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# Liquid Organic Frameworks: The Single-Network "Plumber's Nightmare" Bicontinuous Cubic Liquid Crystal

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**ABSTRACT:** Novel bolapolyphiles, built of a *p*-terphenyl or bistolane core with polar glycerol end-groups and two laterally attached *n*-alkyl or semiperfluoroalkyl chains, form the first "single plumber's nightmare network", the simplest soft-matter cubic phase  $(Pm\overline{3}m)$ . Its cage-like grid comprises bundles of aromatic rods lying along the cubic unit cell edges, connected by six-way hydrogen-bonded junctions. Side-chains fill the remaining volume of this unique noninterpenetrating liquid-crystalline organic framework.

**B** icontinuous cubic (Cub<sub>bi</sub>) phases of amphiphile–solvent systems have found promising applications in biochemistry, biotechnology, and nanotechnology.<sup>1,2</sup> They comprise continua of two chemically different constitutions. Most prominent are the double-gyroid (DG,  $Ia\overline{3}d$ ), double-diamond (DD,  $Pn\overline{3}m$ ), and double-network "plumber's nightmare" structures (DP,  $Im\overline{3}m$ ) (Figure 1a–c).<sup>1,2</sup> Cub<sub>bi</sub> phases, with their unique 3D structures and high surface area, find uses such as templates for porous inorganic solids<sup>3</sup> and membranes with well-defined nanopores.<sup>4</sup>

 $Cub_{bi}$  phases also appear in block copolymers<sup>5</sup> and thermotropic (solvent-free) liquid crystals (LC). In the latter, the DG is predominant, DD is rare, and DP (Figure 1c) nonexistent.<sup>6–8</sup> Beside these double networks a triple network<sup>7</sup> has also been reported, while biophotonic  $Cub_{bi}$  structures with only one network were found in butterflies (single gyroid, SG)<sup>9</sup> and beetles (single diamond, SD).<sup>10,11</sup> However, synthetic versions have been obtained only by top-down fabrication.<sup>11,12</sup> Generation of single-network structures through self-assembly would simplify production of photonic and metamaterials and of extremely porous materials, as the second network is removed.

Recently the first self-assembled single-network LC, the SD with  $Fd\overline{3}m$  symmetry (Figure 1e), has been reported for a sidebranched glycerol-terminated *p*-terphenyl (compounds 1 with n = 18-22, Figure 2a, right).<sup>13</sup> This cubic LC belongs to the so-called rod-bundle phases formed by bundles of rod-like bolaamphiphiles with a laterally attached branched space-filling chain (Figure 2a).<sup>14-17</sup> The bundles lie along the network segments, and in the SD, as in the previously reported DD ( $Pn\overline{3}m$ ),<sup>18</sup> the segments are interconnected by tetrahedral four-way junctions.

The number of consecutive bundles between junctions is either two<sup>18,21</sup> or only one.<sup>13,22</sup> The observed replacement of DG by SD phase (both with single bundles) upon increasing the side-chain length of 1 from n = 16 to 18 (Figure 2a) was attributed to the larger distance between network segments in the SD with the same interjunction segment length. This increased chain length is reflected in the expansion of the dV/dr curve for SD compared to that for DG (Figure 1g).<sup>13</sup> Figure 1g also shows how for double-network phases (DP, DD, DG) dV/dr drops abruptly when the increasing radius r of the network segments results in collision with the second network. Meanwhile, in the absence of the second network, in SP, SG, and SD, side-chains can be further extended until colliding with parts of their own network. Figure 1g also implies that reducing the side-chain volume should lead to a transition from DG to DD and, ultimately, to the densest of all networks, the "plumber's nightmare"-type DP and SP phases ( $Im\bar{3}m$  and  $Pm\bar{3}m$ ). Similarly, coarse-grain simulations predicted the SP in T-shaped bolaamphiphiles beside the SD for smaller side-chains.<sup>23</sup> While the DP is known in lyotropics, the SP has not been experimentally observed in any system.

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From Figure 1g we can deduce a molecular design concept for the envisaged SP phase. Ideally, normalized to the same interjunction or bundle length L, the combined volume of the side-chains should be significantly smaller than required for the DG or SD. Note that L = 1 in Figure 1g, which, for the SP structure, is the unit cell length a. Meanwhile, at least one of the chains must be long enough to reach from the network segment central axis to r = 0.7L, which is where the dV/dr for SP falls to 0. Furthermore, the dV/dr curves for SP and DP show the largest downward departure from the straight line  $dV/dr = 2\pi r$ , which is due to the large overlaps of the widening cylinders at 6-fold junctions. This means that we should avoid excessive fanning-out of the side-chain, and for this reason branched chains should be avoided; note that the limiting case of  $dV/dr = 2\pi r$  applies to uniaxial columnar phases,<sup>7</sup> which require highly divergent chains.

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**Figure 1.** (a-c) Double-network cubic phases with their infinite minimal surfaces (blue) and (d-f) the corresponding single networks; (g) radial volume distribution dV/dr curves, where V(r) is that part of the unit cell volume that is within a distance r from the closest network segment. The curves show the increase in occupied volume as the radius (r) of the cylindrical network segments increases (the length of the segments is normalized to 1).<sup>13</sup>

Therefore, we designed two different molecules (Figure 2b). In compound 2 the terphenyl was retained, but the long branched chain was replaced by inward-pointing shorter ones on the outer benzene rings. This led to a reduced fanning-out of the chains. In this short-chain compound, semiperfluorinated chains were chosen to enhance nanosegregation to ensure LC phase stability. In compound 3 we extended the rod-like core of 2 by two additional ethynyl units<sup>24</sup> and replaced the short side-chain by two appropriately extended linear *n*-alkyls attached to the middle ring. This increased the bundle length *L*, which provided more internetwork space for the longer side-chains to fill.

The synthesis of 2 and 3 by C–C coupling reactions is described in Schemes S1 and S2 of the Supporting Information (SI), where the experimental procedures, analysis, and simulation of diffraction patterns and additional data are also given.

For both compounds cooling from the isotropic liquid (Iso) induces an exothermic transition ( $\Delta H = -1.4$  to -2.6 kJ mol<sup>-1</sup>) (Figure S1) accompanied by a significant increase in viscosity, while the sample remains optically isotropic. The LC character is confirmed by the presence of only diffuse scattering, the maximum being at d = 0.54 nm for compound 2 and at 0.45 nm for 3 (Figure S2). At smaller angles the presence of sharp Bragg reflections indicates a periodic lattice. For both 2 and 3 (Figure 3a,e) their 1/d values stand in the ratio  $1:\sqrt{2}:\sqrt{3}:\sqrt{4}:\sqrt{5}...$ , which can be indexed to a primitive

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**Figure 2.** (a) Compounds 1 forming the double-gyroid (DG) and the single-diamond (SD) cubic LC phases, depending on chain length n, with schematic phase structures.<sup>13</sup> (b) Formulas and molecular dimensions of the new compounds 2 and 3; the volumes were estimated using crystal volume increments.<sup>19,20</sup>

Table 1. Transition Temperatures  $(T/^{\circ}C)$ , Associated Enthalpy Changes  $(\Delta H/kJ \text{ mol}^{-1})$ , and Lattice Parameters of Compounds 2 and 3

compd	$T/^{\circ}C \left[\Delta H/kJ \cdot mol^{-1}\right]^{a}$	$a_{\rm cub}/{\rm nm} (T/{\rm °C})$	n <sub>cell</sub>	n <sub>bundle</sub>
2	H: Cr 122 [26.7] Cub/Pm3m 154 [2.7] Iso	2.89 (150)	19.3	6.4
	C: Iso 151 [-2.6] Cub/Pm3m 44 [-15.4] Cr			
3	H: Cr 98 [74.8] Cub/Pm3m 134 [1.0] Iso	3.61 (100)	26.5	8.8
	C: Iso 130 [-1.4] Cub/Pm3m 79 [-78.0] Cr			

<sup>*a*</sup>Determined by DSC (second heating/cooling, 10 K min<sup>-1</sup>, peak temperatures); abbreviations:  $Cr = crystalline, Cub/Pm\overline{3}m = simple cubic phase (SP), Iso = isotropic liquid, H = heating, C = cooling, for DSCs see Figure S1.$ 

 $Pm\overline{3}m$  or a body-centered  $Im\overline{3}m$  lattice. The distinction was possible by GISAXS on oriented films (Figures 3b and S3a). For the  $Im\overline{3}m$  lattice the fundamental reflection group would have been {110}, thus showing two diffraction spots in addition to the one meridional and two equatorial; see Figure S3b. Their absence means that the reflections belong to the {100} group of the simple cubic lattice, excluding  $Im\overline{3}m$ .

The cubic lattice parameters  $a_{cub}$  of **2** and **3** are 2.89 and 3.61 nm, while the lengths  $L_{mol}$  of their molecules are 2.5 and 3.1 nm (Figure 2b). The similarity of *a* and  $L_{mol}$  suggests a structure in which bundles of coaxial molecular cores lie along

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**Figure 3.** Cub/*Pm* $\overline{3}m$  phases of compounds (a-d) 2 and (e-h) 3 at the indicated temperatures: (a, e) experimental (top) and simulated (bottom) SAXS powder diffractograms; (b) experimental GISAXS pattern (sharp spots are from well-oriented domains, lying on their {100} face); (c, g) ED maps, blue-purple = high-density, red = low-density; schematic molecules are added; (f) model of 2 × 2 × 2 unit cells; (d, h) geometric models used to calculate diffraction intensities shown in (a) and (e) and in Tables S3 and S4; mathematical details are in Section S3.2.

the edges of the cubic unit cell, forming a simple cubic framework with polar glycerol nodes, while the side-chains fill the remaining continuum (Figure 3c,f,g). The number of molecules of volume  $V_{\rm mol}$  in a unit cell is  $n_{\rm cell} = 0.89 a_{\rm cub}^3/V_{\rm mol} = 19.3$  for **2**,  $n_{\rm cell} = 26.5$  for **3**,<sup>19</sup> and the factor 0.89 is a correction<sup>20</sup> (Table S2). Each unit cell contains three network segments, each containing one bundle of 6 (6.4) molecules in **2** and about 9 (8.8) in **3**. The excess cell length  $a-L_{\rm mol}$  of 0.4-0.5 nm is attributed to the excluded volume effect at the sixway junctions (Figure 3f). Thus, in **2**,  $6n_{\rm bundle} = 6 \times 6.4 \approx 38$  glycerols aggregate in each H-bonded junction, adding to the effective bundle length. In **3**  $n_{\rm bundle} = 9$ ; hence their 54-glycerol micelles cause an even larger excess cell length of 0.5 nm.

Geometric models of the cubic structures of 2 and 3 were constructed (Figure 3d,h), and the diffraction intensities were calculated, which compare well with those observed (Figure 3a,e). Next, electron density (ED) maps were reconstructed using the structure factor amplitudes from diffraction intensities and the corresponding phase angles from Fourier analysis of the models (for details see Section S3.1).

In the ED map of compound **3** (Figures 3g and S4b) the high-ED regions (blue-purple) follow the edges of the unit cells forming a network of orthogonal columns with octahedral intersections; this network contains the 1,4-bis-(phenylethynyl)benzene cores and the glycerols, as expected for SP structure (Figure 3f). The low-ED alkyls (enclosed within the red surface) occupy the space between the blue network segments, around the areas that would be hosting the second network in a DP phase. Although Figure 3g may be reminiscent of a common depiction of the DP phase, as seen in lyotropic LCs, note that in that case the two networks would be the same color, while the minimum surface would be intercalated between them.<sup>1</sup>

In the ED map of compound 2 (Figures 3c and S4a) the highest ED regions (blue-purple) are now the face centers stretching toward the body center of the unit cell, dominated

by the fluoroalkyl segments of the side-chains (Figure 3c). In the geometric model this is represented by the network of fused body-centered octahedra (Figure 3d). Aromatic rodbundles together with the attached alkyl segments are now the lowest ED moieties (red), while the glycerol cell corners are intermediate (blue). One might expect that the map for 2 would be essentially the inverse of that for 3. However, in 2 the body center is not part of the highest density region, although the only moieties capable of reaching it are the high-ED perfluoroalkyl segments. In fact, it turns out that the length l of the fully stretched side-chains of 2, including the 0.45 nm core width, is 1.85 nm, falling short of the required distance to the body center (( $a_{cub}/2$ ) ×  $\sqrt{2}$  = 2.04 nm). In other words  $l/a_{cub}$ = 1.85/2.89 = 0.64, i.e., slightly less than  $\sqrt{2/2} = 0.7$ , where the dV/dr for SP falls to 0 (Figure 1g). This shortfall in length of the side-chains in 2 explains the local ED minimum at the center of the unit cell (Figures 3c and S4c) and contributes to the larger number of molecules in the bundles. No such shortfall exists in 3, where *l* is 2.70 + 0.45 = 3.15 nm; hence *l*/  $a_{\rm cub} = 3.15/3.61 = 0.87$ , well above the 0.7 threshold.

As explained in Figure 4, the proposed structure of the Cub/  $Pm\overline{3}m$  phase of 2 was further corroborated by high-resolution atomic force microscopy (AFM). The large domain size seen by AFM is in line with the 0.185  $\mu$ m size (lower limit) obtained by the Scherrer equation from the synchrotron Bragg diffraction line width of 0.034 nm<sup>-1</sup>.

In summary, the first single "plumber's nightmare" (SP) bicontinuous network phase was discovered in two soft-matter systems. It is only the second observed single-network LC phase and is formed by self-assembly of strategically designed  $\pi$ -shaped bolapolyphiles,<sup>26</sup> the design being based on matching the molecular architecture and phase geometry via the dV/dr diagram.<sup>7</sup> It belongs to the cubic bundle phases, being bicontinuous regarding the network and micellar regarding the glycerol spheres. This concept can lead to yet unknown LC phases, including the still missing SG and DP (an "alternating"



**Figure 4.** (a) AFM phase image of 2 in the Cub/ $Pm\overline{3}m$  phase. Inset: Fourier transform. (b) Fourier filtered image in (a); the dark spots are the stiff fluoroalkyl regions.<sup>25</sup> (c) Six unit cells showing the highest density aggregates of fluorinated chains (compare Figure S4c) as spheres around the face centers within an  $a_{cub}/\sqrt{2} = 2$  nm thick (110) plane (yellow box). (d) Frontal view of the cleaved (110) surface with the content of the box in (c), showing the pseudohexagonal arrangement of the fluoroalkyl stiffness maxima, seen in (b), where the white rectangle is an example area shown in (c) and (d). XRD-based distances between rows (d) match closely those measured by AFM (a).

DG has just been reported<sup>27</sup>). These unique LCs could be considered as liquid organic frameworks (LOFs), related to the solid-state covalent and metal—organic frameworks (COFs,<sup>28</sup> MOFs<sup>29</sup>). The dynamic hydrogen-bonded junctions replace the metal or covalent nodes of MOFs and COFs. The cage-like noninterpenetrating grid of the Cub/ $Pm\bar{3}m$ , reminiscent of MOFs, is unknown among bicontinuous LCs. If scaled up, these single-network structures are of interest for photonics and metamaterials.<sup>30</sup>

# ASSOCIATED CONTENT

# **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.9b11073.

Experimental methods; additional experimental data; analysis of X-ray data, construction of maps and simulation from models; synthesis and analytical data; supporting discussion and calculations; additional NMR spectra (PDF)

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## Notes

The authors declare no competing financial interest.

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