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Deconstruction as a Strategy for the Design of Libraries of Self-Assembling Dendrons**

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Dendrons and dendrimers are perfectly branched molecules prepared through convergent or divergent iterative synthesis.[1] Self-assembling dendrons[2] serve as building blocks for self-organizable complex architectures that mimic important biological structures. The study of these supramolecular assemblies has expanded the frontiers of nanoscience by interfacing chemistry, biology, and physics.

The current design of self-assembling dendron libraries involves a generational strategy in which first generation dendrons are sequentially added to constitutional isomeric AB$_n$ ($n \geq 2$) building blocks to produce higher-generation dendrons.[2,3a–d] The synthesis, structural, and retrostructural analysis of generational libraries of self-assembling dendrons,[3a–c,e] as well as of hybrid AB$_n$-(AB)$_y$ dendrons,[3d,f] enabled the discovery of diverse self-organizable supramolecular dendrimers.[4] Despite differences in building-block structure, homologous connective topologies of dendrons from different generational libraries provide a conserved and therefore predictable[3e] assembly of the supramolecular dendrimers that is programmed by their primary structure. This predictability leads to a "nanoperiodic" table[3e,5] of self-assembling dendrons, and enables the rational design of complex supramolecular systems. Unfortunately, the predictability reduces the likelihood of finding new supramolecular structures through the synthesis of additional generational libraries. The discovery of new supramolecular architectures from self-assembling dendrons requires the synthesis of dendritic structures that were not previously accessible through the strategies of generational[3a–c,e] or hybrid dendron libraries.[3d,f–g] Aside from the generational and combined generational hybrid strategies, no other rational method to the design of libraries required to access dendrons with novel primary structures is available.

Herein we report the deconstruction of self-assembling dendrons as a fundamentally different strategy for the design of new libraries of self-assembling dendrons. Starting from any self-assembling dendron or dendrimer, branches are systematically and sequentially removed to provide an array of novel deconstructed structures, which can be synthesized by the same iterative methods that provided the parent molecule. We demonstrate the deconstruction design strategy by using the (3,4BpPr-(3,4,5BpPr)^2)12G3-X[3e] (**6a**: X = CO$_2$CH$_3$, **6b**: X = CH$_2$OH) dendron as the parent compound (Figure 1). Detailed synthesis of all deconstructed dendrons and their structural and retrostructural analysis are given in the Supporting Information.

The design of a dendron library through the deconstruction of **6a,b** provides novel dendritic topologies that result in a variety of previously unencountered 3D phases (Figure 2). Deconstructed dendrons that provide routinely encountered structures are discussed in the Supporting Information.

The parent dendrons **6a,b** self-organize in $Pm\bar{3}n$ cubic phases (Cub, Figure 2). Deconstruction of **6a,b** by sequential removal of two (3,4BpPr-3,4,5BpPr)12G2 subunits from their periphery provides **7a,b** and **8a,b**. Compounds **7a,b** and **8a** form Cub phases. Compound **8b** self-assembles into spherical dendrimers that self-organize into a body-centered $Im\bar{3}m$ cubic lattice (body-centered cubic (BCC), Figure 2).[6] The BCC lattice is rarely encountered for self-organizing dendrons, though it has been observed for dendronized poly(oxazolines),[7] dendritic metal carboxylates,[6] and benzyl ether dendrons.[3a]

Removal of four (3,4BpPr)12G1 subunits from the periphery of **7a,b** results in novel AB$_2$-AB-AB$_2$ dendritic architectures, **15a,b**. At elevated temperatures, **15a** self-organizes in a vesicular Cub phase, observed previously for (4BpPr-3,4BpPr-3,5BpPr)12G2-CO$_2$CH$_3$.[3e] The supramolecular spheres assembled from **15a** by a mechanism similar to that previously reported[3e] are composed of 933 quasi-equivalent dendrons that have a molecular weight of 1.70 × 10^6 g mol^{-1} and a diameter of 171.9 Å. These two structures represent the largest monodisperse supramolecular objects self-assembled from dendrons reported to date and are comparable in size to the most complex biological structures such as the ribosome.[8]

The dendritic alcohol **15b** forms a hexagonal columnar Φ_h phase at low temperatures. At elevated temperatures, this

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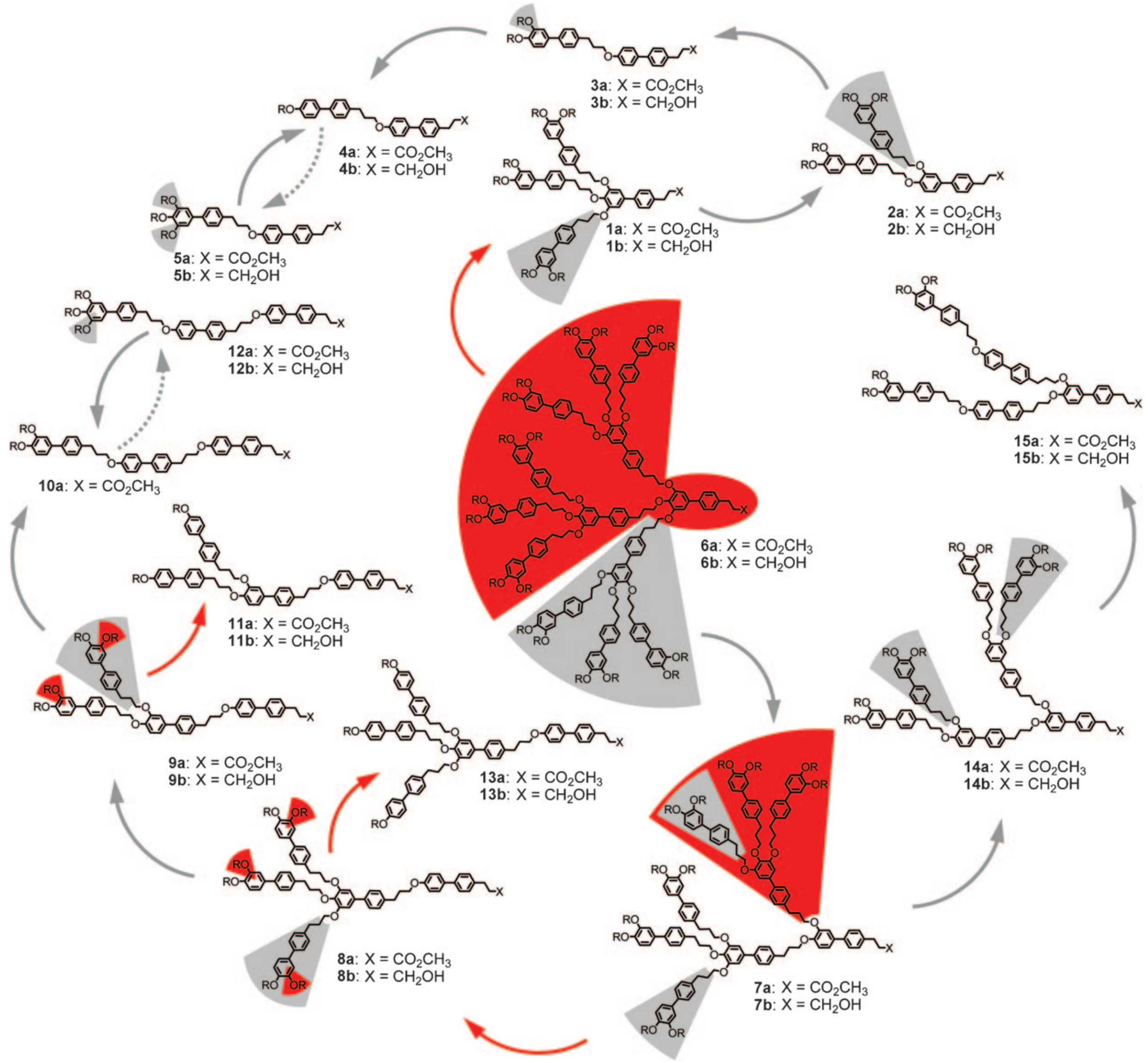

Figure 1. The deconstruction of **6a,b**. In each step of the deconstruction (solid arrows), the fragment highlighted by the wedge of the corresponding color (red or gray) is removed. Dotted arrows indicate construction.

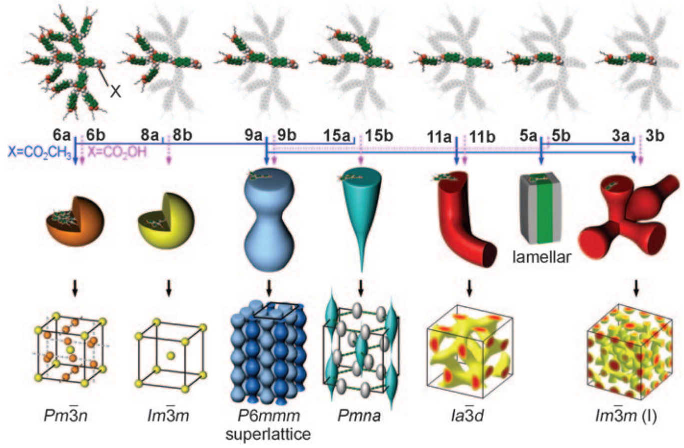

Figure 2. Novel structures from deconstructed dendritic esters (blue arrows) and alcohols (purple dotted arrows).

phase transforms into a new columnar simple orthorhombic $\Phi_{s\text{–}o}$ lattice with *Pmna* symmetry (Figure 3). The reconstructed electron densities suggest that the columns of the Φ_h phase produce shorter segments with comparable diameters upon the Φ_h–$\Phi_{s\text{–}o}$ transition (Figure 3 d).

Deconstruction of **8a,b** can also proceed via removal of (3,4BpPr)12G1 to provide **9a,b**. Oriented-fiber XRD of structures assembled from **9b** show a Φ_h phase at low temperatures and a hexagonal columnar superlattice $\Phi_h^{3D\text{-}SL}$ at high temperatures (Figure 4). $\Phi_h^{3D\text{-}SL}$ phases were observed only in the coassembly of twin-tapered dendritic benzamides with three[9a] and four[9b] cylindrical bundle dendronized polymers. The $\Phi_h^{3D\text{-}SL}$ phases of **5b** and **9a,b** are the first reported examples of these phases generated by self-assembly rather than coassembly. The wide-angle X-ray (WAXS) fiber patterns collected in the $\Phi_h^{3D\text{-}SL}$ of **5b** and of **9a,b** show only diffuse scattering that corresponds to alkyl chain–chain

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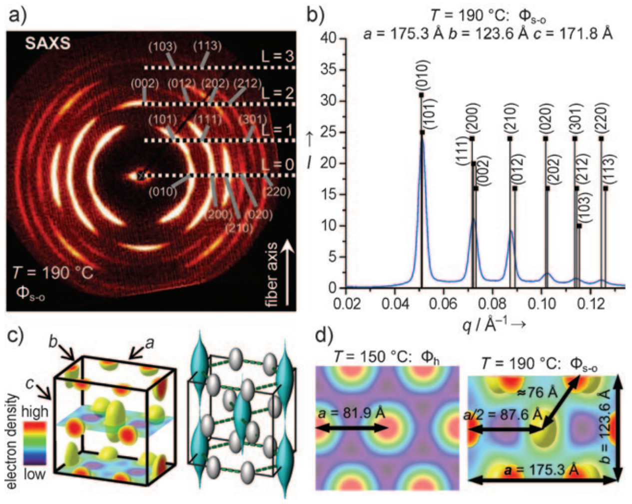

Figure 3. a) Oriented-fiber, b) powder XRD diffractograms, and c) reconstructed 3D electron density and model of the Φ_{s-o} phase with *Pmna* symmetry generated from **15b**. d) The 2D map of the $z=1/2$ plane is shown at scale with the corresponding map from the lower temperature Φ_h phase.

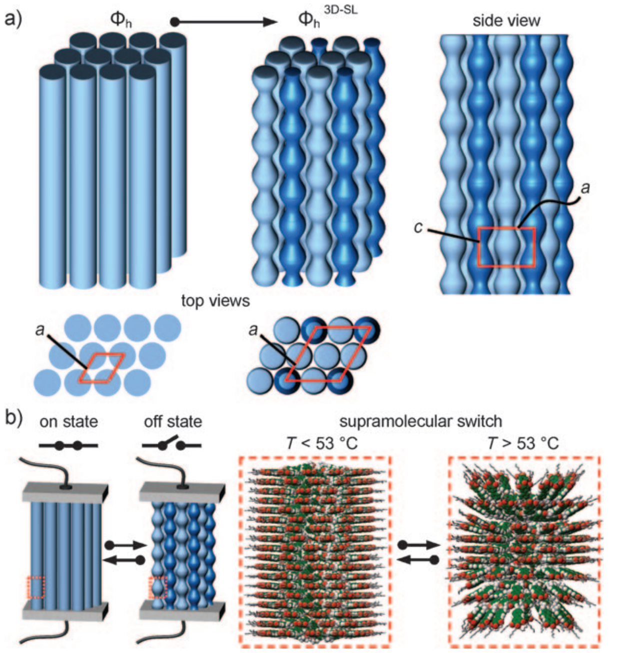

Figure 5. a) Model of the Φ_h–$\Phi_h^{3D\text{-}SL}$ transition and b) its potential role as a supramolecular switch.

correlations around 4.7 Å. This result demonstrates that the columns posses a soft, liquid-like alkyl jacket. Therefore, the presence of 3D column-to-column correlations at high temperatures can be explained only by significant variations of the column profiles. This hypothesis is supported by the relative electron density distributions (Figure 4). The 3D correlations are generated by the periodic coupling of "undulated" columns. This periodicity doubles the size of the low-temperature unit cell, hence generating the $\Phi_h^{3D\text{-}SL}$ phase (Figure 5a). The Φ_h–$\Phi_h^{3D\text{-}SL}$ transition of these assemblies can be utilized as a supramolecular switch for molecular electronics (Figure 5b).

Interestingly, above the $\Phi_h^{3D\text{-}SL}$ of **9a**, a triply continuous $Im\bar{3}m$(I) cubic phase (Cub_{tri}) is observed (Figure 2). This Cub_{tri} phase has been observed in a few phasmidic molecules,[10] but never before in self-assembling dendrons.

Deconstruction of **9** by the removal of (3,4BpPr)12G1 provided **10**. The analogous structures **12a,b** can be derived from the deconstruction of $(3,4,5BpPr)^3$12G3-X, or by addition of one $C_{12}H_{25}$ chain to **10**. At elevated temperatures, compounds **12a,b** self-organize into bicontinous $Ia\bar{3}d$ cubic phases (Cub_{bi}, Figure 6). The Cub_{bi} phase has also been observed for phasmidic molecules[10b] and dendrons with

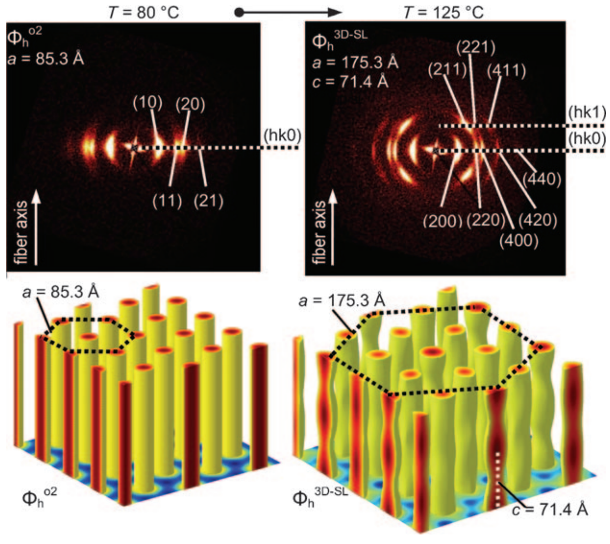

Figure 4. Oriented-fiber XRD and corresponding reconstructed relative electron density distributions of the Φ_h and $\Phi_h^{3D\text{-}SL}$ phases generated from **9b**.

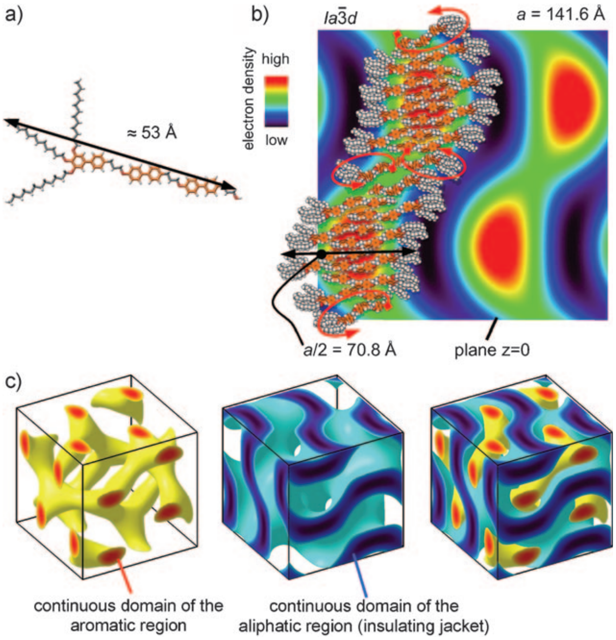

Figure 6. a) The molecular model of **12a**, b) 2D, and c) 3D reconstructed relative electron density distributions of the Cub_{bi} phase.

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semifluorinated periphery,[11] but has not been found in generational libraries of self-assembling dendrons[3a–c,e] or self-assembling hybrid dendrons.[3d,f] The $\mathrm{Cub}_{\mathrm{bi}}$ phase generated from **12a,b** can be approximated by interconnected distorted columnar segments with a diameter of approximately 70 Å (Figure 6). Reconstructed electron density distributions indicate a continuous aromatic domain surrounded by a continuous aliphatic insulating jacket (Figure 6b,c).

The deconstruction of self-assembling dendrons provides access to novel dendron primary structures, thereby overcoming the predictability of the generational approach.[3e] This library of deconstructed dendrons generated self-assembled structures that were not found in previous generational libraries; such structures include triple continuous and bicontinous cubic lattices, hexagonal columnar superlattices, and a novel columnar simple orthorhombic phase. The co-assembly of dendronized donors, dendronized acceptors, or donor and acceptor polymers provided access to self-repairing 2D electronic materials.[12] The approach to the triple continuous and bicontinuous structures discovered here may be used in the design of 3D electronic materials that do not require alignment in order to bridge the space between two electrodes.[13,14] The deconstruction strategy can be applied to any dendron and dendrimer primary structure, regardless of whether or not it has been previously synthesized, thus providing nearly limitless inspiration for new rationally designed structures.

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