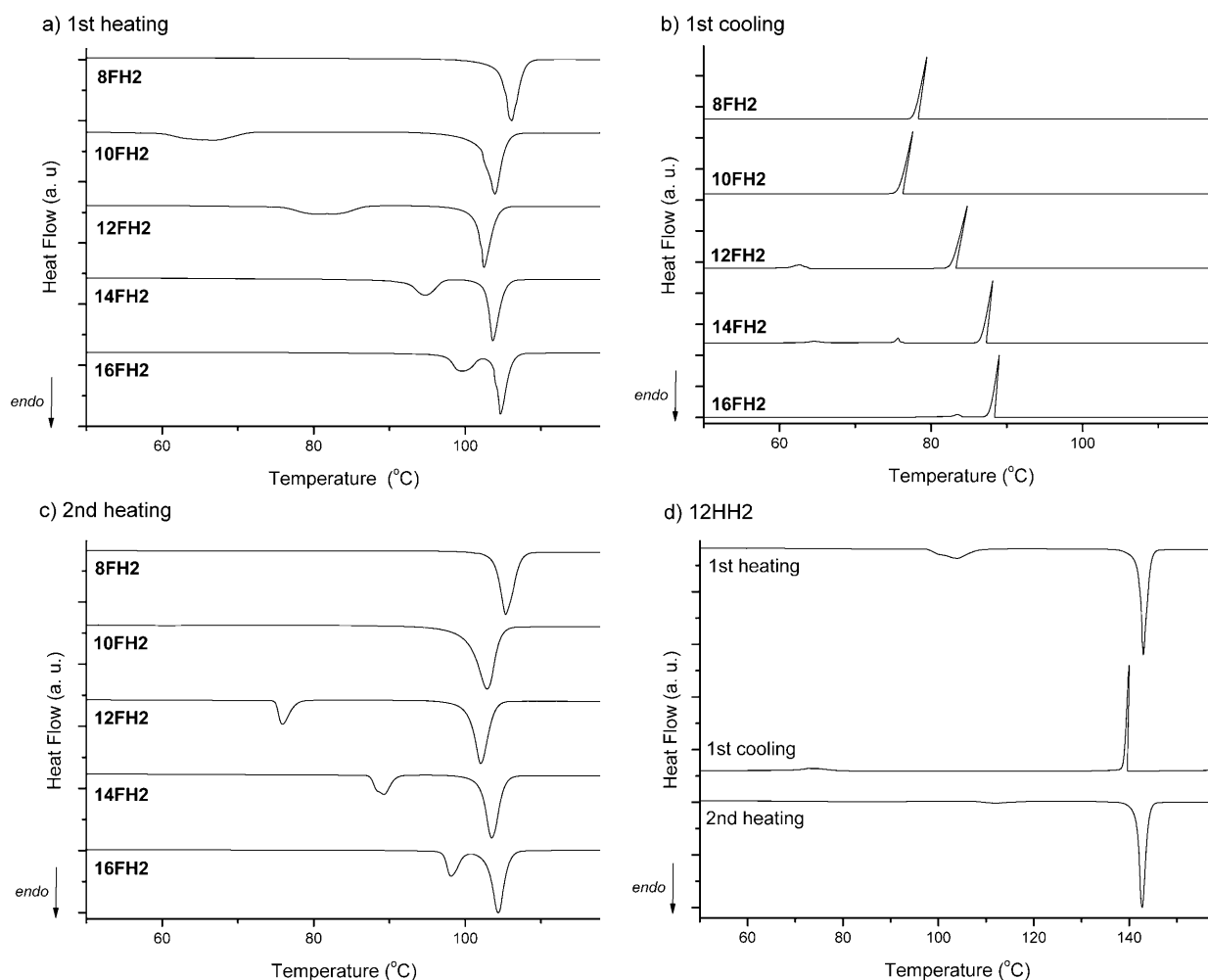


Figure 4. DSC thermograms of the compounds under N_2 at a heating rate of 5°Cmin^{-1} and a cooling rate of 2°Cmin^{-1} . Peak intensities were normalized. a) First heating scan of **8FH2**–**16FH2**. b) First cooling scan of **8FH2**–**16FH2**. c) Second heating scan of **8FH2**–**16FH2**. d) First heating, first cooling, and second heating scan of **12HH2**.

the transition temperature increased with increasing carbon number. However, no morphological change was observed around that temperature under the polarized optical microscope. Thus, it was assigned to the phase transition corresponding to a change in the conformation of the alkyl chain from an ordered to disordered structure.^[28]

Figure 4b shows the thermograms recorded during the first cooling cycle. Large exothermic peaks with a tilted shape were assigned to abrupt crystallization of the compounds from the melt. Compounds **12FH2**, **14FH2**, and **16FH2** showed an additional exothermic peak, and the peak temperature increased with increasing carbon number. This exothermic peak was assigned to rearrangement of alkyl chains. The above DSC results indicate that hydrogen bonding and rearrangement of the alkyl chains occur at different temperatures.

Because crystallization from the melt yields only **L** polymorph, the initial **S** polymorph during the first heating cycle should be transformed into the **L** polymorph. Therefore, the second cycle should show thermal transitions corresponding

to the **L** polymorph. Indeed, the thermograms of the second heating cycle were identical to those of the **L** polymorph, and the transition temperature corresponding to the conformational change of the alkyl group decreased in all cases. This suggests that the conformation of the alkyl groups is different between the **L** and **S** polymorphs. The temperature was maintained during the third and fourth scans (data not shown), that is, the **L** polymorphic form is preserved.

The enthalpies corresponding to the melting of the hydrogen bonds of $30\text{--}40\text{ kJ mol}^{-1}$ reflect the strength of two-dimensional hydrogen bonds between benzamide moieties. The enthalpies corresponding to the transition of alkyl chains were much smaller, in the range of $10\text{--}20\text{ kJ mol}^{-1}$ (17.7 for **12FH2**, 18.9 for **14FH2**, and 16.9 kJ mol^{-1} for **16FH2** in the first heating cycle). When divided by the number of carbon atoms in the alkyl chains, the enthalpies for the transitions during the first heating cycle were about 1 kJ mol^{-1} . These values are similar to the reported premelting transition enthalpies of *n*-alkanes.^[26b]

Also, the effect of the trifluoromethyl group at the *ortho* position of the benzamide moiety was examined for **12FH2** and **12HH2**. Similar to **12FH2**, **12HH2** showed two transitions corresponding to the conformational change of the alkyl group and the cleavage of the hydrogen bonds between benzamide groups. However, the much higher melting temperature (ca. 40 °C) indicated that the hydrogen-bonded network of **12HH2** is stronger due to the absence of the sterically bulky trifluoromethyl group.

Drying-mediated assembly: To utilize the difference between the two polymorphs in assembly, we evaporated ethanolic solutions of **8FH2–16FH2** and **12HH2** on a silicon wafer. Evaporation of a solution on a substrate is in principle a nonequilibrium process: it is complex enough to form dissipative structures, and irreversible because it freezes the final structure.^[5a,8b] Although complete understanding of the structural evolution during evaporation is very difficult, the coffee-stain mechanism and the pinhole mechanism have been applied to explain the formation of unique structures.^[29,30] The coffee-stain mechanism explains the formation of ringlike stains from solution droplets by precipitation of solute at the perimeter of the droplet and subsequent outward flow of liquid from the interior to the edge of the drop. The pinhole mechanism has been applied when the formation of holes in the thinning liquid films accounts for ring formation. The evaporation speed is higher at the edge of the pinhole than in the bulk of the solution film, and inward flow of solute concentrates the ring structure.^[9b]

However, to the best of our knowledge, drying-mediated assembly has not been applied to crystalline compounds. We speculated that rapid evaporation at high temperature would provide an interesting environment in which both crystallization in the solution and crystallization from the melt can occur, yielding unique crystal morphologies composed of two polymorphs. In a typical experiment, 20% (w/v) ethanolic solutions of the compounds at around 100 °C were simply dropped onto a silicon wafer at room temperature and allowed to evaporate. Figure 5 shows selected SEM images of the resulting solids after complete evaporation.

In the cases of **8FH2** (Figure 5a) and **10FH2** (Figure 5b), two-dimensional sheetlike morphologies with cracks and holes formed by evaporation of the solvent were observed. Formation of the structure can be explained by the pinhole mechanism, including thinning of the concentrated solution on the substrate. However, we observed that rapid crystallization during evaporation strongly affected the drying-mediated assembly process by defining the growth direction of the structure, especially at high concentration. In the case of **8FH2**, linear holes developed rather than the usual spherical holes, due to crystalline growth around the boundaries of the pinholes. Compound **10FH2**, which is more crystalline due to the longer alkyl group, developed cracks with lengths of several tenths of a micrometer along the domain boundaries. It appears that the crystallization of **10FH2** was initiated mainly by the decrease in temperature and rapidly propagated in two dimensions. These results also imply that

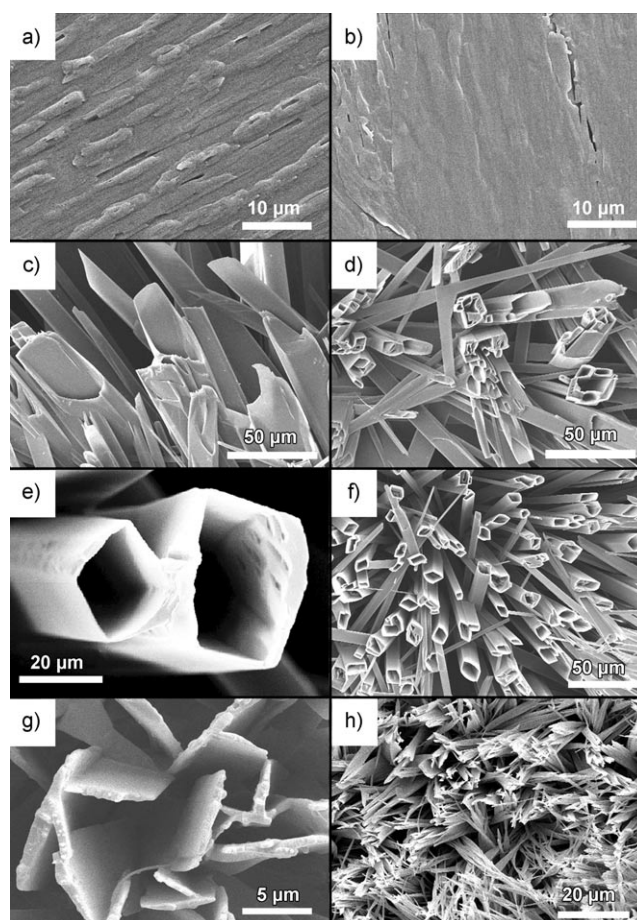


Figure 5. SEM images of solids obtained from ethanolic solution (20% w/v) by drying-mediated assembly process. a) **8FH2**. b) **10FH2**. c, d) **12FH2**. e, f) **14FH2**. g) **16FH2**. h) **12HH2**. Samples were prepared by dropping hot ethanolic solutions of the compounds onto a silicon wafer at room temperature, followed by evaporation of ethanol.

the number of carbon atoms in the alkyl group determines the crystallization rate of the compounds, and this number should exceed ten in order to grow three-dimensional crystals during the evaporation process.

In the cases of **12FH2** (Figure 5c and d) and **14FH2** (Figure 5e and f), evaporation resulted in an unusual crystal growth. The SEM images clearly show that hemispherical bundles of rectangular pipes with micrometer size formed over a wide region. The observation of hemispherical bundles spread over the substrate indicates that Bénard convection flow was locally produced due to the temperature difference between the surface of the solution drop and the substrate. The flow originates from the region near the substrate, where it is relatively hot. Due to the temperature gradient from the surface to the substrate, which is generated by subsequent cooling, the flow rises up with the aid of buoyant force. When the flow reaches the surface of the drop and contacts cold air, the temperature abruptly decreases and drives the flow downward. At that point, crystallization appears to be initiated from a locally supersaturated solution and propagates along the direction of the sinking

flow, forming hemispherical bundles. Because of the appearance of platelike crystals at the boundary of the droplet, the evaporation process is thought to occur by a coffee-stain mechanism.

The cross section of the pipes obtained from **12FH2** was about $20 \times 15 \mu\text{m}$ with an interior angle of -80° and an exterior angle of -100° , similar to those of **14FH2**. The highest end of the pipe was about 1 mm high. The thickness of the wall was about 150 nm for **12FH2** and about 300 nm for **14FH2**. Although most pipes had a parallelogrammatic shape, some were more complex in shape. Platelike crystals were observed in regions around the bundle.

Although a small number of studies have reported the formation of organic self-assembled tubes of micrometer size,^[31,32] macroporous nature of the tubes, which is important for practical applications, has yet to be fully realized. We used mercury-intrusion porosimetry to evaluate the average pore diameter of **12FH2** and **14FH2**. The pore size distribution of **12FH2** and **14FH2** is depicted in Figure 6, which shows that macropores with a median pore diameter of $47.0 \mu\text{m}$ for **12FH2** and $34.4 \mu\text{m}$ for **14FH2** were developed. The total pore area was calculated as $77.2 \text{ m}^2 \text{ g}^{-1}$ for **12FH2** and $50.2 \text{ m}^2 \text{ g}^{-1}$ for **14FH2**. Also, the multimodal shape of the distribution suggests that the size of the initial **S** polymorph, which acts as a template, is broadly distributed because the growth process occurs in heterogeneous environments. The porosity of the samples was 73.0 and 80.6% for **12FH2** and for **14FH2**, respectively.

The next task was to identify the supramolecular structure of the parallelogrammatic pipes, which should have two different faces and junctions between them. Using an atomic force microscope (AFM), we scanned two different faces of the pipe of **12FH2** and obtained the height image of each face. The face depicted in Figure 7a showed a considerably flat surface consisting of several terraces and steps. The height of the steps was about 1.6 nm on average. This value did not match any repeat distance observed in the powder XRD pattern of **12FH2**, but was smaller than the d spacing of 2.39 nm. Thus, it was thought to be a stack of lamellar layers, and we envisioned the whole face as the (100) surface of a horizontally stacked lamellar structure of the **L** polymorph. The other face, depicted in Figure 7b, revealed a highly rough surface on which the ledges of platelike structures all protruded vertically. Following the assignment of the (100) surface, the face should be the (010) surface of the **L** polymorph. The distance between the plates was about

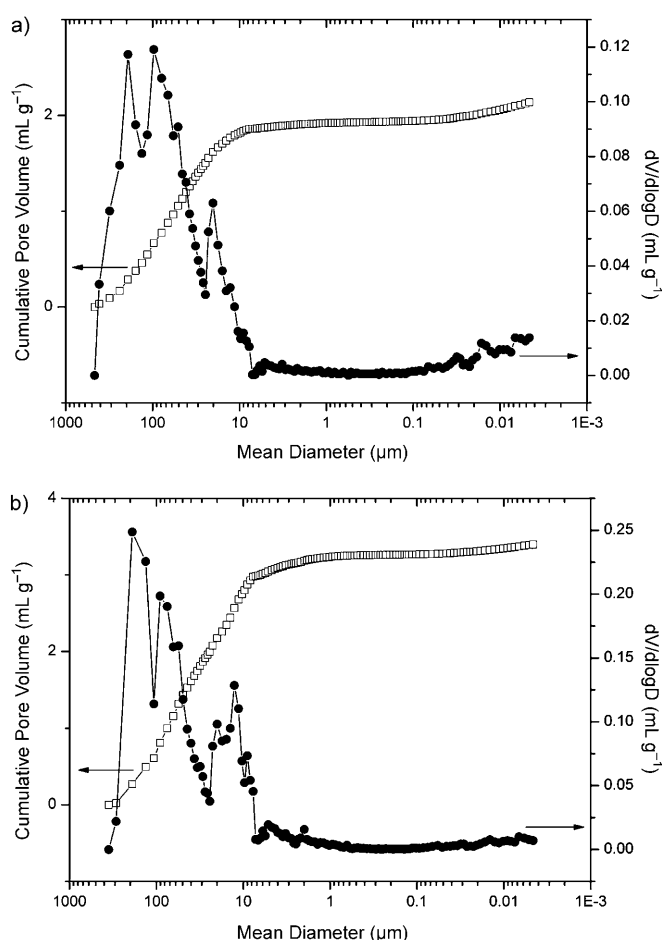


Figure 6. Pore size distribution of parallelogrammatic pipes obtained from ethanolic solution (20% w/v) by drying-mediated assembly. a) **12FH2**. b) **14FH2**.

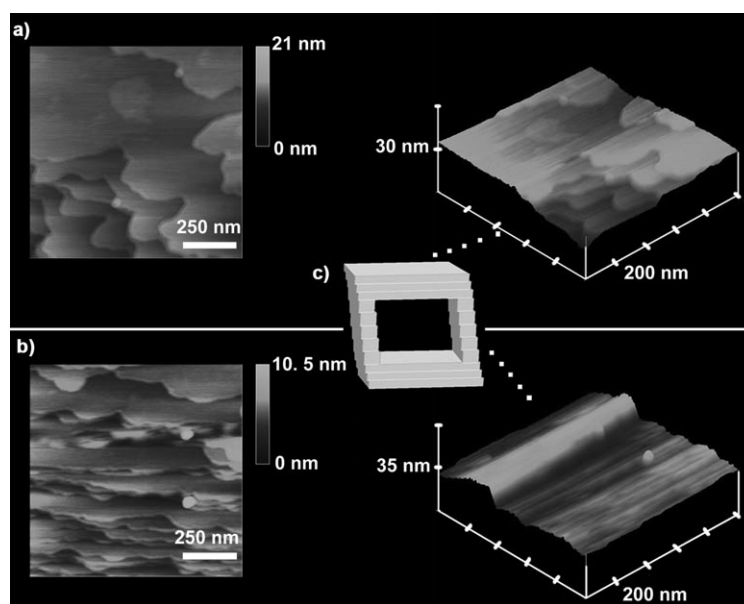


Figure 7. AFM images of pipes of **12FH2**. a) Image of horizontal face. b) Image of vertical face. c) Proposed structure based on the results.

1.8 nm on average, similar to the height of the steps observed in Figure 7a.

Based on the morphology shown in Figure 7 and consideration of the anisotropic unit-cell structure of the **L** polymorph, we could draw the three-dimensional structure of the pipe (Figure 7c). It is reasonable to regard the pipe as a hollow crystal of the **L** polymorph. The stacked lamellar structures of similar thicknesses observed at both faces, however, suggest that the whole pipe is composed of small crystallites, similar to a sectioned column. This picture also fits the drying-mediated assembly process, because rapid nucleation due to evaporation is likely to generate small crystallites and promote their aggregation.

The features described above strongly support the tentative mechanism we previously suggested for the origin of the formation of the unusual parallelogrammatic cross section of micrometer-size, that is, polymorphic transition of **S** into **L** polymorph during evaporation.^[13] An XRD study of quenched samples of **12FH2** and **14FH2** verified that crystallization of the **S** polymorph occurs in the drop of solution as it becomes saturated during evaporation. Thus, the initial solvent-rich crystal composed of the **S** polymorph should be transformed into the **L** polymorph on contact with air. The existence of the hollow space inside the pipes suggests that the transformation is initiated from the surface of the crystal to form a wall, and a subsequent decrease in the amount of solute leaves the inner space solvent-filled. Because of the anisotropic shape of the molecules, growth of crystals of the **L** polymorph would favor a certain direction along the [001] axis and yield large platelike crystals on the (100) surface and small crystallites on the (010) surface. Eventually, macroscopic tubes would be generated by packing of crystals after removal of the solvent.

In the case of **16FH2**, the SEM images showed three-dimensionally grown crystals arranged in a thin platelike morphology. The width of the crystals of about 20 μm is similar to those of **12FH2** and **14FH2**, and several platelike crystals were attached such that they appeared to form half of a pipe. However, no hollow structures were observed, that is, a very sophisticated balance in the molecular structure is required. Compound **12HH2** also revealed a similar but thinner morphology compared to **16FH2**, consisting of fibers with diameters of several hundred nanometers adhering together to form a petal-like structure.

Molecular/mesomorphic structure relationship and criteria for the formation of pipe structures: One of the prerequisites for the formation of parallelogrammatic pipes is the ability to develop three-dimensional structures during evaporation. The SEM study indicates that the molecule should have an alkyl chain length of more than 12 carbon atoms, thus ruling out **8FH2** and **10FH2**. Also, overly crystalline molecules such as **16FH2** and **12HH2** were inappropriate for forming parallelogrammatic pipes, although they formed three-dimensional structures.

The other factor is thought to be a proper polymorphic transition during the evaporation process. It is surprisingly

rare that crystals can be exploited in the formation of unique hollow structures which are macroscopic objects with controlled symmetries.^[32] A previous study for **12FH2** indicated that the appearance of an **L** polymorph consisting of pipes is actually the result of the polymorphic transition from the initial **S** polymorph, and this is crucial for the formation of a parallelogrammatic cross section of micrometer size.^[13] Compared to other methodologies, utilization of polymorphism may be advantageous as it does not require additional materials.

Powder XRD measurements were carried out to investigate the composition of solids obtained by evaporation. Figure 8 depicts XRD patterns of the compounds after com-

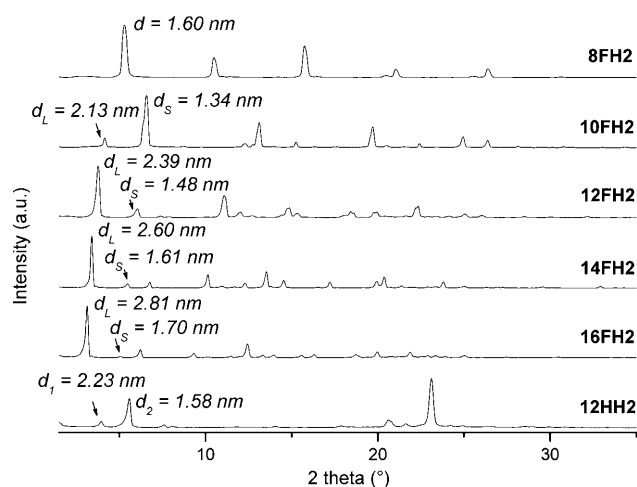


Figure 8. Powder XRD patterns of the solids obtained from ethanol solution (20% w/v) by drying-mediated assembly. d_L and d_S denote peaks corresponding to the (001) diffraction of **L** and **S** polymorphs of **10FH2**–**16FH2**. d_1 and d_2 denote peaks corresponding to the (001) diffraction of each polymorph of **12HH2**.

plete evaporation. The patterns clearly show that both **L** and **S** polymorphs were simultaneously developed in the drying process, except for the case of **8FH2**.

The intensity ratio between the first diffraction peaks of the two polymorphs (**L/S** ratio) varied depending on the length of the alkyl group. The increasing **L/S** ratio from **10FH2** to **16FH2** indicates that compounds with longer alkyl groups favor the **L** polymorph during evaporation. This suggests that rapid crystallization induced by evaporation promotes the formation of the **L** polymorph because of increased intermolecular interaction between alkyl groups. Also, the crystallization rate became faster as the **L/S** ratio increased.

Investigation of structural analogues of **12FH2** reveals that the formation of uniquely shaped pipes occurs under very precise conditions, and also requires a sophisticated molecular structural balance between hydrogen-bonding interactions of benzamide groups and van der Waals interactions of alkyl groups. Given that the benzamide moiety is essential to afford the desired two-dimensional hydrogen

bonds and the subsequent crystallinity, the length of the alkyl group is critical for generating the hollowness based on the alkoxybenzamide backbone. Specifically, an alkyl group with more than ten carbon atoms is necessary for polymorphism. The compounds consisting of an alkyl group with 12 or 14 carbon atoms generate a three-dimensional structure through an appropriate balance between **S** and **L** polymorphs, where one serves as a template and the other as a negative replica. If the process conditions are inclined toward one polymorph, such as in the case of **8FH2** or **16FH2**, a three-dimensional hollow structure cannot form. The relationship between molecular and mesomorphic structure and the criteria for formation of pipe structures are summarized in Figure 9

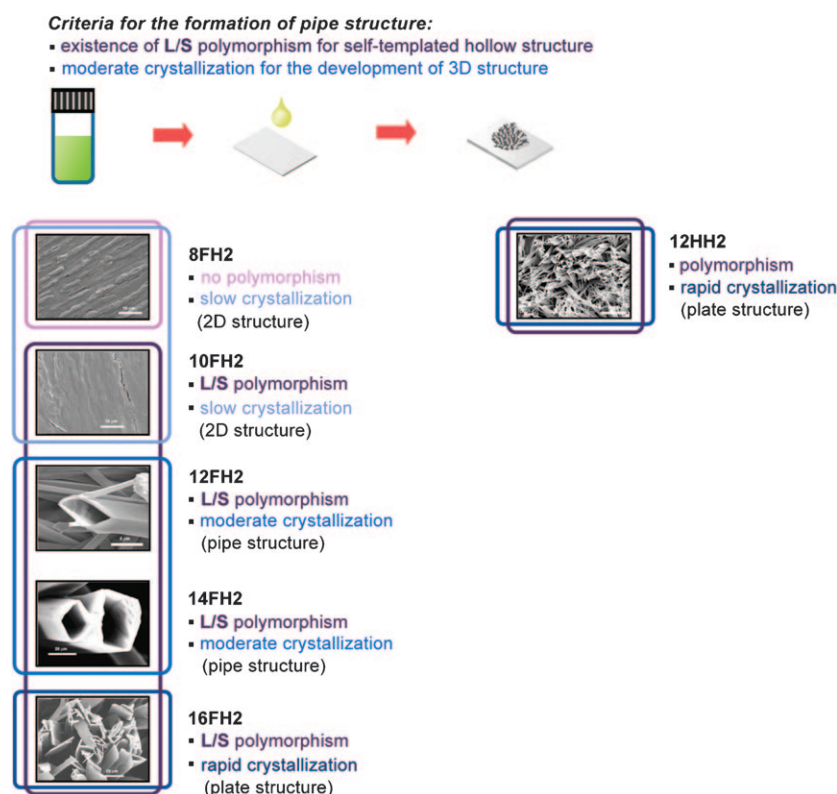


Figure 9. Molecular/mesomorphic structure relationship and criteria for formation of pipe structures.

Conclusion

A series of structural analogues of **12FH2** were synthesized to evaluate their molecular structures in relation to the formation of parallelogrammatic pipes. The polymorphic nature of the analogues, characterized by powder XRD and DSC analyses, originated from the conformation of alkyl groups and was preserved through the series when the number of carbon atoms in the alkyl group was greater than eight. Investigation of the solids obtained by a drying-mediated assembly process revealed that the formation of parallelogrammatic pipes required sophisticated evolution conditions with a moderate crystallization rate that would allow a

polymorphic transition from **S** to **L** polymorph. Only **12FH2** and **14FH2** met the criteria for polymorphic transition and produced parallelogrammatic pipes.

Experimental Section

General: 4-Nitro-2-trifluoromethylbenzonitrile was synthesized according to procedures reported elsewhere.^[13] Other starting materials were obtained from commercial suppliers and used without further purification. MgSO_4 was used to dry all organic solutions during workup procedures. Analytical TLC was performed on a Kieselgel 60 F-254 precoated TLC plates. Silica for flash chromatography was silica 60 (230–400 mesh) from Merck. The ^1H and ^{13}C NMR spectra were recorded on a Bruker Fourier Transform AVANCE 400 spectrometer. Chemical shifts are expressed in

parts per million relative to residual solvent protons. Scanning electron microscopy (SEM) studies were performed on a Philips XL30S field-emission SEM (FE-SEM) and Leo 1455 VP environment SEM (ESEM). Samples prepared on a silicon wafer were sputtered with gold and investigated by SEM. X-ray diffraction patterns were obtained on a Rigaku D/MAX III diffractometer with a scan speed of 2°min^{-1} and a sampling width of 0.01° by using $\text{Cu K}\alpha$ radiation. Mercury-porosimetry isotherms were obtained on an AutoPore III (Micromeritics). Prior to intrusion of mercury the samples were evacuated under vacuum maintained below 3×10^{-2} Torr at room temperature. The Kelvin equation was used to determine the pore size distribution of the samples. The contact angle between the sample and mercury was chosen as 140° . Differential scanning calorimetry (DSC) was conducted on a TA Q100 calorimeter. Samples were measured in aluminum hermetic cells under N_2 atmosphere at a heating rate of 5°Cmin^{-1} and a cooling rate of 2°Cmin^{-1} . Atomic force microscopy (AFM) was conducted on a Veeco Multimode Scanning Probe Microscope in tapping mode.

General method for the synthesis of 4-alkoxy-2-trifluoromethylbenzonitriles:

Aliphatic alcohol (43.74 mmol) was added to a stirred suspension of sodium hydride (60% (w/w) oil dispersion, 1.75 g, 43.85 mmol) in THF (60 mL) at 0°C under N_2 . The mixture was heated to reflux for 30 min and cooled to room temperature. 4-Nitro-2-trifluoromethylbenzonitrile (10 g, 46.27 mmol) was dissolved in THF (60 mL) and dropped into the flask. The reaction mixture was refluxed for 15 h under N_2 and cooled to room temperature. A saturated aqueous solution of NaCl (120 mL) was added to the reaction mixture and an organic layer was collected. The aqueous layer was extracted with ethyl acetate. The combined organic layers were dried and concentrated to give a reddish liquid. The desired product was purified by flash chromatography on silica gel with ethyl acetate/hexane as eluent.

4-Octyloxy-2-trifluoromethylbenzonitrile (2): Yield 58%; m.p. $< \text{RT}$; ^1H NMR (400 MHz, CDCl_3 , 25°C): $\delta = 7.71$ (d, 1H, ArH), 7.23 (d, 1H, ArH), 7.07 (q, 1H, ArH), 4.03 (t, 2H, OCH_2), 1.77 (p, 2H, OCH_2CH_2), 1.27 (m, 10H), 0.85 ppm (t, 3H, CH_2CH_3); ^{13}C NMR (100 MHz, CDCl_3 ,

25°C): δ = 162.3, 136.5, 134.5 (q, $^2J(\text{C},\text{F})$ = 32.5 Hz), 122.0 (q, $^1J(\text{C},\text{F})$ = 272.3 Hz), 117.1, 115.9, 113.8 (q, $^3J(\text{C},\text{F})$ = 4.9 Hz), 100.9, 69.1, 31.7, 29.2, 29.1, 28.8, 25.8, 22.6, 14.0 ppm; MS: m/z : 299.1518 (calcd: 299.1497); elemental analysis calcd (%) for $\text{C}_{16}\text{H}_{20}\text{F}_3\text{NO}$: C 64.20, H 6.73, F 19.04, N 4.68, O 5.35; found: C 63.92, H 7.38, N 5.10.

4-Decyloxy-2-trifluoromethylbenzonitrile (3): Yield 40%; m.p. < RT; ^1H NMR (400 MHz, CDCl_3 , 25°C): δ = 7.71 (d, 1H, ArH), 7.23 (d, 1H, ArH), 7.07 (q, 1H, ArH), 4.03 (t, 2H, OCH_2), 1.77 (p, 2H, OCH_2CH_2), 1.27 (m, 14H), 0.85 ppm (t, 3H, CH_2CH_3); ^{13}C NMR (100 MHz, CDCl_3 , 25°C): δ = 162.2, 136.5, 134.5 (q, $^2J(\text{C},\text{F})$ = 35.0 Hz), 122.3 (q, $^1J(\text{C},\text{F})$ = 277.5 Hz), 117.2, 115.9, 113.8 (q, $^3J(\text{C},\text{F})$ = 4.7 Hz), 100.9, 69.1, 31.9, 29.5, 29.2, 28.8, 25.8, 22.6, 14.1 ppm; MS: m/z : 327.1813 (calcd: 327.1810); elemental analysis calcd (%) for $\text{C}_{18}\text{H}_{24}\text{F}_3\text{NO}$: C 66.04, H 7.39, F 17.41, N 4.28, O 4.89; found: C 66.10, H 8.08, N 4.85.

4-Dodecyloxy-2-trifluoromethylbenzonitrile (4): Yield 55%; m.p. 33–35°C; ^1H NMR (400 MHz, CDCl_3 , 25°C): δ = 7.71 (d, 1H, ArH), 7.22 (d, 1H, ArH), 7.07 (q, 1H, ArH), 4.03 (t, 2H, OCH_2), 1.77 (p, 2H, OCH_2CH_2), 1.27 (m, 18H), 0.85 ppm (t, 3H, CH_2CH_3); ^{13}C NMR (100 MHz, CDCl_3 , 25°C): δ = 162.2, 126.5, 134.1 (q, $^2J(\text{C},\text{F})$ = 32.6 Hz), 122.2 (q, $^1J(\text{C},\text{F})$ = 272.2 Hz), 117.0, 115.6, 113.8 (q, $^3J(\text{C},\text{F})$ = 4.9 Hz), 100.8, 69.0, 31.2, 29.7–28.8 (m), 25.8, 22.6, 14.0 ppm; MS: m/z : 355.2125 (calcd: 355.2123); elemental analysis calcd (%) for $\text{C}_{20}\text{H}_{28}\text{F}_3\text{NO}$: C 67.58, H 7.94, F 16.04, N 3.94, O 4.50; found: C 65.74, H 7.66, N 3.74.

4-Tetradecyloxy-2-trifluoromethylbenzonitrile (5): Yield 47%; m.p. 43–44°C; ^1H NMR (400 MHz, CDCl_3 , 25°C): δ = 7.71 (d, 1H, ArH), 7.23 (d, 1H, ArH), 7.07 (q, 1H, ArH), 4.03 (t, 2H, OCH_2), 1.77 (p, 2H, OCH_2CH_2), 1.27 (m, 10H), 0.85 ppm (t, 3H, CH_2CH_3); ^{13}C NMR (100 MHz, CDCl_3 , 25°C): δ = 162.3, 136.5, 134.5 (q, $^2J(\text{C},\text{F})$ = 30.4 Hz), 122.0 (q, $^1J(\text{C},\text{F})$ = 267.6 Hz), 117.1, 115.9, 113.8 (q, $^3J(\text{C},\text{F})$ = 4.8 Hz), 100.9, 69.1, 31.9, 29.7–29.2 (m), 28.8, 25.8, 22.7, 14.1 ppm; MS: m/z : 383.2401 (calcd: 383.2436); elemental analysis calcd (%) for $\text{C}_{22}\text{H}_{32}\text{F}_3\text{NO}$: C 68.90, H 8.41, F 14.86, N 3.65, O 4.17; found: C 69.43, H 9.32, N 4.10.

4-Hexadecyloxy-2-trifluoromethylbenzonitrile (6): Yield 58%; m.p. 51–52°C; ^1H NMR (400 MHz, CDCl_3 , 25°C): δ = 7.71 (d, 1H, ArH), 7.23 (d, 1H, ArH), 7.07 (q, 1H, ArH), 4.03 (t, 2H, OCH_2), 1.80 (p, 2H, OCH_2CH_2), 1.44 (p, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.27 (m, 24H), 0.85 ppm (t, 3H, CH_2CH_3); ^{13}C NMR (100 MHz, CDCl_3 , 25°C): δ = 162.3, 136.5, 134.5 (q, $^2J(\text{C},\text{F})$ = 31.5 Hz), 122.0 (q, $^1J(\text{C},\text{F})$ = 272.6 Hz), 117.1, 115.9, 113.8 (q, $^3J(\text{C},\text{F})$ = 4.5 Hz), 100.9, 69.1, 31.9, 29.7–28.8 (m), 25.8, 22.7, 14.1 ppm; MS: m/z : 411.2701 (calcd: 411.2749); elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{36}\text{F}_3\text{NO}$: C 70.04, H 8.82, F 13.85, N 3.40, O 3.89; found: C 70.82, H 9.79, N 3.87.

Method I for the synthesis of 4-alkoxy-2-trifluoromethylbenzamides: 4-Alkoxy-2-trifluoromethylbenzonitrile (0.5 g, 1.407 mmol) was dissolved in ethanol (5 mL). Potassium hydroxide (1.34 g, 23.91 mmol) was dissolved in water (5 mL) and the solution was added to the flask. The reaction mixture was heated to reflux for 20 h and cooled to room temperature. Water (3 mL) was added to the reaction mixture. The mixture was filtered to give a white solid, which was dried under vacuum.

4-Octyloxy-2-trifluoromethylbenzamide (8FH2): Yield 88%; m.p. 105°C; ^1H NMR (400 MHz, CDCl_3 , 25°C): δ = 7.52 (d, 1H, ArH), 7.16 (d, 1H, ArH), 7.01 (q, 1H, ArH), 6.27 (s, 1H, NH of amide), 5.89 (s, 1H, other NH of amide), 3.98 (t, 2H, OCH_2), 1.78 (p, 2H, OCH_2CH_2), 1.44 (p, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.30 (m, 8H), 0.86 ppm (t, 3H, CH_2CH_3); ^{13}C NMR (100 MHz, CDCl_3 , 25°C): δ = 169.9, 160.2, 130.6, 128.7 (q, $^2J(\text{C},\text{F})$ = 33.1 Hz), 126.6, 123.3 (q, $^1J(\text{C},\text{F})$ = 272.3 Hz), 117.0, 113.0 (q, $^3J(\text{C},\text{F})$ = 5.0 Hz), 68.6, 31.7, 29.2, 29.1, 29.0, 25.9, 22.6, 14.1 ppm; MS: m/z : 317.1628 (calcd: 317.1603); elemental analysis calcd (%) for $\text{C}_{16}\text{H}_{22}\text{F}_3\text{NO}_2$: C 60.56, H 6.99, F 17.96, N 4.41, O 10.08; found: C 60.67, H 7.32, N 4.94.

4-Decyloxy-2-trifluoromethylbenzamide (10FH2): Yield 79%; m.p. 105°C; ^1H NMR (400 MHz, CDCl_3 , 25°C): δ = 7.49 (d, 1H, ArH), 7.14 (s, 1H, ArH), 6.99 (d, 1H, ArH), 6.52 (s, 1H, NH of amide), 5.98 (s, 1H, other NH of amide), 3.97 (t, 2H, OCH_2), 1.77 (p, 2H, OCH_2CH_2), 1.43 (p, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.30 (m, 12H), 0.85 ppm (t, 3H, CH_2CH_3); ^{13}C NMR (400 MHz, CDCl_3 , 25°C): δ = 170.1, 160.2, 130.5, 128.6 (q, $^2J(\text{C},\text{F})$ = 32.3 Hz), 126.7, 123.3 (q, $^1J(\text{C},\text{F})$ = 272.0 Hz), 116.9, 112.9 (q, $^3J(\text{C},\text{F})$ = 6.0 Hz), 68.5, 31.8, 29.5–29.0 (m), 25.9, 22.6, 14.0 ppm; MS: m/z :

345.1908 (calcd: 345.1916); elemental analysis calcd (%) for $\text{C}_{18}\text{H}_{26}\text{F}_3\text{NO}_2$: C 62.59, H 7.59, F 16.50, N 4.06, O 9.26; found: C 63.08, H 8.04, N 4.58.

4-Dodecyloxy-2-trifluoromethylbenzamide (12FH2): Yield 85%; m.p. 103°C; ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$, 25°C): δ = 7.79 (s, 1H, NH of amide), 7.46 (d, 1H, ArH), 7.43 (s, 1H, other NH of amide), 7.21 (q, 1H, ArH), 7.18 (d, 1H, ArH), 4.04 (t, 2H, OCH_2), 1.69 (p, 2H, OCH_2CH_2), 1.23 (m, 18H), 0.84 ppm (t, 3H, CH_2CH_3); ^{13}C NMR (100 MHz, $[\text{D}_6]\text{DMSO}$, 25°C): δ = 168.8, 159.0, 130.3, 128.9, 128.0 (q, $^2J(\text{C},\text{F})$ = 19.7 Hz), 123.5 (q, $^1J(\text{C},\text{F})$ = 272.2 Hz), 117.0, 112.5 (q, $^3J(\text{C},\text{F})$ = 4.7 Hz), 68.1, 31.4, 29.2–28.5 (m), 25.5, 22.2, 13.8 ppm; MS: m/z : 373.2229 (calcd: 373.2229); elemental analysis calcd (%) for $\text{C}_{20}\text{H}_{30}\text{F}_3\text{NO}_2$: C 64.32, H 8.10, F 15.26, N 3.75, O 8.57; found: C 63.22, H 8.04, N 3.77.

Method II for the synthesis of 4-alkoxy-2-trifluoromethylbenzamides: 4-Alkoxy-2-trifluoromethylbenzonitrile (2.670 mmol) was dissolved in DMSO (10 mL). Potassium carbonate (0.6 g, 4.341 mmol) was added to the flask and aqueous H_2O_2 solution (35%, 2 mL) was dropped into the mixture. The reaction mixture was stirred at 60°C for 10 h and cooled to room temperature. Water (30 mL) was added to the mixture. The brown solid was collected by filtration and purified by flash chromatography on silica gel with ethyl acetate/hexane as eluent.

4-Tetradecyloxy-2-trifluoromethylbenzamide (14FH2): Yield 97%; m.p. 104°C; ^1H NMR (400 MHz, CDCl_3 , 25°C): δ = 7.54 (d, 1H, ArH), 7.17 (d, 1H, ArH), 7.03 (q, 1H, ArH), 5.88 (s, 1H, NH of amide), 5.79 (s, 1H, other NH of amide), 3.98 (t, 2H, OCH_2), 1.78 (p, 2H, OCH_2CH_2), 1.42 (p, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.30 (m, 20H), 0.86 ppm (t, 3H, CH_2CH_3); ^{13}C NMR (400 MHz, CDCl_3 , 25°C): δ = 169.6, 160.3, 130.7, 128.7 (q, $^2J(\text{C},\text{F})$ = 31.9 Hz), 126.6, 123.3 (q, $^1J(\text{C},\text{F})$ = 272.0 Hz), 117.1, 112.9 (q, $^3J(\text{C},\text{F})$ = 5.2 Hz), 68.6, 31.9, 29.6–29.0 (m), 25.9, 22.7, 14.1 ppm; MS: m/z : 401.2506 (calcd: 401.2542); elemental analysis calcd (%) for $\text{C}_{22}\text{H}_{34}\text{F}_3\text{NO}_2$: C 65.81, H 8.54, F 14.20, N 3.49, O 7.97; found: C 65.89, H 9.04, N 3.93.

4-Hexadecyloxy-2-trifluoromethylbenzamide (16FH2): Yield 81%; m.p. 105°C; ^1H NMR (400 MHz, CDCl_3 , 25°C): δ = 7.52 (d, 1H, ArH), 7.16 (d, 1H, ArH), 7.02 (q, 1H, ArH), 6.16 (s, 1H, NH of amide), 5.84 (s, 1H, other NH of amide), 3.98 (t, 2H, OCH_2), 1.78 (p, 2H, OCH_2CH_2), 1.43 (p, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.30 (m, 24H), 0.86 ppm (t, 3H, CH_2CH_3); ^{13}C NMR (400 MHz, CDCl_3 , 25°C): δ = 169.8, 160.2, 130.6, 128.8 (q, $^2J(\text{C},\text{F})$ = 31.3 Hz), 126.7, 123.3 (q, $^1J(\text{C},\text{F})$ = 273.6 Hz), 117.0, 113.0 (q, $^3J(\text{C},\text{F})$ = 5.5 Hz), 68.6, 31.9, 29.7–29.0 (m), 25.9, 22.7, 14.1 ppm; MS: m/z : 429.2917 (calcd: 429.2855); elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{38}\text{F}_3\text{NO}_2$: C 67.11, H 8.92, F 13.27, N 3.26, O 7.45; found: C 66.72, H 9.74, N 3.74.

4-Dodecyloxybenzonitrile (7): A procedure reported in the literature^[33] was adjusted as follows. 4-cyanophenol (0.361 g, 3.029 mmol) and 1-bromododecane (0.906 g, 3.635 mmol) were dissolved in acetone (20 mL). Potassium carbonate (2.344 g, 16.96 mmol) was added and the mixture was heated to reflux for 2 days with vigorous stirring. After cooling to room temperature, the mixture was filtered and the residue washed with acetone. The filtrate was concentrated in a rotary evaporator and redissolved in ethyl acetate. The solution was washed with water (2 × 20 mL) and brine (20 mL). Finally, the solution was dried on MgSO_4 and evaporated to yield the product (0.720 g, 83%). M.p. 40°C; ^1H NMR (400 MHz, CDCl_3 , 25°C): δ = 7.55 (d, 2H, ArH), 6.90 (d, 2H, ArH), 3.97 (t, 2H, OCH_2), 1.76 (p, 2H, OCH_2CH_2), 1.44 (p, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.24 (m, 18H), 0.86 ppm (t, 3H, CH_2CH_3); ^{13}C NMR (400 MHz, CDCl_3 , 25°C): δ = 162.5, 133.9, 121.9, 115.2, 103.6, 68.4, 31.9, 29.7–29.0 (m), 25.9, 22.7, 14.1 ppm; MS: m/z : 287.2241 (calcd: 287.2249); elemental analysis calcd (%) for $\text{C}_{19}\text{H}_{29}\text{NO}$: C 79.39, H 10.17, N 4.87, O 5.57. Found: C, 75.80; H, 9.97; N, 4.33.

4-Dodecyloxybenzamide (12HH2): A mixture of acetone (90 mL) and water (60 mL) was added to 4-dodecyloxybenzonitrile (0.915 g, 3.183 mmol) and sodium percarbonate (11.07 g, 70.50 mmol). The mixture was heated for 9 h at 50°C. The mixture was cooled to room temperature and acetone was removed on a rotary evaporator. Water (100 mL) was added and the solid was collected by filtration to yield crude product. Reprecipitation from ethanol/water gave the product (0.901 g, 93%). M.p. 143°C (Lit. 96–98°C^[34]); ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$, 25°C):

δ = 7.78 (dd, 2H, ArH), 7.76 (s, 1H, NH of amide), 7.10 (s, 1H, other NH of amide), 6.90 (dd, 2H, ArH), 3.96 (t, 2H, OCH₂), 1.67 (p, 2H, OCH₂CH₂), 1.36 (p, 2H, OCH₂CH₂CH₂), 1.20 (m, 18H), 0.81 ppm (t, 3H, CH₂CH₃); ¹³C NMR (100 MHz, [D₆]DMSO, 25°C): δ = 167.4, 161.0, 129.3, 126.3, 113.7, 67.6, 31.2, 30.0–28.5 (m), 25.4, 22.0, 13.9 ppm; MS: *m/z*: 305.2357 (calcd: 305.2355); elemental analysis calcd (%) for C₁₀H₃₁NO₂: C 74.71, H 10.23, N 4.59, O 10.48; found: C 71.79, H 9.46, N 4.43.

Preparation of pipes: The compound (0.2 g) and ethanol (1 mL) were put into a vial. The vial was closed and heated in a silicone oil bath at 96°C (for **12FH2**) or 101°C (for **14FH2**) until the whole compound dissolved. The vial was then removed from the bath and opened, and one drop of the hot solution was dropped onto a silicon wafer. Evaporation of ethanol in ambient atmosphere produced parallelogrammatic pipes on the wafer.

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