

## LIQUID CRYSTALS

## Forced to line up for perfect order

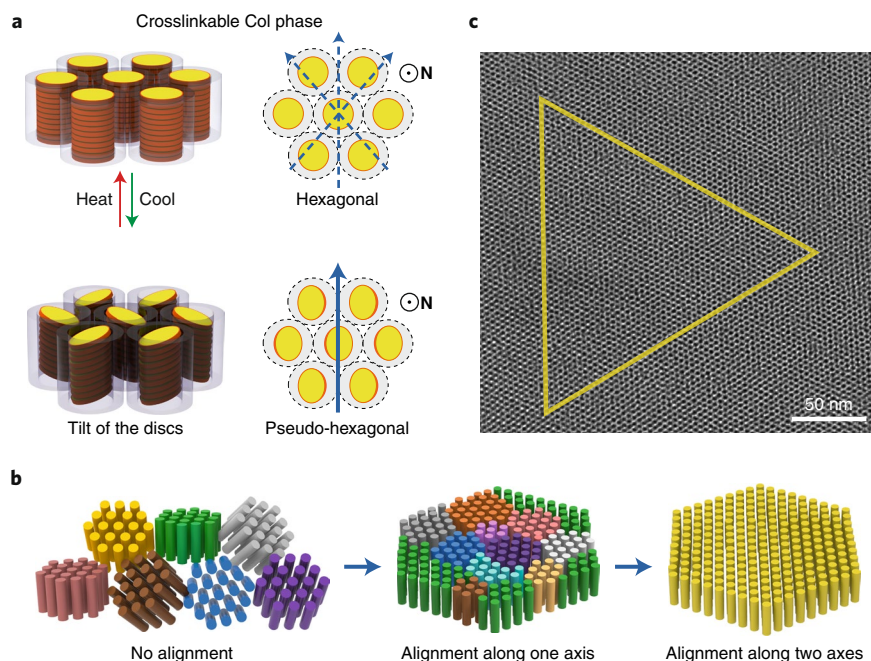
Physical confinement and magnetic fields are used to align organic molecules that self-assemble into large-size single crystals with perfect positional order.

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As a liquid solidifies, crystals usually start growing at different locations with random orientation, resulting in polycrystalline materials composed of many small crystallites. However, for many technological applications, macroscopic single crystals are required. Now, writing in *Nature Materials*, Chinedum Osuji and colleagues<sup>1</sup> report that a mosaic of pre-formed randomly oriented columnar liquid crystals of disc-shaped macromolecules can be subsequently aligned into a macroscopically large and highly ordered single crystal. This is achieved by the simultaneous application of two orthogonal fields: (1) physical confinement of the columnar liquid crystals in a thin film and (2) alignment of the columnar network along an applied magnetic field. The resulting photo-crosslinkable films have very high positional order and can be readily used as templates for the fabrication of novel crystalline nanomaterials with single texture.

For hard materials such as silicon, the transformation from a polycrystalline state to a single crystal necessarily proceeds via a liquid state with subsequent recrystallization. The so-called Czochralski method<sup>2</sup> is often used, in which the crystallization can only occur from a unique seed at a temperature close to the melting point. In contrast, soft condensed matter is constructed from larger building blocks that have weaker interactions. Soft materials are therefore much more susceptible to external stimuli and can be more easily manipulated by external fields after casting<sup>3</sup>.

Osuji and colleagues studied the structure of liquid-crystalline phases of large disc-shaped organic molecules, consisting of an aromatic core (1,3,5-tris(4,5-dihydroimidazol-2-yl)benzene, TDIB) and three wedge-shaped benzoic acid species (3,4,5-tris(11'-acryloyloxyundecyloxy)benzoic acid, TABA) hydrogen-bonded to the core. A small amount of butyl acrylate was added to lower the melting point of the compound. On cooling, the isotropic phase transforms to the columnar phase at about 62 °C. At this point the discotic molecules stack on top of each other to form columns, which



**Fig. 1 | Molecular packing and orientation of discotic shaped organic molecules under different experimental conditions.** **a**, Structural sketch of the non-tilted and tilted columnar (Col) phases in side and aerial views. The magnetic interaction energy is independent of the in-plane field orientation in the non-tilted phase (dashed blue arrows), while in the tilted phase it is minimized for a unique field orientation relative to the tilt directions (solid blue arrow). The system can reversibly switch between each phase by cooling or heating the sample. **b**, Schematics of a polycrystalline sample with no alignment and aligned along one and two directions. In the last case, the orientation of the third axis is set by the fixed biaxial alignment resulting in a highly ordered crystalline arrangement of the Col phase. **c**, Transmission electron microscope image of a liquid crystal sample aligned by a magnetic field in confinement. A 60° triangle is drawn to highlight the quality of the positional intercolumnar order. Adapted from ref. <sup>1</sup>, Springer Nature Ltd.

in turn arrange themselves into a hexagonal structure with two-dimensional periodicity. On further cooling to temperatures below 58 °C, disc-shaped cores of the molecule tilt with respect to the column direction (Fig. 1a). Interestingly, molecular tilt removes the six-fold symmetry of the structure. However, the intercolumnar distance along the three principal directions remain practically the same, probably due to the flexibility of the TABA tails, strongly reducing the distortion of the original hexagonal lattice. A similar observation of a pseudohexagonal tilted columnar phase of somewhat smaller

disc-shaped molecules was reported in the seminal work of Frank and Chandrasekhar<sup>4</sup>.

The application of a uniaxial field is able to align one crystallographic direction while the structure can still explore any orientations obtained by rotating around the field direction. For some applications, such as liquid-crystal displays, this uniaxial alignment is already sufficient to control the state of the pixels — that is, transmitting or blocking light. However, to fully control the three-dimensional crystal orientation, it is necessary to use a second non-collinear field. In this way, it is possible to fix two

crystallographic directions while the orientation of the third crystal axis naturally arises from the two directions imposed and from the internal crystal symmetry (Fig. 1b).

Osuji and colleagues sandwich the sample in between two parallel plates 10  $\mu\text{m}$  apart. The flat disc-like molecules tend to align parallel to the flat walls. For the liquid-crystalline phase with long-range orientational order, the molecular alignment at the surface defines the orientation of the columns through the whole sample thickness. However, the lateral orientation of the hexagonal columnar network is still random. To remove this ambiguity, the authors apply a magnetic field along the film, which aligns the flat TDIB cores parallel to the field direction. This condition is automatically fulfilled in the non-tilted columnar phase and the magnetic field does not provide any lateral alignment of the structure. However, at a temperature below 58  $^{\circ}\text{C}$  the tilt defines a unique direction that minimizes the magnetic interaction energy (Fig. 1a). By slowly cooling the sample in the magnetic field, it is possible to obtain high-quality single-crystal films where the hexagonally arranged columns are separated by as little as 4.12 nm. In contrast to hard matter, here the alignment can

be performed after casting, which can be advantageous for technological processing. Despite the fact that self-organized soft matter systems are prone to various defects<sup>5</sup>, the alignment treatment leads to very high-quality periodic positional order with nanometre precision (Fig. 1c).

Applications of this approach can be envisioned, for example, in magnetic recording. The hexagonal nanostructure can be fixed in position on light irradiation and readily used as a template. The molecule cores could be etched away and filled with a magnetic material. In this way, materials with  $7 \times 10^{12}$  magnetic nanocylinders per square centimetre can be obtained where the diameter and length of each nanocylinder can be controlled by the chemical etching process. Using the magnetization state of each nanoparticle as one bit of information, an information density of more than 40 Tbit per square inch is easily reached, which is an order of magnitude higher than the current state of the art<sup>6,7</sup>. The next challenge would consist of developing a technology that allows for the modification and reading of the magnetization states of the individual particles. Alternatively, the single crystals described by Osuji and colleagues could be subjected to selective etching to remove

the TABA tails while leaving the TDIB core intact to create a template for a honeycomb nanostructure with massless electrons<sup>8</sup>. In addition, the use of non-collinear fields during or after the crystal growth could also prove useful for other applications such as protein crystallography<sup>9</sup>.  $\square$

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## PLASMONICS

# Lasing under ultralow pumping

Ultralow-threshold plasmonic lasers under continuous-wave pumping at room temperature have been created using lattice plasmonic cavities integrated with gain material consisting of upconverting nanoparticles.

Ren-Min Ma

Threshold is one of the most important figures of merit for laser devices. It characterizes the minimum pump power for the onset of lasing emission (Fig. 1a). Threshold power consists of two major parts, one for achieving population inversion of the gain material (that is, to make the gain medium transparent), and the other for compensating the cavity loss. In the past decade, plasmonic nanolasers emerged as a new class of lasers with great potential for shrinking the size of integrated photonic circuits to be comparable to modern electronic devices<sup>1–4</sup>. In order to realize such an unprecedented miniaturization, part of the light energy of a plasmonic nanolaser has to be stored in the form of free-electron oscillation inside the metal. However, free-electron oscillation dissipates energy

to heat rapidly; this additional metallic loss has led so far to plasmonic nanolasers with high lasing thresholds. Writing in *Nature Materials*, P. James Schuck, Teri W. Odom and colleagues<sup>5</sup> have now achieved a record low threshold of 70  $\text{W cm}^{-2}$  in plasmonic lasers under continuous-wave pumping at room temperature, which is about two orders of magnitude lower than commercialized laser diodes.

Because the stimulated emission needs to dominate in the lasing state, laser threshold can be unambiguously defined as the condition in which the rates of spontaneous and stimulated emission into the laser mode are equal (Fig. 1b). According to Einstein's 1917 paper on spontaneous emission and stimulated emission coefficients, this condition is equivalent to saying that a lasing

mode should contain one photon to reach the threshold<sup>6</sup>. Hence for a given cavity loss, the minimum power to maintain a photon in the laser mode requires a power ( $P_{\text{cavity}}$ ) of  $\gamma_{\text{c}} \times \hbar\nu \times \frac{1}{\beta}$ , where  $\gamma_{\text{c}}$  is the cavity photon loss rate,  $\hbar\nu$  is the energy of the one photon, and  $\beta$  is the spontaneous emission factor, the fraction of spontaneous emission directed into the laser mode. In a conventional laser, the photon loss rate can be significantly suppressed by cavity feedback optimization. However, in a plasmonic laser cavity, the photon loss rate usually reaches  $10^{13}$ – $10^{14} \text{ s}^{-1}$  due to the parasitic metallic loss. Assuming an emitted photon energy  $\hbar\nu$  of  $\sim 1 \text{ eV}$  and a  $\beta$  factor of 1, we can obtain a minimum threshold power of plasmonic nanolasers around 1–10  $\mu\text{W}$ . This may not sound like a very high power but given the very small