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Complex Arrangement of Orthogonal Nanoscale Columns *via* a Supramolecular Orientational Memory Effect

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Abstract

Memory effects, including shape, chiral and liquid crystalline, have enabled macroscopic materials with novel functions. However, the generation of complex supramolecular nanosystems *via* memory effects has not yet been investigated. Here we report a cyclotrimeratrylene-crown (CTV) compound that self-assembles into supramolecular columns and spheres forming respectively hexagonal and cubic mesophases. Upon transition from one phase to the other an epitaxial relationship holds, *via* an unprecedented *supramolecular orientational memory* effect. Specifically, the molecular orientation and columnar character of supramolecular packing is preserved in the cubic phase, providing an otherwise inaccessible structure comprising orthogonally oriented domains of supramolecular columns. The continuous columnar character of tetrahedrally distorted supramolecular spheres self-organized from the CTV derivative in the faces of the $Pm\bar{3}n$ lattice is the basis of this *supramolecular orientational memory*, which holds throughout cycling in temperature between the two phases. This concept is expected to be general for other combinations of periodic and quasiperiodic arrays generated from supramolecular spheres upon transition to supramolecular columns.

Graphical abstract

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Supporting Information

Synthetic scheme, comparison of previous epitaxy relationships, additional electron density maps and histograms. This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

The authors declare no competing financial interests.

Keywords

memory effect; complex arrangement; orthogonal columns; supramolecular; self-assembly

Memory effects, in science and in society at large, allow “a past event [to be] inferred from a present state”.¹ Ölander discovered shape memory in AuCd alloys in 1932.² Since then shape memory has been observed in other alloys, in ceramics and in metals such as titanium.^{3–6} Recently memory effects have been transplanted from hard to soft materials. Shape-memory polymers,^{7–9} which adopt different macroscopic shapes in response to an external stimulus, have been designed for use as self-tying sutures¹⁰ and for other biomedical applications.¹¹ Chiral memory refers to the preservation of induced chirality after removal of a chiral inducer,^{12–14} whereas orientational memory in nematic liquid crystals¹⁵ has been employed to develop liquid crystal displays.^{16,17} Additional memory effects are expected to provide new complex architectures with novel functions and applications.

Libraries of self-assembling dendrons and dendrimers have been utilized to discover a variety of nanoscale periodic and quasiperiodic arrays self-organized from supramolecular spheres, including $Pm\bar{3}n$ cubic,^{18–20} $Im\bar{3}m$ body-centered cubic,²¹ $P4_2/mnm$ tetragonal²² and 12-fold liquid quasicrystalline (LQC).²³ These assemblies were recently generalized for self-organized soft condensed matter including block copolymers and surfactants^{24–30} and have been studied computationally.^{31–36} In this report the supramolecular columns generated from a self-assembling cyclotrimeratrylene-crown (CTV)^{37–39} were discovered to display an unprecedented *supramolecular orientational memory* effect at the transition between columnar hexagonal with intracolumnar order (Φ_h^{io} , $P6mm$) and cubic ($Pm\bar{3}n$) phases. A complex arrangement of orthogonal supramolecular columns, whose orientations are preserved from the cubic phase upon cooling to the columnar hexagonal phase, was observed. This new architecture cannot be constructed by any other methodology except the *supramolecular orientational memory* introduced here.

RESULTS AND DISCUSSION

Thermal, Structural and Retrostructural Analysis by Differential Scanning Calorimetry (DSC) and X-Ray Diffraction (XRD)

The (3,4,5)12G1-CTV dendrimer employed (Figure 1A) self-organizes into hexagonal and cubic phases.³⁷ This organization was enabled by the crown conformation of CTV (Figure 1A), which facilitates packing of the molecules into supramolecular columns and spheres. Thermal and structural analysis by differential scanning calorimetry (DSC) and X-ray

diffraction (XRD) on powder and oriented fibers revealed the formation of a columnar hexagonal crystal (Φ_h^k) below 18 °C which transforms into a 2D Φ_h^{io} ($P6mm$) array at 18 °C during first heating and to a cubic ($Pm\bar{3}n$) lattice above 69 °C (Figure 1B–E). Upon cooling at 1 °C/min, the cubic phase is observed below 56 °C, followed by Φ_h^{io} at 30 °C and Φ_h^k at –12 °C. Faster cooling requires annealing at 25 °C to replicate the phase behavior observed upon initial heating.

Orientational Relationship Observed in XRD Patterns of Oriented Fibers

XRD measurements were made on extruded fibers of (3,4,5)12G1-CTV assemblies (Figure 2). Extrusion of the fiber in Φ_h^{io} preferentially aligns the supramolecular columns along the fiber axis, which is the $(001)_{\text{hex}}$ direction (Figure 1B).³⁸ Unexpectedly an orientational relationship (Supporting Figure S1) was observed, first upon heating from the Φ_h^{io} to the cubic ($Pm\bar{3}n$) phase and subsequently upon cooling from the cubic to the Φ_h^{io} phase (compare Figure 2A, left and right panels). Such orientational relationships may also be termed “epitaxy” or “epitaxial relationships” to indicate the preservation of certain crystallographic directions upon the indicated phase transition.^{40–44}

During a first order transition between different phases, the new phase often grows from “seeds” within the previous phase, in which case there is no reason for any orientational relationship between the two phases

If such a relationship does exist, one would expect that it would either preserve local structural units or some symmetry feature of the two lattices. In the present case Φ_h^{io} consists of columns dominated by π – π interactions between aromatic units which are orthogonal to the column axes,³⁷ while the cubic ($Pm\bar{3}n$) phase comprises eight supramolecular spheres (Figure 1B and Supporting Figure S1).^{18,19} Columnar hexagonal phases have a single axis with six-fold rotational symmetry, while cubic $Pm\bar{3}n$ lattices have multiple four-fold axes of rotation, and four $(111)_{\text{cub}}$ axes with three-fold symmetry along the body diagonals of the cube (Figure 1B and Supporting Figure S1). One potential orientational relationship would preserve an axis of three-fold rotational symmetry, *via* alignment of one of the four $(111)_{\text{cub}}$ cubic axes (Supporting Figure S1) with the columnar $(001)_{\text{hex}}$ axis (Figure 1B and Supporting Figure S1). This particular orientational relationship has been observed in lipids^{40–42} and mixtures of block copolymers⁴³ forming a bicontinuous $Ia\bar{3}d$ cubic phase, and in lipids⁴⁴ and supramolecular dendrimers⁴⁵ forming a $Pm\bar{3}n$ cubic phase. However, no mechanism of this process has been proposed.

An alternative epitaxial relationship would preserve local structural units insofar as possible so that, upon transformation of the cubic phase to the hexagonal phase, adjacent tetrahedrally distorted supramolecular spheres along one of the three $(200)_{\text{cub}}$ directions merge to form columns aligned along the $(200)_{\text{cub}}$ direction. To our knowledge, this relationship has not been observed in any system to date. Small-angle X-ray scattering (SAXS) oriented fiber measurements (Figure 2A, C) demonstrate that this latter path is obtained in assemblies of (3,4,5)12G1-CTV. Upon heating, the original orientation of the column axis ($(001)_{\text{hex}}$) becomes the orientation of nearest-neighbor spheres in the cubic ($Pm\bar{3}n$) phase ($(200)_{\text{cub}}$), and upon cooling, supramolecular columns in the Φ_h^{io} phase orient in the direction defined by nearest-neighbor spheres at the face positions of the cubic unit

cell, that is, along the $(200)_{\text{cub}}$, $(020)_{\text{cub}}$ and $(002)_{\text{cub}}$ directions (Figure 1B). Hence the orientation of the nearest-neighbor spheres in the cubic phase can be inferred from the orthogonal orientation of the supramolecular columns of the $\Phi_{\text{h}}^{\text{io}}$ phase. This represents the first example of $(001)_{\text{hex}}$ to $(200)_{\text{cub}}$ epitaxy (Supporting Figure S1) in a structure organized from a single self-assembling building block.

Wide-angle X-ray scattering (WAXS) fiber and powder experiments (Figure 2B, D, E) provide additional information on the structures self-organized from **(3,4,5)12G1-CTV** in the $\Phi_{\text{h}}^{\text{io}}$ and cubic ($Pm\bar{3}n$) phases. A strong 3.9 Å feature associated with π - π stacking correlations between dendrons in $\Phi_{\text{h}}^{\text{io}}$ is observed both in the original oriented fiber and in a cycled fiber, which was heated to 80 °C and cooled to 25 °C four times (Figure 2B, E). Due to the three-dimensional orthogonal reorientation of the columns, in the cycled fiber the 3.9 Å π - π stacking features appear in the equatorial position, as well as in the meridional position. This supports the hypothesis that the supramolecular orientational memory of the hexagonal-to-cubic phase transition is mainly dictated by the strong core-core aromatic interactions which preserve local packing. Core stacking features at 4.9 Å and diffuse off-meridional helical features were identified in the XRD pattern of the original oriented fiber (Figure 2B). This stacking value was used to calculate a density of one molecule per 4.9 Å column stratum in the $\Phi_{\text{h}}^{\text{io}}$ array (Supporting Table ST1). Tilt features in the original oriented fiber and cycled fiber indicate that the alkyl chains of **(3,4,5)12G1-CTV** are tilted down from the molecular stratum by 26°, in agreement with the expected tilt value of the CTV (Figure 2B, D, F).^{37,39} These alkyl chains are melted in the high temperature cubic ($Pm\bar{3}n$) phase, as indicated by the presence of a broad peak at the 4.5 Å average alkyl chain correlation length (Figure 2E).

These structural results demonstrate that the cycled structure recovers the $\Phi_{\text{h}}^{\text{io}}$ phase, but oriented in multiple orthogonal directions. The $(001)_{\text{hex}}$ axis of the original $\Phi_{\text{h}}^{\text{io}}$ phase establishes one of three $(200)_{\text{cub}}$ directions such that the other $(200)_{\text{cub}}$ directions are orthogonally distributed randomly about that axis. Each $(200)_{\text{cub}}$ direction then establishes a $(001)_{\text{hex}}$ direction in the re-formed $\Phi_{\text{h}}^{\text{io}}$ phase to produce columnar hexagonal domains aligned along all of the former $(200)_{\text{cub}}$ directions. The cycled fiber orientation was investigated in both the $\Phi_{\text{h}}^{\text{io}}$ (fibers monitored at 23 °C over several months) and the $Pm\bar{3}n$ phase (fiber monitored for 3 h at 85 °C) and the preferred orthogonal orientation was found stable in time. The data reported in Figure 2 were repeated with different batches of fibers in which the cycling between phases was repeated six times. These fibers were re-measured three months later to confirm the stability of the preferred orientation.

Molecular Model of **(3,4,5)12G1-CTV**

The model for **(3,4,5)12G1-CTV** packing in columns based on SAXS and WAXS powder and oriented fiber data is shown in Figure 2F. Tilt features in oriented XRD patterns (Figure 2B, D) suggest an angle of 26°, consistent with the crown conformation of the CTV (Figure 2F). This intramolecular tilt facilitates stronger interaction between the outer aromatic regions of adjacent molecules (denoted by the 3.9 Å π - π stacking feature in Figure 2B, E) than between the relatively large CTV of adjacent molecules (denoted by the 4.9 Å separation feature in Figure 2B, E). The helical features at 14.8 Å (Figure 2B), taken with

the 4.9 Å separation distance, imply that there are three molecules per repeating unit of the helical column (Figure 2F). Due to the three-fold axis of rotational symmetry in **(3,4,5)12G1-CTV**, this suggests that molecules are rotated by 40° with respect to their neighbor in the column.

The Φ_h^{i0} phase comprises cofacially stacked **(3,4,5)12G1-CTV** which maximize aromatic π - π interactions, while the $Pm\bar{3}n$ phase contains eight supramolecular spheres whose assembly is driven by phase segregation of high electron density aromatic regions and low electron density melted aliphatic domains. This phase segregation is demonstrated by Figure 3A, B, which compares the reconstructed electron density map of the hexagonal Φ_h^{i0} phase with the volumetric representation of the electron density of the $Pm\bar{3}n$ phase based on the powder XRD data from Figure 1D (histograms in Supporting Figure S5).

Mechanism of Supramolecular Orientational Memory and Structure of Supramolecular Spheres

The mechanism of the cubic-hexagonal supramolecular orientational memory can be understood by examining the structure of the two phases (Figure 4). The tetrahedrally distorted spheres from the faces of the $Pm\bar{3}n$ lattice^{18,20} exhibit columnar character along the three $(200)_{\text{cub}}$ directions,^{18–20} (see orange, red, and blue in Figure 4B). These tetrahedrally distorted spheres^{18,20} form pseudohexagonal structures deformed by less than 6% from true hexagonal symmetry (Figure 3A, B). If the path for the orientational memory had been $(001)_{\text{hex}}$ to $(111)_{\text{cub}}$, as will be reported for other cases, rather than $(001)_{\text{hex}}$ to $(200)_{\text{cub}}$ as reported here (Figure 1B and Supporting Figure S1), face spheres (Figure 4A, yellow) would require a large translation to integrate into the hexagonal columns. This process would involve substantial disruption to the strong aromatic core interactions. Instead, the tetrahedrally distorted face spheres merge along the $(200)_{\text{cub}}$ direction dictated by their continuous columnar character into supramolecular columns (Figure 4C, path A), which shift slightly to form hexagonal symmetry (Figure 4B). In the reverse process, formation of the corner spheres requires only a short translation, while formation of the face spheres requires local reorientations of the molecules but almost no translation of the columns since the lattice parameter of the cubic phase is almost double that of the hexagonal phase (Figure 3A, B).

A simplified way to envision the mechanism of the supramolecular orientational memory effect is to introduce conceptually a non-covalently bonded supramolecular unit containing multiple molecules. The helical features (Figure 2B) demonstrated that the intrinsic 3-fold symmetry of the **(3,4,5)12G1-CTV** unit generated a long range 3_1 -helical columnar packing (Figure 2F). It is probable that the high order rotational symmetry of **(3,4,5)12G1-CTV** coupled with the observed tilt (Figure 2B, F) can generate a supramolecular unit of n dendrimers. The interior of this n -dendrimer unit comprises an interlocked aromatic core defined by the strongly interacting CTV which dictates the well-defined preferential orientational axis of the n -molecule unit at all temperatures (Figure 3E), while the exterior of the n -molecule unit is a “softer” spherical (at high temperature) or “harder” cylindrical (at low temperature) with outer shell formed by alkyl chains. This n -dendrimer unit acts as a single structural entity upon cycling between the two phases: the tetrahedrally distorted

spheres re-couple into columns at low temperatures and separate back into spheres at high temperatures, while retaining their specific preferred direction at any temperature below the isotropization temperature.

Figure 3D, E depicts two models for the formation of supramolecular spheres with columnar character from the supramolecular columns of **(3,4,5)12G1-CTV**. The supramolecular orientational memory observed by XRD (Figure 2) indicates that molecules are distributed into supramolecular spheres in the cubic phase. The experimental density ($\rho = 0.96 \text{ g/cm}^3$ at 20 °C; Supporting Table ST1) and lattice parameters of the $Pm\bar{3}n$ cubic phase (Figure 2) indicate that there are, on average, 6 dendrimers per supramolecular sphere. This is consistent with three packing models for the aromatic CTV, as shown in Figure 3E. The lattice parameter of the cubic phase ($a = 72 \text{ Å}$) represents 15–16 molecules within a column of the Φ_h^{i0} phase divided into two distorted spherical units (Figure 3D, E). A possible saddle conformation,^{39,46} rather than a crown conformation, for the CTV of the middle dendrimer of the spheres in Figure 3E (center) cannot be excluded. However, the saddle conformation has been demonstrated to be a transient metastable conformation and is therefore unlikely to persist in the supramolecular assemblies.^{39,46}

The orientational memory observed in the hexagonal phase on cooling relies on the continuous columnar character of the tetrahedrally distorted spheres from the faces of the cubic phase (Figure 3E and 4C). During the transition from the $Pm\bar{3}n$ to the Φ_h^{i0} phase, each of the three $(200)_{\text{cub}}$ directions in a given domain is inherited as a $(001)_{\text{hex}}$ columnar direction, so that new columnar orientations are established perpendicular to the original direction (Figure 4B). The orientation of the face spheres inherited from the Φ_h^{i0} phase (blue in Figure 4B, C) induces orthogonal reorientation in the other two directions (red and orange in Figure 4C). The mechanism *via* which center and corner spheres are integrated into the supramolecular columns is not yet elucidated. Information about the cubic axes can be inferred from the orientation of supramolecular columns in the hexagonal phase, and hence we term this new memory effect, *supramolecular orientational memory*.

Visualizing Supramolecular Reorientation by Polarized Birefringence Microscopy

To determine whether the orthogonal reorientation is a local process on the unit cell scale (Figure 4C, path B) or a larger scale process (Figure 4C, path A), birefringence microscopy experiments were performed (Figure 5A). A thin film in which the supramolecular columns of the hexagonal phase were oriented in the plane of the film (Figure 5A), was heated to 71 °C where it was held for 1 h (Figure 5B). It was then heated at 1 °C/min to 75 °C and held for 5 min. After cooling at 0.4 °C/min to 26 °C and reheating at 2 °C/min to 60 °C the birefringence was measured. A bimodal orientation with two peaks of comparable intensity separated by 90° orientation was observed (Figure 5D, E). The lack of intermediate orientations is apparent from the dearth of green shades in the orientation maps (Figure 5F, G). One prominent orientation was parallel to the original orientation ($\phi \sim 149^\circ$) and the other perpendicular ($\phi \sim 59^\circ$), consistent with a reversible epitaxial relationship between the cubic and columnar phases. The two in-plane columnar orientations arising from epitaxy from the cubic phase are well mixed (Figure 5F), with the proportion of one or the other in a particular neighborhood having some randomness (Figure 5G). The structure coarsens with

annealing, while regions of one orientation swallow the other. This behavior signals that columnar orientation, by epitaxy from the cubic, is a local statistically random process, supporting strongly the concept of shared supramolecular arrangement between the cubic and hexagonal phases.

CONCLUSIONS

We have demonstrated that supramolecular spheres self-assembled from (3,4,5)12G1-CTV-crown self-organize into Φ_h^{i0} ($P6mm$) and cubic ($Pm\bar{3}n$) phases with preferred orientation. The orientational preference of the supramolecular spheres in an aligned Φ_h^{i0} is preserved upon heating to $Pm\bar{3}n$ and again upon cooling to Φ_h^{i0} , generating a complex architecture featuring orthogonally-oriented columnar hexagonal microdomains which cannot be generated through any other mechanism known to us. The only mechanism that explains both the direction and the reversibility of this memory effect invokes the formation of supramolecular tetrahedrally distorted spheres with a preferred orientation. This orientational relationship is introduced here as the concept of *supramolecular orientational memory*.

The supramolecular structural units of materials with *supramolecular orientational memory* remember their orientations during phase transitions

In the present system, we observe a $(001)_{\text{hex}}$ to $(200)_{\text{cub}}$ *supramolecular orientational memory* effect in the assemblies of (3,4,5)12G1-CTV. The strong interactions between CTV molecules are preserved by a $(001)_{\text{hex}}$ to $(200)_{\text{cub}}$ epitaxial relationship and provide a driving force for $(001)_{\text{hex}}$ to $(200)_{\text{cub}}$ memory rather than the $(001)_{\text{hex}}$ to $(111)_{\text{cub}}$ relationship to be reported soon and also observed in biphasic mixtures.^{40–44} This concept is expected to be elaborated for further $Pm\bar{3}n$ cubic known also as Frank-Kasper A15 structures⁴⁷ and will be reported soon in other 3D phases generated from spheres, such as $Im\bar{3}m$ BCC cubic,³⁰ $P4_2/mnm$ tetragonal,^{24,29} and LQC^{26,28} at their transition to various columnar phases. It is also expected that this concept will be transplanted from self-assembling dendrimers to block copolymers,^{24,26,28,29} surfactants,²⁵ and other soft matter^{27,28} displaying this combination of phases. Therefore, *supramolecular orientational memory* is expected to become a general concept for the creation of otherwise inaccessible complex supramolecular architectures with as yet unknown functions. Novel functions derived from these new complex arrangements of orthogonal columns *via* the supramolecular orientational memory effect reported here are under investigation and will be reported soon.

METHODS

Synthesis of (3,4,5)12G1-CTV

(3,4,5)12G1-CTV³⁷ was synthesized from (3,4,5)12G1-CH₂OH^{48–50} according to previously reported procedures (Supporting Scheme SS1). The purity and the structure identity of the intermediary and final products were assessed by a combination of techniques that includes thin-layer chromatography, high pressure liquid chromatography, ¹H and ¹³C NMR, and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry.

Differential Scanning Calorimetry (DSC)

Thermal transitions were measured on TA instrument 2920 modulated, and Q100 differential scanning calorimeter (DSC) integrated with a refrigerated cooling system (RCS). Heating and cooling rates are indicated in Figure 1C. The transition temperatures were measured as the maxima, and minima of their endothermic, and exothermic peaks. Indium was used as the standard for the calibration.

Density Measurements

For density measurements, a small mass of sample (~0.4 mg) was placed in a vial filled with water followed by ultrasonication to remove the air bubbles embedded within the sample. The sample sank to the bottom of the vial due to its high density compared with water. A saturated aqueous solution of potassium iodide (KI) was then added into the solution at ~0.1 g per aliquot to gradually increase the solution density. KI was added at an interval of at least 20 min to ensure equilibrium within the solution. When the sample was suspended in the middle of the solution, the density of the sample was identical to that of the solution, which was measured by a 10 mL volumetric flask.

X-ray Diffraction (XRD)

X-ray diffraction (XRD) measurements were performed using Cu-K α_1 radiation ($\lambda = 1.542$ Å) from a Bruker-Nonius FR-591 rotating anode X-ray source equipped with a 0.2×0.2 mm² filament, and operated at 3.4 kW. Osmic Max-Flux optics, and triple pinhole collimation were used to obtain a highly collimated beam with a 0.3×0.3 mm² spot on a Bruker-AXS Hi-Star multiwire area detector. To minimize attenuation, and background scattering, an integral vacuum was maintained along the length of the flight tube, and within the sample chamber. Samples were held in glass capillaries (1.0 mm in diameter), mounted in a temperature-controlled oven (temperature precision: ± 0.1 °C, temperature range from -10 °C to 210 °C). Aligned samples for fiber XRD experiments were prepared using a custom made extrusion device.⁵¹ The powdered sample (~10 mg) was heated inside the extrusion device. After slow cooling, the fiber was extruded in the liquid crystal phase, and cooled to 23 °C. Typically, the aligned samples had a thickness of 0.3 – 0.7 mm, and a length of 3 – 7 mm. All XRD measurements were done with the aligned sample axis perpendicular to the beam direction. Primary XRD analysis was performed using Datasqueeze (version 3.0.5).⁵²

Molecular Modeling and Simulation

Structural and retrostructural analysis^{53,54} was performed *via* molecular modeling and simulation experiments as reported previously.^{18,39,55,56} XRD patterns were measured of oriented fiber and powder samples. Diffraction features and lattice parameters obtained using Datasqueeze (version 3.0.5)⁵² were used with helical diffraction theory⁵⁵ to generate initial molecular and supramolecular models, using Accelrys Materials Studio (versions 3.1 and 5.0). Geometry optimization was performed using the VAMP module. The XRD pattern expected from this model was simulated using Accelrys Cerius². The simulated and experimental XRD patterns were compared and the supramolecular model refined.³⁹ Electron density maps reconstructed from XRD were also used to assess the validity of the

proposed supramolecular model (Supporting Figure S3).^{18,56} This process of XRD simulation and model refinement was repeated iteratively until the level of agreement between simulated and experimental XRD patterns was agreeable.

Polarized Light Microscopy and Birefringence Measurements

Birefringence measurements were performed with a Metripol birefringence microscope (Oxford Cryosystems), which is based on the Wood and Glazer method.⁵⁷ Monochromatic light ($\lambda = 550$ nm) is sent through a rotating polarizer into the sample, then through a quarter wave plate and an analyzer into a CCD camera (10 bit Firewire; Scion CFW-1310M high-resolution; 1360×1024 pixels), which measures the light intensity I . Other measured quantities are the phase difference, θ , between two orthogonally polarized components and the orientation angle, ϕ of the sample's principal axis. I , θ and ϕ are inter-related:

$$I = \frac{1}{2} I_o [1 + \sin \{2(\omega_{pol} \tau_m - \varphi)\} \sin \theta]$$

I_o is the transmittance, while ω_{pol} and τ_m denote the polarizer's rotational frequency and the measurement time, respectively. A map of the orientation angle ϕ is shown in Figure 5. Checks and calibrations performed on the system included alignment and light intensity uniformity check, assessment of optical path polarization state without the sample, and assessment of the camera's dark noise and linear response from 0% to 80% of its dynamic range. A 40 $\times$ objective lens (NA = 0.65; magnification = 0.116 μm / pixel) was used.

A few small grains of **(3,4,5)12G1-CTV** were sheared between two microscope coverslips held at approximately 49 °C. Shearing the material thus in the Φ_h^{i0} phase produced a high degree of alignment of the columns parallel to the shearing direction. Shearing was continued until the slides easily separated, leaving highly aligned films on each surface (Figure 5A, C). One slide was removed and the remaining slide was observed during heat treatment. After holding the sample momentarily at 49 °C, it was then first heated to 71 °C and the birefringence was monitored. At this temperature, the cubic phase is stable and the birefringence associated with the columnar phase decayed over a period of several minutes (Figure 5B). The sample was then heated to 75 °C. and subsequently cooled from 75 °C at 0.4 °C/min to 26 °C and then heated at 2 °C/min to 60 °C and held at that temperature for 2 h. As birefringence returned, the orientation distribution became bimodal (Figure 5D, E), exhibiting two mutually orthogonal column orientations, one being parallel to the original direction.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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REFERENCES

1. Shigeno M, Kushida Y, Yamaguchi M. Molecular Switching Involving Metastable States: Molecular Thermal Hysteresis and Sensing of Environmental Changes by Chiral Helicene Oligomeric Foldamers. *Chem. Commun.* 2016; 52:4955–4970.
2. Ölander A. An Electrochemical Investigation of Solid Cadmium-Gold Alloys. *J. Am. Chem. Soc.* 1932; 54:3819–3833.
3. Schurch KE, Ashbee KHG. A Near Perfect Shape-Memory Ceramic Material. *Nature.* 1977; 266:706–707.
4. Swain MV. Shape Memory Behaviour in Partially Stabilized Zirconia Ceramics. *Nature.* 1986; 322:234–236.
5. Wenk HR, Kaercher P, Kanitpanyacharoen W, Zepeda-Alarcon E, Wang Y. Orientation Relations during the α - ω Phase Transition of Zirconium: *In Situ* Texture Observations at High Pressure and Temperature. *Phys. Rev Lett.* 2013; 111:1–5.
6. Lai A, Du Z, Gan CL, Schuh CA. Shape Memory and Superelastic Ceramics at Small Scales. *Science.* 2013; 341:1505–1508. [PubMed: 24072920]
7. Lendlein A, Jiang H, Junger O, Langer R. Light-Induced Shape-Memory Polymers. *Nature.* 2005; 434:879–882. [PubMed: 15829960]
8. Xie T. Tunable Polymer Multi-Shape Memory Effect. *Nature.* 2010; 464:267–270. [PubMed: 20220846]
9. Shah AA, Schultz B, Zhang W, Glotzer SC, Solomon MJ. Actuation of Shape-Memory Colloidal Fibres of Janus Ellipsoids. *Nat. Mater.* 2014; 14:117–124. [PubMed: 25384169]
10. Lendlein A, Langer R. Biodegradable, Elastic Shape-Memory Polymers for Potential Biomedical Applications. *Science.* 2002; 296:1673–1676. [PubMed: 11976407]
11. Sokolowski W, Metcalfe A, Hayashi S, Yahia L, Raymond J. Medical Applications of Shape Memory Polymers. *Biomed. Mater.* 2007; 2:S23–S27. [PubMed: 18458416]
12. Furusho Y, Kimura T, Mizuno Y, Aida T. Chirality-Memory Molecule: A D_2 -Symmetric Fully Substituted Porphyrin as a Conceptually New Chirality Sensor. *J. Am. Chem. Soc.* 1997; 119:5267–5268.
13. Yashima E, Maeda K, Okamoto Y. Memory of Macromolecular Helicity Assisted by Interaction with Achiral Small Molecules. *Nature.* 1999; 399:449–451.
14. Helmich F, Smulders MMJ, Lee CC, Schenning APHJ, Meijer EW. Effect of Stereogenic Centers on the Self-Sorting, Depolymerization, and Atropisomerization Kinetics of Porphyrin-Based Aggregates. *J. Am. Chem. Soc.* 2011; 133:12238–12246. [PubMed: 21714481]
15. Dozov I, Nobili M, Durand G. Fast Bistable Nematic Display Using Monostable Surface Switching. *Appl. Phys. Lett.* 1997; 70:1179–1181.
16. Araki T, Buscaglia M, Bellini T, Tanaka H. Memory and Topological Frustration in Nematic Liquid Crystals Confined in Porous Materials. *Nat. Mater.* 2011; 10:303–309. [PubMed: 21423186]
17. Serra F, Buscaglia M, Bellini T. The Emergence of Memory in Liquid Crystals. *Mater. Today.* 2011; 14:488–494.
18. Balagurusamy VSK, Ungar G, Percec V, Johansson G. Rational Design of the First Spherical Supramolecular Dendrimers Self-Organized in a Novel Thermotropic Cubic Liquid-Crystalline Phase and the Determination of Their Shape by X-Ray Analysis. *J. Am. Chem. Soc.* 1997; 119:1539–1555.
19. Hudson SD, Jung H-T, Percec V, Cho W-D, Johansson G, Ungar G, Balagurusamy VSK. Direct Visualization of Individual Cylindrical and Spherical Supramolecular Dendrimers. *Science.* 1997; 278:449–452.
20. Dukeson DR, Ungar G, Balagurusamy VSK, Percec V, Johansson GA, Glodde M. Application of Isomorphous Replacement in the Structure Determination of a Cubic Liquid Crystal Phase and Location of Counterions. *J. Am. Chem. Soc.* 2003; 125:15974–15980. [PubMed: 14677989]

21. Yeardley DJP, Ungar G, Percec V, Holerca MN, Johansson G. Spherical Supramolecular Minidendrimers Self-Organized in an “Inverse Micellar”-Like Thermotropic Body-Centered Cubic Liquid Crystalline Phase. *J. Am. Chem. Soc.* 2000; 122:1684–1689.
22. Ungar G, Liu Y, Zeng X, Percec V, Cho W-D. Giant Supramolecular Liquid Crystal Lattice. *Science*. 2003; 299:1208–1211. [PubMed: 12595686]
23. Zeng X, Ungar G, Liu Y, Percec V, Dulcey AE, Hobbs JK. Supramolecular Dendritic Liquid Quasicrystals. *Nature*. 2004; 428:157–160. [PubMed: 15014524]
24. Lee S, Bluemle MJ, Bates FS. Discovery of a Frank-Kasper σ -Phase in Sphere-Forming Block Copolymer Melts. *Science*. 2010; 330:349–353. [PubMed: 20947759]
25. Perroni DV, Mahanthappa MK. Inverse $Pm\bar{3}n$ Cubic Micellar Lyotropic Phases from Zwitterionic Triazolium Gemini Surfactants. *Soft Matter*. 2013; 9:7919–7922.
26. Lee S, Leighton C, Bates FS. Sphericity and Symmetry Breaking in the Formation of Frank-Kasper Phases from One Component Materials. *Proc. Natl. Acad. Sci. U. S. A.* 2014; 111:17723–17731. [PubMed: 25378703]
27. Huang M, Hsu C-H, Wang J, Mei S, Dong X, Li Y, Li M, Liu H, Zhang W, Aida T, Zhang W-B, Yue K, Cheng SZD. Selective Assemblies of Giant Tetrahedra *via* Precisely Controlled Positional Interactions. *Science*. 2015; 348:424–428. [PubMed: 25908818]
28. Gillard TM, Lee S, Bates FS. Dodecagonal Quasicrystalline Order in a Diblock Copolymer Melt. *Proc. Natl. Acad. Sci. U. S. A.* 2016; 113:5167–5172.
29. Chanpuriya S, Kim K, Zhang J, Lee S, Arora A, Dorfman KD, Delaney KT, Fredrickson GH, Bates FS. Cornucopia of Nanoscale Ordered Phases in Sphere-Forming Tetrablock Terpolymers. *ACS Nano*. 2016; 10:4961–4972. [PubMed: 27055118]
30. Zhang W, Huang M, Su H, Zhang S, Yue K, Dong X-H, Li X, Liu H, Zhang S, Wesdemiotis C, Lotz B, Zhang W-B, Li Y, Cheng SZD. Toward Controlled Hierarchical Heterogeneities in Giant Molecules with Precisely Arranged Nano Building Blocks. *ACS Cent. Sci.* 2016; 2:48–54. [PubMed: 27163025]
31. Zihl P, Kamien RD. Maximizing Entropy by Minimizing Area: Towards a New Principle of Self-Organization. *J. Phys. Chem. B*. 2001; 105:10147–10158.
32. Li Y, Lin S-T, Goddard WA III. Efficiency of Various Lattice from Hard Ball to Soft Ball; Theoretical Study of Thermodynamic Properties of Dendrimer Liquid Crystal from Atomistic Simulation. *J. Am. Chem. Soc.* 2004; 126:1872–1885. [PubMed: 14871120]
33. Lifshitz R, Diamant H. Soft Quasicrystals – Why are They Stable? *Philos. Mag.* 2007; 87:3021–3030.
34. Barkan K, Diamant H, Lifshitz R. Stability of Quasicrystals Composed of Soft Isotropic Particles. *Phys. Rev. B*. 2001; 83:172201.
35. Iacovella CR, Keys AS, Glotzer SC. Self-Assembly of Soft-Matter Quasicrystals and their Approximants. *Proc. Natl. Acad. Sci. U. S. A.* 2011; 108:20935–20940. [PubMed: 22160672]
36. Engle M, Damasceno PF, Phillips CL, Glotzer SC. Computational Self-Assembly of a One-Component Icosahedral Quasicrystal. *Nat. Mater.* 2015; 14:109–116. [PubMed: 25485986]
37. Percec V, Imam MR, Peterca M, Wilson DA, Heiney PA. Self-Assembly of Dendritic Crowns into Chiral Supramolecular Spheres. *J. Am. Chem. Soc.* 2009; 131:1294–1304. [PubMed: 19115859]
38. Percec V, Imam MR, Peterca M, Wilson DA, Graf R, Spiess HW, Balagurusamy VSK, Heiney PA. Self-Assembly of Dendronized Triphenylenes into Helical Pyramidal Columns and Chiral Spheres. *J. Am. Chem. Soc.* 2009; 131:7662–7677. [PubMed: 19309145]
39. Roche C, Sun H-J, Prendergast ME, Leowanawat P, Partridge BE, Heiney PA, Araoka F, Graf R, Spiess HW, Zeng X, Ungar G, Percec V. Homochiral Columns Constructed by Chiral Self-Sorting During Supramolecular Helical Organization of Hat-Shaped Molecules. *J. Am. Chem. Soc.* 2014; 136:7169–7185. [PubMed: 24758745]
40. Rancon Y, Charvolin J. Epitaxial Relationships during Phase Transformations in a Lyotropic Liquid Crystal. *J. Phys. Chem.* 1988; 92:2646–2651.
41. Clerc M, Levelut AM, Sadoc JF. Transitions between Mesophases Involving Cubic Phases in the Surfactant-Water Systems. Epitaxial Relations and Their Consequences in a Geometrical Framework. *J. Phys. II Fr.* 1991; 1:1263–1276.

42. Sakya P, Seddon JM, Templer RH, Mirkin RJ, Tiddy GJT. Micellar Cubic Phases and Their Structural Relationships: The Nonionic Surfactant System C₁₂EO₁₂/Water. *Langmuir*. 1997; 13:3706–3714.
43. Koppi KA, Tirrell M, Bates FS, Almdal K, Mortensen K. Epitaxial Growth and Shearing of the Body Centered Cubic Phase in Diblock Copolymer Melts. *J. Rheol.* 1994; 38:999–1027.
44. Mariani P, Amaral LQ, Saturni L, Delacroix H. Hexagonal-Cubic Phase Transitions in Lipid Containing Systems: Epitaxial Relationships and Cylinder Growth. *J. Phys. II*. 1994; 4:1393–1416.
45. Peterca M, Imam MR, Leowanawat P, Rosen BM, Wilson DA, Wilson CJ, Zeng X, Ungar G, Heiney PA, Percec V. Self-Assembly of Hybrid Dendrons into Doubly Segregated Supramolecular Polyhedral Columns and Vesicles. *J. Am. Chem. Soc.* 2010; 132:11288–11305. [PubMed: 20698696]
46. Zimmermann H, Tolstoy P, Limbach HH, Poupko R, Luz Z. The Saddle Form of Cyclotrimeratrylene. *J. Phys. Chem. B*. 2004; 108:18772–18778.
47. Klein ML, Levesque D, Weis J-J. Molecular-Dynamics Study of Solid γ -O₂. *Phys. Rev. B*. 1980; 21:5785–5792.
48. Percec V, Cho W-D, Mosier PE, Ungar G, Yeardley DJP. Structural Analysis of Cylindrical and Spherical Supramolecular Dendrimers Quantifies the Concept of Monodendron Shape Control by Generation Number. *J. Am. Chem. Soc.* 1998; 120:11061–11070.
49. Percec V, Cho WD, Ungar G. Increasing the Diameter of Cylindrical and Spherical Supramolecular Dendrimers by Decreasing the Solid Angle of Their Monodendrons *via* Periphery Functionalization. *J. Am. Chem. Soc.* 2000; 122:10273–10281.
50. Percec V, Cho W-D, Ungar G, Yeardley DJP. From Molecular Flat Tapers, Discs, and Cones to Supramolecular Cylinders and Spheres Using Fréchet-Type Monodendrons Modified on Their Periphery. *Angew. Chem. Int. Ed.* 2000; 39:1597–1602.
51. Percec V, Sun H-J, Leowanawat P, Peterca M, Graf R, Spiess HW, Zeng X, Ungar G, Heiney PA. Transformation from Kinetically into Thermodynamically Controlled Self-Organization of Complex Helical Columns with 3D Periodicity Assembled from Dendronized Perylene Bisimides. *J. Am. Chem. Soc.* 2013; 135:4129–4148. [PubMed: 23406582]
52. Heiney PA. Datasqueeze: A Software Tool for Powder and Small-Angle X-Ray Diffraction Analysis. *Commission on Powder Diffraction Newsletter*. 2005; 32:9–11.
53. Rosen BM, Wilson CJ, Wilson DA, Peterca M, Imam MR, Percec V. Dendron-Mediated Self-Assembly, Disassembly, and Self-Organization of Complex Systems. *Chem. Rev.* 2009; 109:6275–6540. [PubMed: 19877614]
54. Sun H-J, Zhang S, Percec V. From Structure to Function *via* Complex Supramolecular Dendrimer Systems. *Chem. Soc. Rev.* 2015; 44:3900–3923. [PubMed: 25325787]
55. Peterca M, Percec V, Imam MR, Leowanawat P, Morimitsu K, Heiney PA. Molecular Structure of Helical Supramolecular Dendrimers. *J. Am. Chem. Soc.* 2008; 130:14840–14852. [PubMed: 18841962]
56. Wu Y-C, Leowanawat P, Sun H-J, Partridge BE, Peterca M, Graf R, Spiess HW, Zeng X, Ungar G, Hsu C-S, Heiney PA, Percec V. Complex Columnar Hexagonal Polymorphism in Supramolecular Assemblies of a Semifluorinated Electron-Accepting Naphthalene Bisimide. *J. Am. Chem. Soc.* 2015; 137:807–819. [PubMed: 25549011]
57. Wood IG, Glazer AM. Ferroelastic Phase Transition in BiVO₄. I. Birefringence Measurements Using the Rotating-Analyser Method. *J. Appl. Crystallogr.* 1980; 13:217–223.

Figure 1.

(A) Molecular structure of (3,4,5)12G1-CTV. (B) Schematic representation of columnar hexagonal with intracolumnar order, Φ_h^{io} ($P6mm$) and cubic ($Pm\bar{3}n$) periodic arrays. In the cubic unit cell, flattened disk-like units represent tetrahedrally distorted supramolecular spheres. (C) DSC traces of (top) first heating and cooling at 10 °C/min and (bottom) heating at 5 °C/min after annealing at 25 °C for 28 days. (D) Small angle powder XRD plots measured at indicated temperature and phase. (E) Selected wide angle XRD plots of the (top) cubic ($Pm\bar{3}n$) and (bottom) Φ_h^{io} ($P6mm$) phases. Vertical lines indicate calculated diffraction peak positions.

Figure 2.

(A) SAXS and (B) WAXS patterns of (3,4,5)12G1-CTV. (C) and (D) Azimuthal plots of the patterns in (A) at q_{10} and q_{200} , and (B) at $q = 1.4 \text{ \AA}^{-1}$, respectively. (E) Meridional q plots of the patterns in (B). (F) Molecular model of (left) a (3,4,5)12G1-CTV molecule and (right) a supramolecular column self-assembled from (3,4,5)12G1-CTV. Molecular models of the supramolecular sphere are presented in Figure 3D, E.

Figure 3.

(**A, B**) Electron density maps of the (**A**) Φ_h^{io} and (**B**) cubic ($Pm\bar{3}n$) phases reconstructed from XRD data. The top of the figure illustrates the pseudohexagonal symmetry adopted during the phase transition. In (**B**) the three colored arrows point toward the three orthogonal directions with pseudohexagonal symmetry. (**C**) Schematic representation of face (blue) and center (yellow) tetrahedrally distorted spheres of the $Pm\bar{3}n$ lattice. (**D, E**) Possible mechanisms of transformation from the supramolecular column (**D**) to spheres with columnar character in the faces of the cubic phase (**E**). For simplicity in (**D, E**) alkyl chains are not shown. Color code: H atoms–white; O atoms–red; C atoms of the dendron aromatic benzyl–green, dark or light blue; all other C atoms–gray.

Figure 4.

(A) Upon the phase transition the expected rotational symmetry is broken to conserve the pseudo-hexagonal and hexagonal symmetries. Color code in (A): blue—original orientation preserved by the corner/center spheres; yellow—face spheres of the cubic phase. (B) Depiction of reorientation of hexagonal microdomains according to the cubic lattice. In the cubic unit cell, flattened disk-like units represent tetrahedrally distorted spheres. (C) Columnar character in the supramolecular spheres of the cubic phase. Color code in (B, C): blue—original orientation; red and orange—columns or spheres “reoriented” in a direction perpendicular to the original one; yellow—center or corner spheres of the cubic phase that can adopt the blue, red or orange orientation.

Figure 5.

(A) Hexagonal phase after shearing. Columns are nearly uniformly oriented perpendicular to the director lines shown. (B) Decay of birefringence in the cubic phase. (C, D, E) Orientation distributions of (C) the original film before heating and cooling and (D, E) selected regions of the film after heating and cooling as described in the main text. (F, G) Two representative regions with 90° separated bimodal birefringence in the hexagonal phase after cooling from the cubic phase. Each image (A, F, G) spans 60 μm from top to bottom

(scale bars indicated). Color code: orange–original orientation ($\phi \approx 149^\circ$); blue–second orientation ($\phi \approx 59^\circ$).