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2,6-Dibromogallates as a new building block for controlling π -stacking, network formation and mirror symmetry breaking[†]

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Achiral multi-chain (polycatenar) compounds based on the 2,7-diphenyl substituted [1]benzothieno[3,2-b]benzothiophene (BTBT) unit and a 2,6-dibromo-3,4,5-trialkoxybenzoate end group lead to materials forming bicontinuous cubic liquid crystalline phases with helical network structures over wide temperature ranges.

Supramolecular self-assembly¹ is an effective route to design nanostructured materials with tailored properties.² Among them, liquid crystalline (LC) and solution processable π -conjugated compounds are of growing interest for optical, electronic, light harvesting^{3a} and photonic applications.⁴ The 3,4,5-trialkoxybenzoate unit derived from gallic acid has developed to an important building block for the design of such materials, allowing the control of the mode of self-assembly from lamellar *via* columnar to spherical.⁵⁻⁷ A single 3,4,5-trialkoxybenzoate unit attached to one end of an extended π -conjugated rod-like unit could even lead to bicontinuous cubic phases (Cub_{bi}, Fig. 1c and d),⁸⁻¹⁰ being composed of interwoven networks and representing an intermediate structure at the transition from lamellar to columnar self-assembly.¹¹ In these networks the molecular rods are organized antiparallel to each other and almost perpendicular to the local network direction, and the collision of the bulky trisubstituted ends induces a helical twist (Fig. 1b).⁸ The network junctions provide a long range synchronization of the helix sense along the networks.¹⁰ If the Cub_{bi} phase is formed by only two networks, an achiral Ia3d phase composed of two enantiomorphic networks is formed (double gyroid, Fig. 1c). If there are three networks, as in the I23 structure¹² (previously known as "Im3m", 11,13,14a see Fig. 1d), the network chirality cannot cancel

out, and macroscopic chirality develops by mirror symmetry breaking. Polycatenar molecules involving a π -conjugated core-unit, such as [1]benzothieno[3,2-*b*]benzothiophene (BTBT)¹⁵ provide access to new charge carrier materials with conduction pathways in all three spatial direction (Fig. 1).¹⁶ However, often an unfavourable herringbone packing is assumed, reducing the charge carrier mobility,^{3b,16} and in addition, the Cub_{bi} phases are accompanied by parasitic birefringent mesophases with non-cubic 3D lattices.^{14,16}

Herein, we introduce the 2,6-dibromo-3,4,5-trialkoxybenzoate unit as a new building block for solution processable and soft selfassembled functional materials, more specifically, for the molecular design of compounds being capable of forming surprisingly broad ranges of mirror symmetry broken helical network phases, and we compare them with related non- and mono-brominated analogues.§ It is surprising that the bulky bromines at both sides of the molecule do not significantly reduce the LC phase stability, but widen the LC



Fig. 1 (a) Structures of the discussed compounds **H***n*, **B***n* and **BB***n* and (b) chirality developing due to the twist along the networks of the Cub_{bi} phases; (c) double network structure of the la3d phase and (d) the triple network of the l23 phase; (c and d) were reproduced with permission,¹² The Royal Society of Chemistry 2020.

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Scheme 1 Synthesis of compounds **Hn** and **BBn**. *Reagents and conditions*: (i) 1. SOCl₂, 2. dry pyridine, RT; (ii) 1.1 eq. Br₂, (iii) 2.2 eq. Br₂, or (iv) 3.3 eq. Br₂, DCM, RT; (v) THF, sat. aqu. NaHCO₃, [Pd(PPh₃)₄], reflux; (vi) $C_nH_{2n+1}Br$, 2-butanone, K₂CO₃; TBAI; reflux. See Schemes S2–S4 (ESI†) for details. Compounds **Bn** have been reported previously.¹⁶

ranges, remove the birefringent phases and change the preferred π -stacking mode from edge-to-face to face-to-face.

The synthesis of the new non-brominated and dibrominated compounds **H***n* and **BB***n*, respectively, is shown in Scheme 1 (see also, ESI[†]). Compounds **BB***n* can be prepared by bromination of the boronate 1 to give 1**Br**₂, followed by Suzuki coupling reaction with 1.5 equivalents of 3**B***m* (Scheme 1, blue). Alternatively, by using a Pd[PPh₃]₄ catalyst, prepared according to ref. 17 the Suzuki coupling¹⁸ of the boronate 1 with 2**Br**₃ takes place preferentially with the bromine at the BTBT unit, leading to the phenol **BBOH** which was alkylated in the final step.

In all three series of compounds (Fig. 2a) there are two different types of optically isotropic Cub_{bi} phases which can be distinguished by the small angle X-ray scattering (SAXS) patterns and chiroptical properties (see Fig. S4-S8 and Tables S4-S9, ESI⁺). The dibrominated compound BB7 with the shortest apex chain shows an $Ia\bar{3}d$ lattice with $a_{cub} = 9.80$ nm (Fig. 3a). The reconstructed electron density (ED) map confirms a double gyroid structure, where the aromatic cores with the highest ED (purple \rightarrow green) form the networks and the alkyl chains form the continuum around them (Fig. 3b). The same network phase is found for BB8, but the Cub_{bi} phases of the longer homologues have three main SAXS peaks which can be indexed to the (321), (400) and (420) reflections of the *I*23 lattice (a_{cub} = 14.72 nm for **BB9**, Fig. 3c). This cubic phase with a lattice parameter being about 50% larger than in the $Ia\bar{3}d$ phase has a triple network structure, again with the aromatic cores forming the networks and the alkyl chains in the continuum (Fig. 3d). The lattice parameters are collated in Table S11 (ESI⁺) and the method of selecting the correct phase



Fig. 2 (a) Phase transitions as observed by DSC on cooling (10 K min⁻¹); the data for **Bn** were taken from ref. 16. The related transitions on heating are shown in Fig. S3, ESI;⁺ the numerical data and enthalpy values are collated in Tables S1–S3 (ESI⁺) (for DSCs, see Fig. S1 and S2, for XRD, see Fig. S6–S11 and Tables S4–S11, ESI⁺); abbreviations: Cr = crystalline solid, Cub_{bl}^{|4|}/|23 = Cub_{bl} phase with chiral /23 lattice; Cub_{bl}/la3d = Cub_{bl} phase with achiral *la*3d lattice; Tet = tetragonal 3D phase; M = highly birefringent 3D phase with unknown structure; Iso₁^{|4|} = isotropic liquid with chiral conglomerate structure; the achiral isotropic liquid (Iso) is at the right; (b–d) representative WAXS patterns of selected compounds from each series at the indicated temperatures.



Fig. 3 SAXS patterns at the indicated temperatures. (a) Cub_{bl}/ $Ia\bar{3}d$ phase of **BB7** and (c) the Cub_{bl}^[*]/I23 phase of compound **BB9** with (b and d) the corresponding ED maps reconstructed from the diffraction patterns, the aromatic cores are located in the networks formed by the green iso-surfaces, the space in between is filled by the alkyl chains, as shown in Fig. S12 and S13 (ESI†); for the network models, see Fig. 1c and d; for numerical values and additional XRD date, see Fig. S4–S8 and Tables S4–S11 (ESI†).

combination for ED reconstruction is described in previous work. 9,10,12

The Cub_{bi} phase of **BB7** and **BB8** is achiral (Fig. 4a and Fig. S4b, ESI[†]), in line with the $Ia\bar{3}d$ lattice (Fig. 1c). In contrast, the Cub_{bi}

phase of BB9-BB11 shows a conglomerate of dark and bright domains (Fig. S4d, ESI⁺), if observed by optical microscopy between polarizers rotated by a small angle out of the precise 90° orientation. The domain brightness is inverted by changing the sense of rotation, thus indicating that this optically isotropic Cub_{bi} phase is chiral, confirming a triple network *I*23 structure (Fig. 1d).⁸⁻¹² The transition from the achiral $Ia\bar{3}d$ to the chiral I23phase upon chain elongation (Fig. 2a) is due to the growing volume of the periphery which increases the twist between the molecules (Φ) .^{9,21} At a certain critical twist angle ($\Phi > 9.2^{\circ}$, see Table S11, ESI[†]) the transition from $Ia\bar{3}d$ to I23 takes place in all three series of compound. However, the $Ia\bar{3}d \rightarrow I23$ transition is shifted by bromination to shorter chain length (Hn: 9 \rightarrow 12; Bn: 8 \rightarrow 11; **BBn**: $8 \rightarrow 9$, see Fig. 2a). This means that the bromines obviously contribute to the expansion of the molecular periphery and thus favour mirror symmetry breaking by inducing the $Ia\bar{3}d \rightarrow I23$ transition. Thus, substitution of H by Br has a similar effect as an elongation of the apex chain by one additional CH₂ unit, being in line with the similar volumes of Br $(3.3 \times 10^{-2} \text{ nm}^3)$ and $CH_2 (2.5 \times 10^{-2} \text{ nm}^3)$.¹⁹ Though the melting temperatures are almost the same in all three series (see Tables S1-S3 and Fig. S1, S2, ESI[†]), there is a reduction of the crystallization tendency, leading to an improved supercooling of the crystallization with growing number of bromines, allowing the formation of long time persistent Cub_{bi} phases down to ambient temperature (Fig. 2a and Fig. S2a-e, ESI⁺).

At the transition between the two different Cub_{bi} phases two types of birefringent mesophases occur (Tet, M in Fig. 4). Comparison of the three series shows that an increasing degree of bromination reduces the Tet and M phase ranges and even completely eliminates the Tet phase for compounds **BBn** (Fig. 2a). The Tet phases of **Hn** and **Bn** have very similar low birefringent optical textures (Fig. 4c) and comparable *a*-parameters of the tetragonal lattices (a = 17.7 and 17.8 nm, respectively), and therefore, both should belong to the same kind. Only the parameter *c* is increased by bromination from $c = \sim 16$ nm for **H10** to $c = \sim 20-22$ nm for **Bn** (Table S11, ESI†).¹⁶ The transition between the double and triple network Cub_{bi} phase is also associated with the formation of an additional small range of a metastable mesophase M, growing as



(b)

la3d

(a)

Fig. 4 Optical textures of (a) **BB7** at 226 °C as observed on cooling between two polarizers slightly rotated out of the 90° twisted configuration (arrows) and showing the transition from the $lso_1^{[*]}$ phase (chiral conglomerate) to $Cub_{bi}/la\bar{3}d$ with simultaneous growth of the M-phase and (b and c) of **H10** between fully crossed polarizers; (b) high birefringent M phase developing from the $lso_1^{[*]}$ phase and the co-developing low birefringent Tet phase (bottom, right) at 215 °C and (c) fully developed texture of the Tet phase at 205 °C (longer exposure time).

highly birefringent platelets, which rapidly transforms into Cub_{bi} or Tet with time or upon cooling (Fig. 4a and b). This mesophase is observed in all three series of compounds in a very narrow temperature range during the transition from $\text{Iso}_1^{[*]}$ to $\text{Cub}_{bi}/Ia\bar{3}d$ or Tet on cooling. It is metastable, rapidly transforms into the Cub_{bi} or Tet phase, and therefore it cannot be studied in more detail. It appears to be associated with the $Ia\bar{3}d \rightarrow (\text{Tet}) \rightarrow I23$ transition upon chain elongation and it is removed as soon as either the $\text{Cub}_{bi}/I23$ or the $Ia\bar{3}d$ phase becomes the dominating phase. Double bromination removes the M-phase for n > 7 (Fig. 2).

In all mesophases (Cub_{bi}, Tet, M, Col_{bex}), the wide-angle scattering (WAXS) is diffuse with a maximum around 0.45-0.46 nm, as typical for LC phases (Fig. 2b and c). For H10 there is a very weak shoulder at larger 2θ values which for **B***n* and **BB***n* becomes a second diffuse scattering with increased intensity around 0.35-0.37 nm. (Fig. 2d and Fig. S10 ESI[†]). This is independent on the phase type, but decreases in intensity with rising temperature (Fig. S11, ESI⁺). We attribute this additional scattering to a change of the selfassembly of the π -conjugated rods. For Hn the preferred average organization is edge-to-face, leading to a dominating WAXS maximum at 0.45-0.46 nm, whereas bromination disfavour this arrangement and supports a parallel face-to-face stacking of the π -systems of compounds **B***n* and **BB***n* with a mean distance of 0.35–0.37 nm.²⁰ It appears that the face-to-face packing is mainly caused by the increased aspect ratio of the brominated compounds ($Hn \ll Bn < BBn$). This disfavours the edge-toface and supports the face-to-face packing of the aromatic cores, which then allows the overlapping of adjacent π systems.²⁰ However, the coherence length of the face-to-face stacking is still relatively short, as indicated by the diffuse WAXS.

For all investigated compounds the viscoelastic 3D mesophases are accompanied by additional highly fluid mesophases. One is a mirror symmetry broken isotropic liquid Iso₁[*] phase (Fig. S4a, ESI[†]) which is observed on cooling from the achiral isotropic liquid (Iso).^{21,22} Its temperature range is the largest for Hn and it decreases with increasing bromination in the order $Hn > Bn \gg$ BBn. In the series BBn it is only observed in a small temperature range on cooling the shortest compound BB7 before the transition to the M and $Ia\bar{3}d$ phases, whereas for all compounds **BB***n* with longer chains it is replaced by a Col_{bex} phase (Fig. 2 and Fig. S4c, S9, S11, ESI[†]). This effect of bromination could be attributed to the increase of interface curvature by the bulky bromines. Columnar self-assembly is additionally supported by the change of the preferred mode of packing from edge-to-face to face-to-face (see above), thus providing a taper-like molecular shape. In this Col_{hex} phase the lattice parameter $a_{hex} = 4.33$ nm (B11) is in good agreement with the total molecular length L_{mol} = 4.8 nm (see Fig. S14, ESI[†]) after considering the chain folding. The calculated number of ~4.5 molecules per 0.45 nm thick raft of the columns $(n_{raft}, Table S11, ESI^{\dagger})$ is close to the number of molecules organized in the rafts of the networks of the $Ia\bar{3}d$ phases, ranging from 3 (BB11) to 4 (H8) molecules.

In both series **H***n* and **B***n* an $Iso_1^{[*]}$ phase is found at the high temperature side of the *I*23, *Ia* $\bar{3}d$ and Tet phases. The proximity to the chiral *I*23 phase suggests a local *I*23-like structure of these $Iso_1^{[*]}$

phases retaining long range chirality synchronization, even after loss of the long-range cubic lattice in the liquid state.¹⁰ Because the *I*23 phase can develop from the *Ia*3*d* phase upon increasing twist along the networks,^{8–12} it is likely that thermal chain expansion can increase the helical twist and transforms the achiral Cub_{bi}/*Ia*3*d* lattice into a chiral *I*23-like local structure in the adjacent mirror symmetry broken Iso₁^[*] phase.

Remarkably, the LC \rightarrow Iso/Iso₁^[*] transition temperatures are almost the same in all three series of compounds if the same chain lengths are compared (Fig. S3, ESI†). This is surprising, as it is known from previous work, that bulky substituents in the 2,6-positions at opposite sides of an aromatic core have a dramatic destabilizing effect on LC phases (see for example Scheme S1, ESI†).²³ Hence, it appears that the unfavourable steric effect of bromination is compensated by mesophase stabilizing effects. Besides the different π -stacking modes, the increased London dispersion interactions of the highly polarizable bromines could stabilize the LC phases. Moreover, the bromines can in an antiparallel arrangement efficiently fill the free space around the adjacent ester linkage (Fig. S14, ESI†), and this increases the contact area between the molecules, thus strengthening the dispersion interactions.

Overall, peripheral double bromination of the tapered end of the π -conjugated polycatenars allows the formation of broad regions of mirror symmetry broken network phases, even covering ambient temperature. It also leads to a removal of birefringent 3D phases occurring at the $Ia\bar{3}d$ -I23 transition and hinders the crystallization. These surprising effects of double-bromination are opposite to the effect observed for halogenation of related molecules at other positions. Especially, halogenation in the centre of the core unit of polycatenars is known to suppress Cub_{bi} phase formation.²⁴ Even more remarkable is the formation of a parallel alignment of the π -faces of the aromatic cores which is important for the tailoring of photophysical properties and expected to support charge transportation.^{15,16} Hence, the work provides general guidelines for the controlled design of helical network forming and mirror symmetry broken soft materials based on π -conjugated rods. These are of current interest for numerous applications, as mentioned in the introduction.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

§ Previously, the 2,6-dichloro-3,4,5-trialkoxybenzoate unit was used for bent-core molecules.²⁵ In polycatenars one or two alkyl chains were

replaced by $\mathrm{Br}, {}^{\scriptscriptstyle 5}$ whereas in this work the bromines represent additional substituents.

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