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# Controlling mirror symmetry breaking and network formation in liquid crystalline cubic, isotropic liquid and crystalline phases of benzil-based polycatenars

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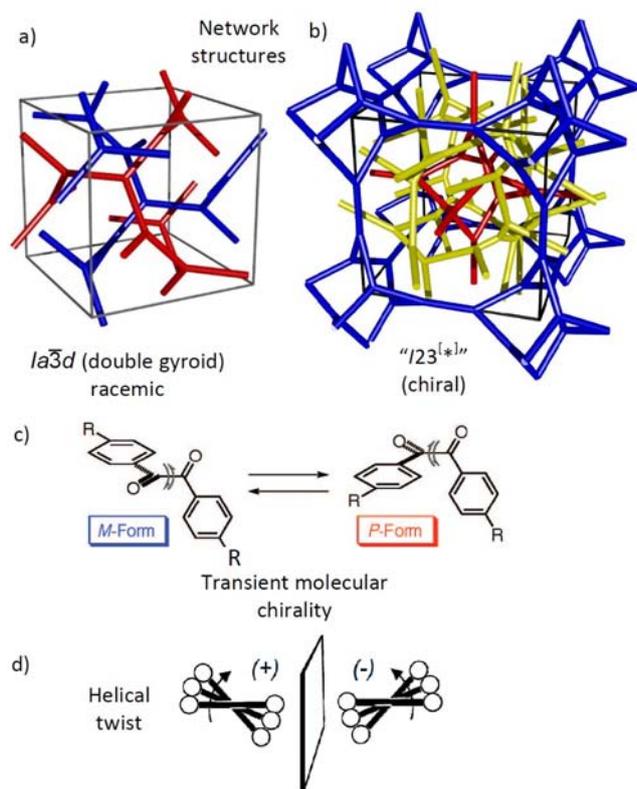
## Abstract

Spontaneous development of chirality in systems composed of achiral molecules is important for new routes to asymmetric synthesis, chiral superstructures and materials, as well as for the understanding of the mechanisms of emergence of prebiotic chirality. Herein it is shown that the 4,4'-diphenylbenzil unit is a universal transiently chiral bent building block for the design of multi-chained (polycatenar) rod-like molecules capable of forming a wide variety of helically twisted network structures in the liquid, the liquid crystalline (LC) and the crystalline state. Single polar substituents at the apex of tricatener molecules support the formation of the achiral (racemic) cubic double network phase with  $Ia\bar{3}d$  symmetry and relatively small twist along the networks. The combination of an alkyl chain with fluorine substitution leads to the homogeneously chiral triple network phase with  $I23$  space group, and in addition, provides a mirror symmetry broken liquid and also a crystalline conglomerate. Replacing F by Cl or Br further increases the twist, leading to a short pitch double gyroid  $Ia\bar{3}d$  phase which is achiral again. The effects of the structural variations on the network structures, either leading to achiral phases or chiral conglomerates are analyzed.

**Keywords:** Liquid crystals, mirror symmetry breaking, chirality, cubic phases, benzil, soft matter

## 1. Introduction

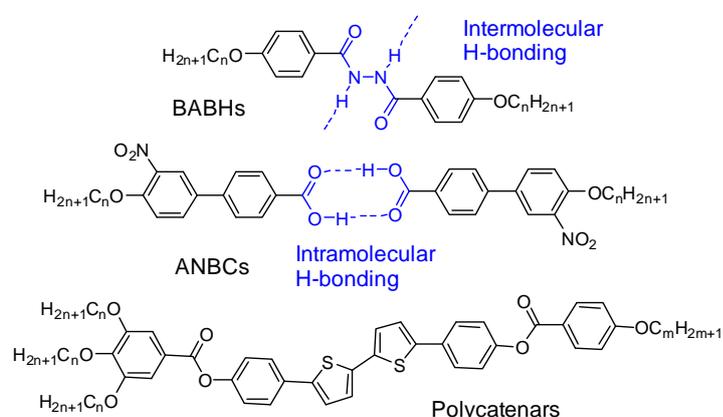
Dynamic self-assembled networks of any kind represent the fundamental basis of open-end development in complex systems. For example, neural networks are responsible for the development of the brain and consciousness, chemical networks are the basis of metabolism, data networks for information technology and so on.<sup>[1-4]</sup> Bicontinuous cubic ( $Cub_{bi}$ ) liquid crystalline phases can be considered as soft self-assembled networks, which have attracted a lot of interest for conducting and photonic materials, as matrices for protein crystallization and as templates for sol-gel syntheses.<sup>[5,6]</sup> Recently, these fluid networks were recognized to be responsible for transmission and amplification of chirality in fluid systems, and thus could provide a new potential route to prebiotic chirality.<sup>[7,8]</sup>  $Cub_{bi}$  phases are known for different types of small molecular<sup>[9-11]</sup> or polymeric<sup>[12]</sup> amphiphilic compounds, either in aqueous systems (lyotropic phases)<sup>[6,13]</sup> or as pure compounds (thermotropic phases).<sup>[9,10,14]</sup> Amphiphilicity can be based on any intramolecular difference of intermolecular interactions leading to nano-segregation of incompatible units,<sup>[15]</sup> like polar and apolar<sup>[11]</sup> or rod-like polyaromatic cores and flexible chains.<sup>[16-27]</sup>



**Figure 1.** Schematics showing the networks of a) the  $Cub_{bi}/Ia\bar{3}d$  phase and b) the triple network  $I23^{[*]}$  phase; c) shows the transient chirality of the benzil unit and d) the development of the helical twist by clashing of bulky end groups attached to the cores. The polyaromatic cores are located in the networks and aligned perpendicular to the network

directions, the continuum between them is filled by the terminal alkyl chains. b) was reproduced from ref. 31 by permission of The Royal Society of Chemistry.

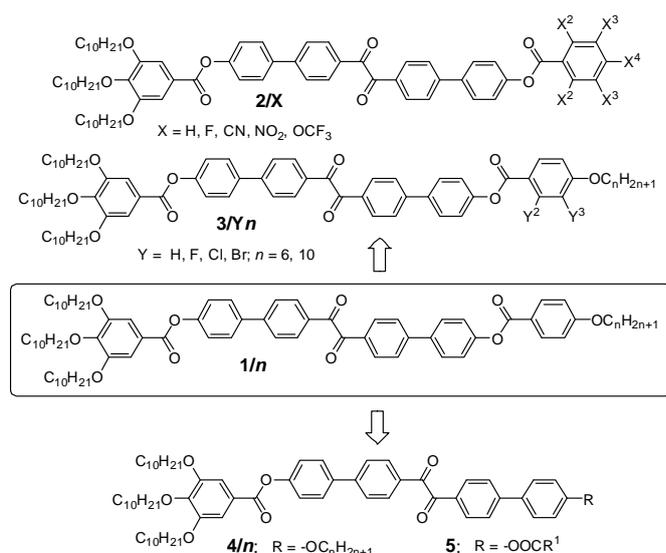
In the  $Cub_{bi}$  phases of rod-like compounds the double gyroid phase with space group  $Ia\bar{3}d$  involving two networks with three-way junctions (see Fig. 1a)<sup>[6,9]</sup> and a more complex triple network structure with larger lattice parameters and  $I23$  space group, also involving exclusively three-way junctions, were observed.<sup>[9,22,23]</sup> The networks are separated by the alkyl chains organized around the infinite minimal surfaces located in the middle between them.<sup>[28]</sup> The  $I23^{[*]}$ -type  $Cub_{bi}$  phase is exceptional, not only as it is the only presently known  $Cub_{bi}$  phase with triple network structure, it was recently also found to be inherently chiral<sup>[29-31]</sup> and the discovery of this supramolecular chirality provided an improved general understanding of the cubic phases formed by rod-like compounds.



**Scheme 1.** Structures of the BABH and ANBC based rod-like hydrogen bonded molecules and supramolecules, and an example of a polycatenar mesogens forming  $Cub_{bi}$  phases.

The most prominent are the 4'-*n*-alkyloxy-3'-nitrobenzyl-4-carboxylic acids (ANBCs)<sup>[32]</sup> and the 1,2-bis(4'-*n*-alkyloxybenzoyl)hydrazines (BABHs),<sup>[33,34]</sup> both involving hydrogen bonding and having only one alkyl chain at each end, and the so-called polycatenar compounds, having more than only two terminal chains (Scheme 1).<sup>[35-37]</sup> In the  $Cub_{bi}$  phase of these compounds the rod-like cores are organized in the networks with the long axes perpendicular to the local net direction, and the clashing of the bulky molecular peripheries leads to a helical twist along the networks (Fig. 1d) which is transmitted by the junctions to the macroscopic scale.<sup>[38,29]</sup> The  $Ia\bar{3}d$  phase with only two enantiomorphous networks with opposite handedness is macroscopically achiral (Fig. 1a),<sup>[39]</sup> whereas in the triple network phase this degeneracy is broken by the third network (Fig. 1b) and a synchronization of the helix sense between the interwoven networks leads to uniform chirality ( $I23^{[*]}$  phase, the spontaneous chirality is indicated by  $^{[*]}$ ).<sup>[40-43]</sup>

Notably, there are two distinct type of  $Ia\bar{3}d$  phases, occurring on either side of the  $I23^{[*]}$  phase, a long pitch (low twist)  $Ia\bar{3}d_{(L)}$  and a short pitch (high twist)  $Ia\bar{3}d_{(S)}$  phase, leading to the phase sequence  $Ia\bar{3}d_{(L)} - I23^{[*]} - Ia\bar{3}d_{(S)}$  with growing twist between the molecules along the networks.<sup>[44-46]</sup> In previous work we have shown that these rod-like molecules do not only form mirror symmetry broken cubic phases, mirror symmetry breaking is in some cases even observed in the adjacent isotropic liquid phases ( $Iso_1^{[*]}$ ), forming liquid conglomerates.<sup>[45,47]</sup> These  $Iso_1^{[*]}$  phases usually occur besides one of the  $Cub_{bi}$  phases and therefore they are considered as liquid network phases.<sup>[38,44]</sup>



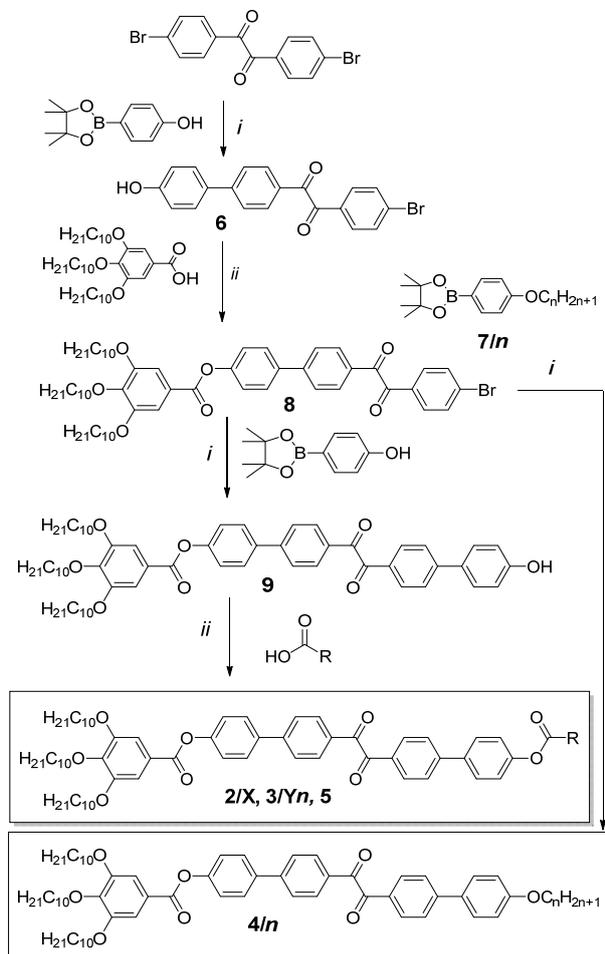
**Scheme 2.** Structures of the compounds under investigation, for details of the structures, see Tables 1-4.

The 4,4'-diphenylbenzil derived polycatenars **1/n** (Scheme 2) with a torsion of the  $O=C-C=O$  bond,<sup>[48]</sup> represent transiently chiral molecules<sup>[38]</sup> which were recently shown to even form a sequence of three mirror symmetry broken mesophases, thus transferring chirality from the isotropic liquid ( $Iso_1^{[*]}$ ) via the liquid crystalline ( $Cub_{bi}/I23^{[*]}$ ) to the crystalline state ( $Cr_{Iso}^{[*]}$ ).<sup>[44]</sup> Herein we expand this class of compounds by investigating the importance of the core length (compounds **4/n** and **5** in Scheme 2) and the effect of polar substituents in lateral position (compounds **3/Yn**) and at one end (at the apex, compounds **2/X** in Scheme 2) on the self assembly, network formation, cubic phase formation and spontaneous mirror symmetry breaking in the liquid state.

## 2. Methods

### 2.1 Synthesis

The target compounds were synthesized according to Scheme 3. Compounds **2/X**, and **5** were obtained by acylation of the phenol **9**<sup>[44]</sup> using the experimental procedures given in the Supporting Information (SI). The alkoxy compounds **4/n** were synthesized from the aryl bromide **8** by Suzuki cross-coupling with 4-alkoxyphenylboronic acid pinacol esters **7/n**.

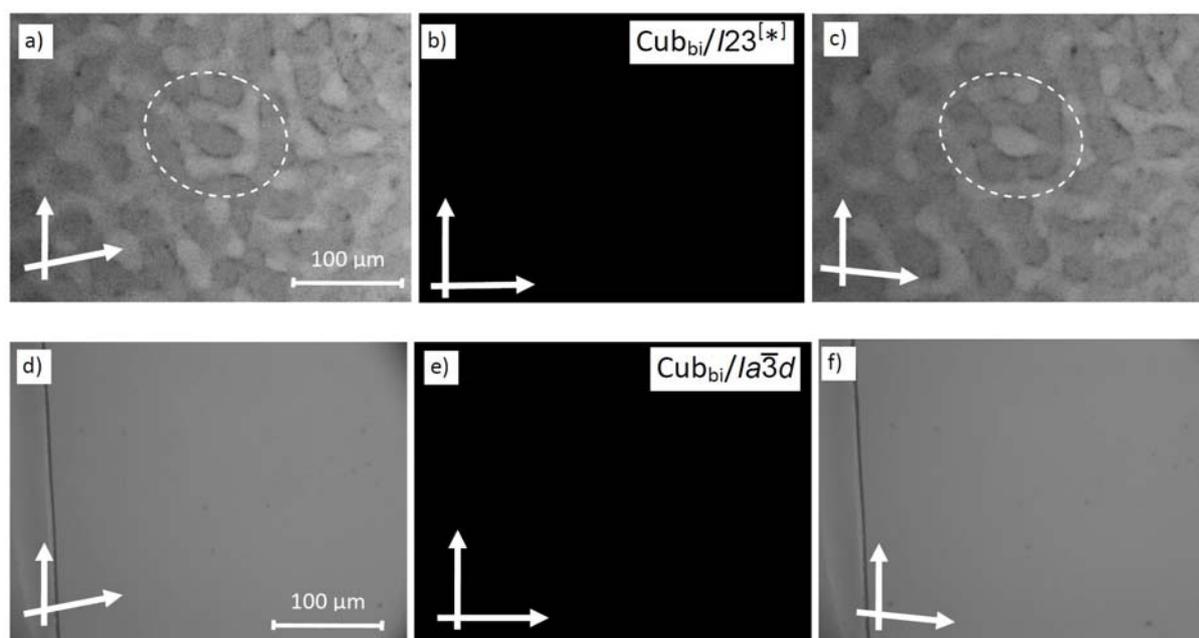


**Scheme 3.** Synthesis of the benzil based compounds **2-5**. Reagents and conditions: (i) THF, sat. NaHCO<sub>3</sub> solution, [Pd(PPh<sub>3</sub>)<sub>4</sub>], reflux; (ii) SOCl<sub>2</sub>, abs. pyridine, DCM, DMAP, 25 °C.

## 2.2 Investigations

Investigations of the compounds were performed by polarizing optical microscopy between crossed and slightly uncrossed polarizers (POM), differential scanning calorimetry (DSC) and X-ray scattering (XRD) with the instrumentation described in the SI. The transition from the isotropic liquid state to the Cub<sub>bi</sub> phases on cooling was identified by an increase of viscosity associated with a small DSC peak (Fig. S1) while the phase remains optically isotropic (Fig. 2b,e). In the X-ray diffraction (XRD) patterns of the Cub<sub>bi</sub> phases there are several small angle scatterings besides the diffuse wide angle scattering. The diffuse character of the wide angle scattering with a maximum around  $d = 0.45$  nm (Figs. S3b and S4b) confirms the LC state

having no fixed positions of the individual molecules. The small angle reflections can be indexed either to (211) and (220) of a  $Ia\bar{3}d$  lattice or to (321), (400) and (420) of the  $I23^{[*]}$  lattice (Tables S2, S3). Figures S3 and S4 show representative XRD patterns of these two cubic phase types. Additional confirmation of the cubic phase type was gained from optical investigation under a polarizing microscope between polarizers slightly rotated by a few degrees out of the exactly  $90^\circ$  twisted orientation where only the  $I23^{[*]}$  phase shows a conglomerate of chiral (dark and bright) domains which invert their brightness by changing the twist direction of the analyzer (see Fig. 2a-c) whereas the  $Ia\bar{3}d$  phase does not, and therefore is achiral (Fig. 2c-f).<sup>[29]</sup> In a similar way the achiral isotropic melted state (Iso, Iso<sub>1</sub>) is distinguished from the conglomerates formed by the mirror symmetry broken Iso<sub>1</sub><sup>[\*]</sup> phase. The non-cubic LC phases were indicated by their typical birefringent textures as observed by POM between crossed polarizers and confirmed by XRD investigation (see Section 3.3 and Table S4).



**Figure 2.** POM images as observed between crossed (middle) and slightly uncrossed polarizers (left, right) for a-c) the  $I23^{[*]}$  phase of **1/10** at  $105^\circ\text{C}$  as obtained after cooling from the Iso<sub>1</sub><sup>[\*]</sup> phase and d-f) the achiral  $Ia\bar{3}d$  phase of **3<sup>2</sup>Br6** at  $70^\circ\text{C}$  as observed on cooling from Iso<sub>1</sub>.

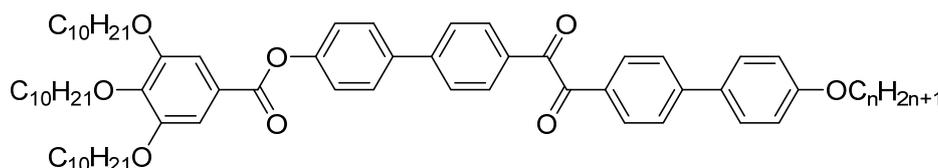
### 3. Results and Discussion

#### 3.1 The series of tetracatenar compounds $4/n$

In the series of compounds  $4/n$  with one benzoate unit shorter core than compounds  $1/n$  only the homologues with a chain length between  $n = 14$  and  $18$  form a monotropic Cub<sub>bi</sub> phase on cooling, whereas all other compounds have only crystalline phases (Table 1). Even for these three compounds, due to rapid crystallization, the phase transitions can only be recorded on

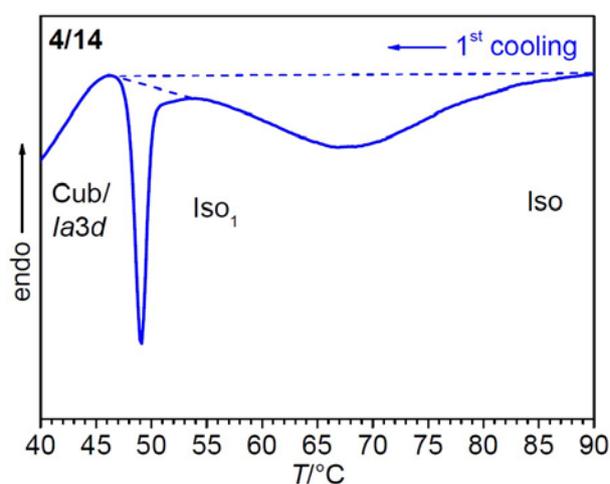
cooling and the investigations are therefore only based on DSC and optical investigations, whereas crystallization takes place during the exposure time of attempted XRD investigations. The assignment to the  $Ia\bar{3}d$  space group is therefore only based on optical investigations, indicating the absence of chiral domains in the optical isotropic mesophases with high viscosity.

**Table 1.** Melting and crystallization temperatures of the homologous series of compounds **4/n** measured on heating and cooling ( $10\text{ K min}^{-1}$ ).<sup>[a]</sup>



Compd.	<i>n</i>	Heating: $T/^\circ\text{C}$ [ $\Delta H/\text{kJ mol}^{-1}$ ]	Cooling: $T/^\circ\text{C}$ [ $\Delta H/\text{kJ mol}^{-1}$ ]
<b>4/4</b>	4	Cr 82 [48.0] Iso	Iso 45 [19.5] Cr
<b>4/6</b>	6	Cr 91 [64.2] Iso	Iso 42 [21.7] Cr
<b>4/8</b>	8	Cr 96 [51.4] Iso	Iso 63 [45.2] Cr
<b>4/10</b> <sup>[44]</sup>	10	Cr 102 [54.7] Iso	Iso 81 [53.3] Cr
<b>4/12</b>	12	Cr 80 [66.5] Iso	Iso 57 [49.4] Cr
<b>4/14</b>	14	Cr 82 [78.3] Iso	Iso 69 [6.5] Iso <sub>1</sub> 49 [1.3] Cub/ $Ia\bar{3}d$ 31 [6.0] Cr <sup>[c]</sup>
<b>4/16</b>	16	Cr 83 [75.3] Iso	Iso 70 [6.1] Iso <sub>1</sub> 55 [1.9] Cub/ $Ia\bar{3}d$ 31 [2.5] Cr <sup>[c]</sup>
<b>4/18</b>	18	Cr 84 [92.3] Iso	Iso 66 [19.9] <sup>[b]</sup> Iso <sub>1</sub> 56 [1.3] Cub/ $Ia\bar{3}d$ 37 [7.7] Cr <sup>[c]</sup>
<b>4/20</b>	20	Cr 86 [110.0] Iso	Iso 66 [83.8] Cr

<sup>[a]</sup> DSC peak temperatures on heating at  $10\text{ K min}^{-1}$ , Abbreviations: Cr = crystalline solid, Iso = achiral isotropic liquid; Cub/ $Ia\bar{3}d$  = achiral bicontinuous cubic phase; though the direct assignment of the  $Ia\bar{3}d$  type was not possible, based on the large chain length a  $Ia\bar{3}d_{(s)}$  type appears more likely; for DSCs of compounds **4/14-4/18**, see Figs. 3 and S1a-c. <sup>[b]</sup> Transition is accompanied by partial crystallization. <sup>[c]</sup> Partial crystallization.

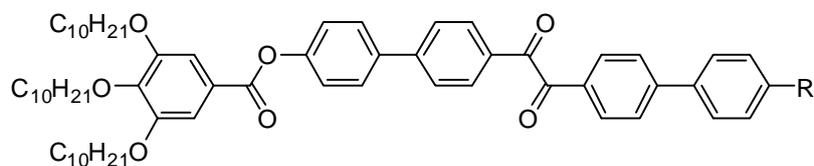


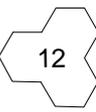
**Figure 3.** DSC of compound **4/14** showing the Iso-Iso<sub>1</sub>-Cub<sub>bi</sub>/ $Ia\bar{3}d$  transition ranges; full heating and cooling scans are shown in Fig. S1a, the DSCs of **4/16** and **4/18** are shown in Fig. S1b-c.

Only for **4/14** and **4/16** the transition from Iso to Cub/ $Ia\bar{3}d$  takes place without partial crystallization on cooling. The most interesting feature of these compound is an additional transition in the liquid before the transition to the cubic phase (Table 1, Figs. 3 and 1a-c). On cooling compound **4/14**, as example, a broad feature occurs in the DSC traces in the temperature range of the isotropic liquid phase, indicating a liquid state polyamorphism (liquid-liquid transitions, see Fig. 3).<sup>[38,44,46,49]</sup> An additional sharp peak indicates the transition to the cubic phase, associated with a sudden change from fluidity to viscoelasticity. The majority of the enthalpy of this Iso-Iso<sub>1</sub>-Cub<sub>bi</sub> transition is involved in this broad feature (6-7 kJ mol<sup>-1</sup>) which is interpreted as a growth of aggregates which fuse to a network structure and continuously increases network connectivity (Iso<sub>1</sub> phase).<sup>[49]</sup> At a certain degree of network connectivity, the long range cubic lattice composed of two interwoven gyroid networks with three way junctions is formed. This is indicated by a sharp peak with small enthalpy (1.3-1.9 kJ mol<sup>-1</sup>). There is no indication of any mirror symmetry breaking in the Iso<sub>1</sub> phase range and therefore we assume a similar  $Ia\bar{3}d$ -like network with three way junctions, but without long range order for the structure of the achiral Iso<sub>1</sub> phase. As the Iso<sub>1</sub> phase flows under gravity like any other ordinary liquid, the network must be highly dynamic and we consider it as a kind of percolated network liquid.<sup>[44]</sup> The very broad Iso-Iso<sub>1</sub> transition is interpreted as a continuous growth process fusing the cybotactic clusters to dynamic networks.<sup>[38a,44]</sup> Though this broad DSC feature was also observed for compound **4/18**, the Iso-Iso<sub>1</sub> transition is in this case accompanied by a partial crystallization, as indicated by the changed shape and larger enthalpy of this broad transition (Fig. S1c).

### 3.2 Tetracatenar compound **5/n** with an acyl chain and tricatener compounds **5** with cyclic units at the apex

Attempts to widen the cubic range of compounds **4/n** by using acyloxy chains (**5/12**) or alicyclic and polycyclic units (compounds **5/c4**, **5/c12** and **5/Ad**) instead of alkyloxy chains failed (see Table 2), though in the series of polycatenar dicarboxylates of 5,5'-diphenyl-2,2'-dithiophene (Scheme 1) a significant mesophases stabilizing effect of these cycloaliphatic units was found.<sup>[45]</sup> As shown in Table 2 all these compound are crystalline solids, some of them can be supercooled even down to room temperature without mesophases formation before the onset of crystallization. It appears that the capability of the non-symmetric 5-ring tetracatenars **4** for mesophases formation is limited to only few examples with long aliphatic chains. Therefore, the focus of the following work is on compounds **2** and **3** with a polyaromatic core involving six benzene rings.

**Table 2.** Phase transitions of compounds **5** on heating and cooling (DSC at 10 K min<sup>-1</sup>).

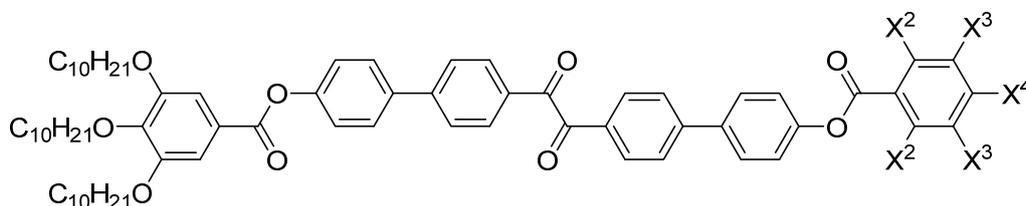
Compd.	R	$T/^\circ\text{C}$ [ $\Delta H$ kJ mol <sup>-1</sup> ]
<b>4/12</b> <sup>[b]</sup>	OC <sub>12</sub> H <sub>25</sub>	H: Cr 80 [66.5] Iso C: Iso 57 [49.4] Cr
<b>5/12</b>	OOC C <sub>12</sub> H <sub>25</sub>	H: Cr 87 [53.4] Iso C: Iso 65 [45.4] Cr
<b>5/c4</b>	OOC 	H: Cr 104 [67.0] Iso C: Iso 45 [19.8] Cr
<b>5/c12</b>	OOC 	H: Cr 106 [66.8] Iso C: Iso < 20 Cr
<b>5/Ad</b>	OOC 	H: Cr 79 [35.5] Iso C: Iso < 20 Cr

### 3.3 Tricatenar compounds with polar substituents at the apex

We expanded the structure of the tetracatenar six-ring compounds **1/n** either by introduction of halogens in lateral positions of the apex or by replacing the alkyl chain at the apex by polar electron withdrawing substituents (tricatenar compounds **2/X**). As shown in Table 3 electron withdrawing groups, especially CN and NO<sub>2</sub> lead to compounds with wide ranges of LC phases, most probably due to increasing polar core-core interactions between the electron deficit aromatics as well as by donor-acceptor interactions with the electron donor substituted trialkoxylated ends in an antiparallel packing.<sup>[45,50]</sup> **2/CN** and **2/NO<sub>2</sub>** show an enantiotropic phase sequence Iso-Iso<sub>1</sub>-SmA-Cub<sub>bi</sub> on cooling. The SmA phases were confirmed by their typical fan-like textures with extinctions parallel to the directions of analyzer and polarizer (Fig. 4a,b), and the optically isotropic appearance of their homeotropic aligned samples (see insets in Fig. 4a,b), thus confirming optically uniaxial non-tilted SmA phases. The XRD patterns show only one sharp small angle scattering with  $d = 5.5$  (**2/CN**) or  $d = 5.3$  nm (**2/NO<sub>2</sub>**, see Table S4), being a bit larger than the molecular lengths  $L_{\text{mol}} = 4.5$  and 4.6 nm, respectively, measured for the most extended conformation of space filling models (Fig. 5a).

Thus, it can be concluded that an almost fully intercalated antiparallel organization of the molecules in the layers, providing a layer distance of 5.5 nm, is present (Fig. 5b).

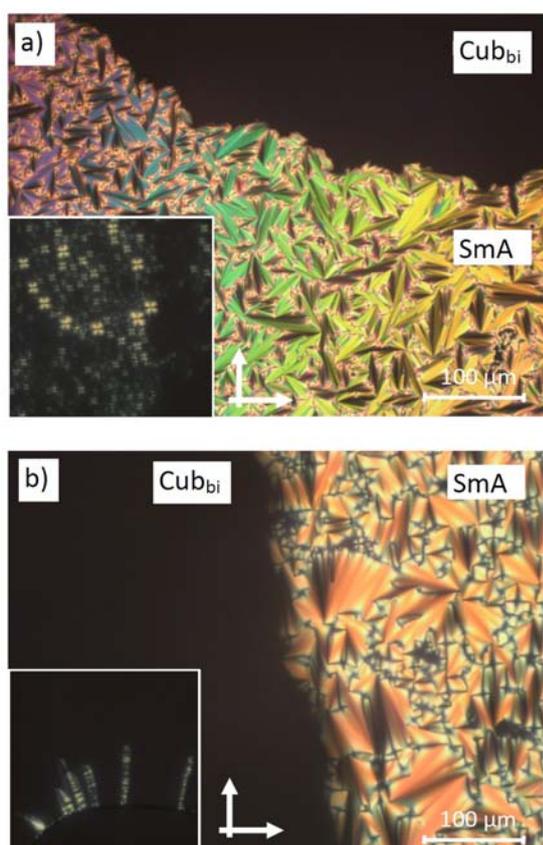
**Table 3.** Phase transitions, lattice parameters ( $a_{\text{cub}}$ ) and twist angles between the molecules in neighboring rafts ( $\Phi/^\circ$ ) in the  $\text{Cub}_{\text{bi}}$  phases of compounds **2/X**.<sup>[a]</sup>



Comp.	X <sup>4</sup>	X <sup>3</sup>	X <sup>2</sup>	T/°C [ $\Delta H$ kJ mol <sup>-1</sup> ]	$n_{\text{raft}}$	$a_{\text{cub}}$ / nm ( $\Phi/^\circ$ )
<b>1/0</b> <sup>[44]</sup>	H	H	H	H: Cr 126 [52.2] Iso; C: Iso 110 [27.3] Cr	-	-
<b>1/1</b> <sup>[44]</sup>	OMe	H	H	H: Cr 127 [36.3] Iso; C: Iso 115 [36.4] Cr	-	-
<b>1/2</b> <sup>[44]</sup>	OEt	H	H	H: Cr 120 [37.9] $Ia\bar{3}d_{(L)}$ 127 [1.8] Iso <sub>1</sub> 135 [1.9] Iso C: Iso 133 [1.3] Iso <sub>1</sub> 121 [0.2] <b>Iso<sub>1</sub></b> <sup>[*]</sup> 110 [0.3] $Ia\bar{3}d_{(L)}$ 105 [31.3] Cr	4.9	12.9 (6.9)
<b>1/14</b> <sup>[44]</sup>	OC <sub>14</sub> H <sub>29</sub>	H	H	H: Cr 108 [44.1] $Ia\bar{3}d_{(S)}$ 135 [2.9] Iso <sub>1</sub> 138 [7.0] Iso C: Iso 136 [3.1] Iso <sub>1</sub> 129 [1.2] Col <sub>hex</sub> 125 [0.4] $Ia\bar{3}d_{(S)}$ 42 [16.9] Cr <sub>Iso</sub> <20 Cr	3.2	11.3 (7.9)
<b>2/F</b>	F	H	H	H: Cr 126 [26.5] Iso; C: Iso 110 [27.3] Cr	-	-
<b>2/CN</b>	CN	H	H	H: Cr 145 [25.0] $Ia\bar{3}d_{(L)}$ 165 [1.2] SmA <sup>[b]</sup> 176 [1.0] Iso <sub>1</sub> 183 Iso C: Iso 178 [2.9] Iso <sub>1</sub> 173 [0.8] SmA 145 [0.9] $Ia\bar{3}d_{(L)}$ 124 [34.4] Cr	4.6	12.4 (7.2)
<b>2/NO<sub>2</sub></b>	NO <sub>2</sub>	H	H	H: Cr 149 [38.9] $Ia\bar{3}d_{(L)}$ 181 [2.0] SmA <sup>[c]</sup> 187 [1.7] Iso <sub>1</sub> 193 [2.5] Iso C: Iso 190 [3.0] Iso <sub>1</sub> 184 [1.5] SmA 167 [1.8] $Ia\bar{3}d_{(L)}$ 130 [41.0] Cr	4.5	12.1 (7.4)
<b>2/OCF<sub>3</sub></b>	OCF <sub>3</sub>	H	H	H: Cr 123 [24.9] $Ia\bar{3}d_{(L)}$ 135 [2.2] Iso <sub>1</sub> 143 [4.0] Iso C: Iso 141 [2.4] Iso <sub>1</sub> 126 [1.6] $Ia\bar{3}d_{(L)}$ 115 [25.3] Cr	3.8	11.3 (7.9)
<b>2/F<sub>3</sub></b>	F	<b>F</b>	H	H: Cr 123 [28.1] $Ia\bar{3}d_{(L)}$ 130 [2.9] Iso <sub>1</sub> 138 [3.4] Iso C: Iso 134 [3.4] Iso <sub>1</sub> 121 [2.2] $Ia\bar{3}d_{(L)}$ 103 [26.4] Cr	3.6	10.9 (8.2)
<b>2/F<sub>5</sub></b>	F	<b>F</b>	<b>F</b>	H: Cr 103 [39.7] $Ia\bar{3}d_{(L)}$ 112 [2.0] Iso <sub>1</sub> 123 [5.2] Iso C: Iso 118 [7.7] Iso <sub>1</sub> 100 [1.6] $Ia\bar{3}d_{(L)}$ 84 [43.1] Cr	3.5	10.8 (8.3)

<sup>[a]</sup> DSC peak temperatures on heating/cooling (H/C) at 10 K min<sup>-1</sup>;  $n_{\text{raft}}$  = number of molecules in the cross section of the networks, calculated for rafts with a height of 0.45 nm; for details of the calculations see Table S5;  $a_{\text{cub}}$  = cubic lattice parameter;  $\Phi(Ia\bar{3}d)$  = twist between adjacent molecules (rafts), calculated according to  $\Phi(Ia\bar{3}d) = 70.5^\circ/[0.354a_{\text{cub}}/0.45\text{nm}]$ ; <sup>[29a]</sup> for DSCs, see Figs. 7 and S1 and for XRD data Tables S2-S5 and Figs. S3-S4; for the Iso-Iso<sub>1</sub> transitions, representing broad features the maxima of the features are given, the complete temperature ranges are listed in Table S1; abbreviations: SmA = non-tilted lamellar (smectic A) phase;  $Ia\bar{3}d_{(L)}$  = long pitch (small  $\Phi$ )  $Ia\bar{3}d$  phase;  $Ia\bar{3}d_{(L)}$  = short pitch (large  $\Phi$ )  $Ia\bar{3}d$  phase for the other abbreviations, see Table 1; [b]  $d = 5.5$  nm; [c]  $d = 5.3$  nm.

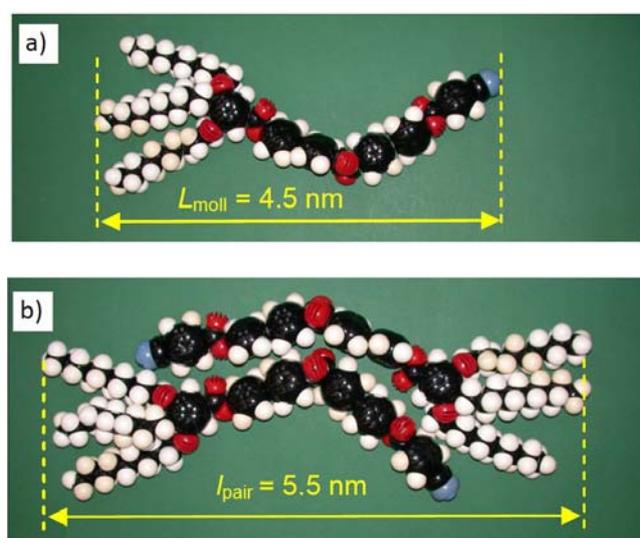
In the cubic phases two main reflections are observed which can be indexed to (211) and (220) of a  $Ia\bar{3}d$  lattice; the calculated lattice parameters  $a_{\text{cub}}$  are 12.4 nm for **2/CN** (155 °C) and 12.1 nm for **2/NO<sub>2</sub>** (160 °C, see Tables 3, S2 and S4). According to  $d_{\text{rod}} = \sqrt{3} \times a_{\text{cub}}/4$  the distance between the two networks is  $d_{\text{rod}} = 5.4$  and 5.2 nm, respectively (see Table S5). This distance corresponds to the separation of the minimal surface and is similar to the layer distances measured in the adjacent SmA phases. This is in line with a non-tilted fully intercalated organization of the polyaromatic rods in the networks (Fig. 5b). The cubic phase stability (and mesophases stability in general) of the 4-substituted compounds **2/X** grows in the order  $X = \text{F} < \text{OCF}_3 < \text{CN} < \text{NO}_2$  with rising Hammett constants of the substituents ( $\sigma_{\text{m}} + \sigma_{\text{p}}$  for  $\text{F} = 0.4$ ;  $\text{OCF}_3 = 0.7$ ;  $\text{CN} = 1.2$  and  $\text{NO}_2 = 1.5$ ).<sup>[51]</sup>



**Figure 4.** Textures of a) **2/CN** at  $T = 147$  °C and b) **2/NO<sub>2</sub>** at  $T = 167$  °C in planar aligned samples showing the growth of the  $\text{Cub}_{\text{bi}}/Ia\bar{3}d$  phase (dark area) into the fan textures of the birefringent SmA phases on cooling; the insets show the homeotropic textures of the SmA phases at 150 and 170 °C, respectively; the arrows indicate the orientation of polarizer and analyzer. The width of the images is 0.8 mm.

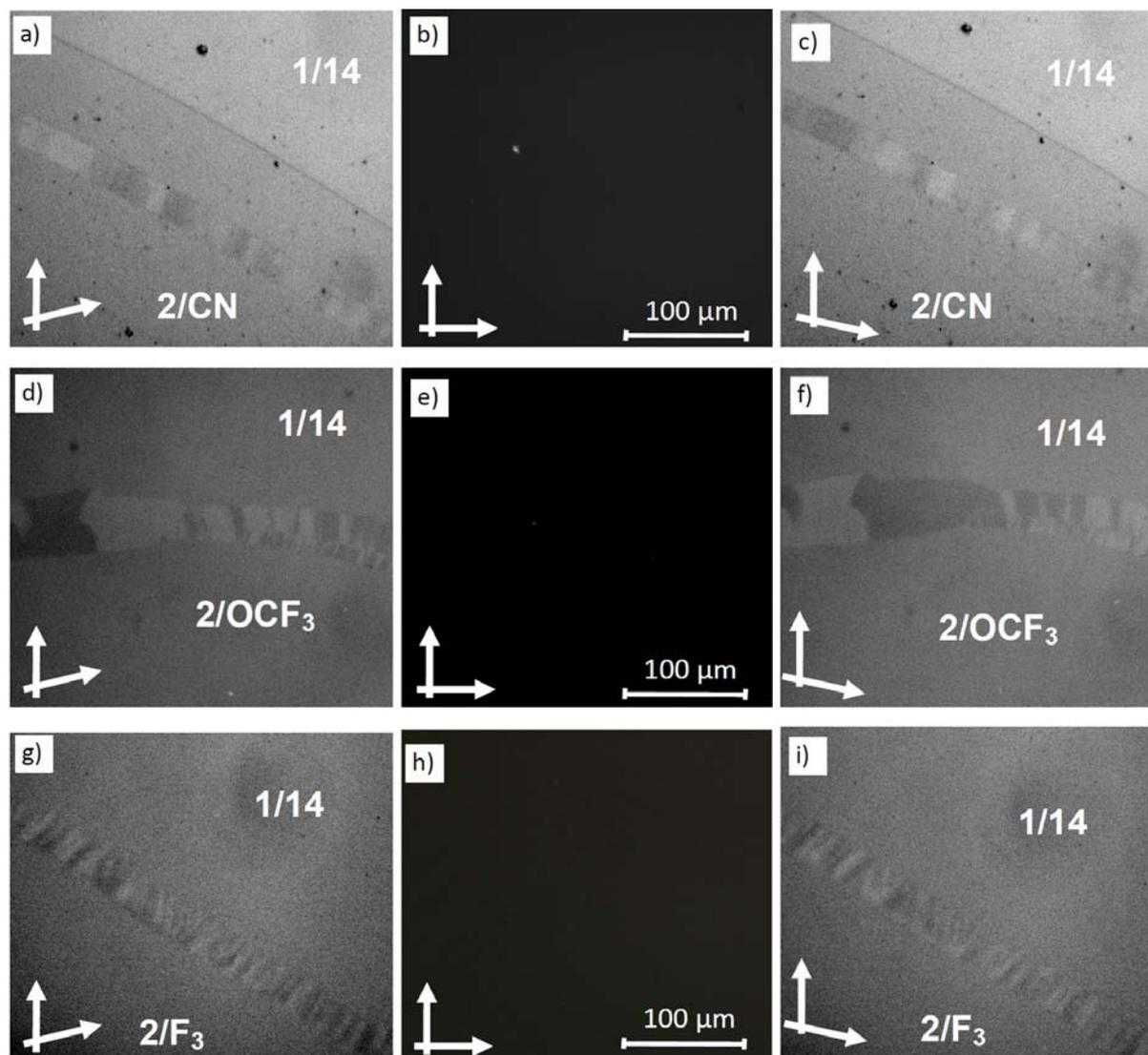
Increasing degree of fluorination at the apex has a similar effect as CN/NO<sub>2</sub> substitution. Though the monofluorinated compound **2/F** does not show any LC phase, probably due to its rapid crystallization on cooling, taking place already at 110 °C, the further increase of the number of fluorines induces cubic phases. This works for aromatic

fluorination<sup>[52]</sup> (**2/F<sub>3</sub>** and **2/F<sub>5</sub>**) as well as for the fluorination of the OCH<sub>3</sub> group (compound **2/OCF<sub>3</sub>**, see Table 3), though there is a competition with the simultaneously growing steric effect of fluorination. All compounds **2/X** with polar substituents form exclusively the achiral  $Ia\bar{3}d$  phase and no  $I23^{[*]}$  or  $Iso_1^{[*]}$  phase can be observed, whereas compounds with alkyloxy chains, acting as donor-substituents ( $\sigma_m + \sigma_p = -0.22$  for OC<sub>4</sub>H<sub>9</sub>)<sup>[51]</sup> form a sequence  $Ia\bar{3}d_{(L)}$  -  $I23^{[*]}$  -  $Ia\bar{3}d_{(S)}$  upon chain elongation.<sup>[9b,44,45,53]</sup> The number of molecules in the cross-section of the networks ( $n_{raft}$ , see Tables 3 and S5) is 3.5-3.8 for the fluorinated compounds and 4.5-4.6 for the NO<sub>2</sub> and CN substituted compounds.



**Figure 5.** a) Space filling models of compound **2/CN** and b) its antiparallel pair with fully intercalated aromatic cores.

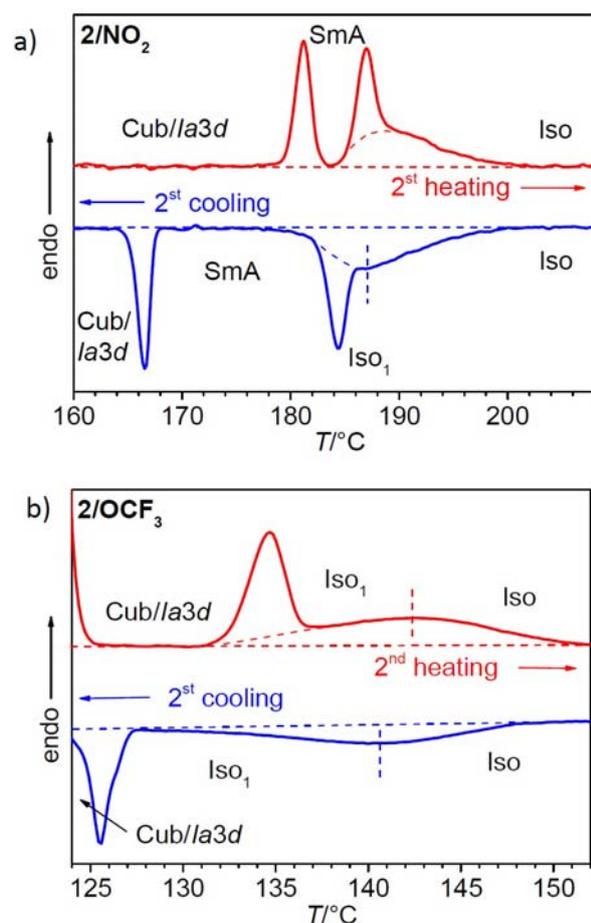
The question arises to which kind the  $Ia\bar{3}d$  phases of compounds **2/X** actually belong. The twist angles of 7.9-8.3° for the fluorinated and 7.2-7.4° for the CN/NO<sub>2</sub> substituted compounds are intermediate between the values expected for the two cases (<7° for  $Ia\bar{3}d_{(S)}$  and >9° for  $Ia\bar{3}d_{(L)}$ , respectively).<sup>[31,44,45]</sup> As previously shown, the chiral  $I23^{[*]}$  phase can be induced between different  $Ia\bar{3}d$  phase types, whereas no such phase is induced between  $Ia\bar{3}d$  phases belonging to the same type.<sup>[44,45,54-56]</sup> As shown in Fig. 6 a stripe of an  $I23^{[*]}$  phase with chiral conglomerate texture is observed in the contact region between the  $Cub_{bi}$  phase of **1/14**,<sup>[44]</sup> known to form the  $Ia\bar{3}d_{(S)}$  type, and the  $Ia\bar{3}d$  phases of the compounds **2/CN**, **2/OCF<sub>3</sub>** and **2/F<sub>3</sub>**. This means that the developing concentration gradient leads to the sequence  $Ia\bar{3}d_{(L)}$  -  $I23^{[*]}$  -  $Ia\bar{3}d_{(S)}$  with increasing concentration of compounds **2**. Therefore, the  $Ia\bar{3}d$  phases of all these polar substituted compounds **2/X** must be considered as long pitch (low twist)  $Ia\bar{3}d_{(L)}$  type phases.



**Figure 6.** Development of chiral conglomerates of the induced  $I23^{[*]}$  phase in the contact regions between the achiral  $Ia\bar{3}d$  phases of a-c) **1/14** ( $Ia\bar{3}d_{(S)}$ )<sup>44</sup> and **2/CN** at 149 °C, d-f) **1/14** and **2/OCF<sub>3</sub>** at 121 °C and g-i) **1/14** with **2/F<sub>3</sub>** at 126 °C, at the left and right between slightly rotated polarizers and in the middle between crossed polarizers. The induction of a  $I23^{[*]}$  ribbon indicates that both  $Ia\bar{3}d$  phases should have different structure, i.e. that they represent  $Ia\bar{3}d_{(L)}$  phases for compounds **2/X**. The absence of any birefringence between crossed polarizers indicates the absence of any birefringent non-cubic induced phases and the inversion of the brightness by inverting the direction of the analyzer indicates the presence of a chiral conglomerate in the  $I23^{[*]}$  ribbons; the phase boundary in a, c) corresponds to the Iso<sub>1</sub>-Cub<sub>bi</sub> transition of the **1/14+2/CN** mixture.

No mirror symmetry broken Iso<sub>1</sub><sup>[\*]</sup> phase can be found besides any of the  $Ia\bar{3}d_{(L)}$  phases of the polar substituted compounds **2/X** (Table 3), though, as shown in Fig. 7 for compounds **2/NO<sub>2</sub>** and **2/OCF<sub>3</sub>**, a broad feature occurs in the DSC traces in the temperature range of the isotropic liquid state. This indicates a transition to a percolated Iso<sub>1</sub> phase before the cubic phase is formed (see also Fig S1), independent if the  $Ia\bar{3}d_{(L)}$  phase is separated from the isotropic liquid phase by an additional SmA range (**2/NO<sub>2</sub>**, **2/CN**, Figs. 7a and S1e) or not

(**2/OCF<sub>3</sub>**, **2/F<sub>n</sub>**, Figs. 7b and S1h-j). This shape of the diffuse DSC feature is similar to that observed for compound **4/14** (Fig. 3a). In contrast, other polycatenar compounds, like the more linear 5,5'-diphenyl-2,2'-dithiophene bisbenzoates (Scheme 1), allowing a denser core packing, do not show this kind of Iso-Iso<sub>1</sub> transition.<sup>[29,45]</sup> Related Iso-Iso<sub>1</sub> transitions were previously reported in the series of the hydrogen bonded dimers of the ANBCs with hydrogen bonding within the cores, but not for the BABHs with *intermolecular* hydrogen bonding between the cores (see Scheme 1),<sup>[9b,49]</sup> thus providing stronger core-core interactions. The absence of an Iso-Iso<sub>1</sub> transition in some cases could therefore be interpreted by a network structure of the liquid phase, being present in the whole range of the isotropic liquid state. This would mean that the isotropic liquids of the strongly aggregating molecules can be considered as Iso<sub>1</sub> phases, being present in the whole investigated temperature range of the liquid state even at high temperatures, whereas for the weakly aggregating bent benzil derivatives they develop only shortly before the transition to the Cub<sub>bi</sub> phase. Overall, the broad Iso-Iso<sub>1</sub> transition appears adjacent to LC network phases if the network develops in a limited pre-transitional temperature range of the liquid phase.<sup>[37,49]</sup>

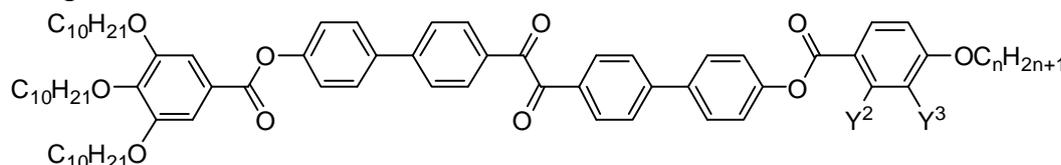


**Figure 7.** Representative DSC heating and cooling traces of compounds **2/X** showing a) the Iso-Iso<sub>1</sub>-SmA-Cub<sub>bi</sub>/*Ia* $\bar{3}d_L$  transition of **2/NO<sub>2</sub>** and b) the Iso-Iso<sub>1</sub>-Cub<sub>bi</sub>/*Ia* $\bar{3}d_L$  transition of **2/OCF<sub>3</sub>**; for full scans and the DSC traces of the other compounds, see Fig. S1d,g.

Chirality synchronization by transition to the mirror symmetry broken  $\text{Iso}_1^{[*]}$  phase, takes place after reaching a certain degree of network connectivity, which is independent if there is an observable Iso-Iso<sub>1</sub> transition (Fig. 8a,b,d) or not,<sup>[45,47]</sup> meaning that chirality synchronization in the liquid state takes place after the dynamic network with a sufficient degree of connectivity has developed. However, not in all cases of liquid network phases (Iso<sub>1</sub>) mirror symmetry breaking with formation of the  $\text{Iso}_1^{[*]}$  phase takes place (Figs. 7 and 8c,d). The reason could either be an insufficient connectivity of the network achieved in the liquid state or a tendency to develop a racemic  $Ia\bar{3}d$ -like network structure (see further below).

### 3.4 Non-symmetric tetracatenars with additional fluorine substitution at the less substituted terminal

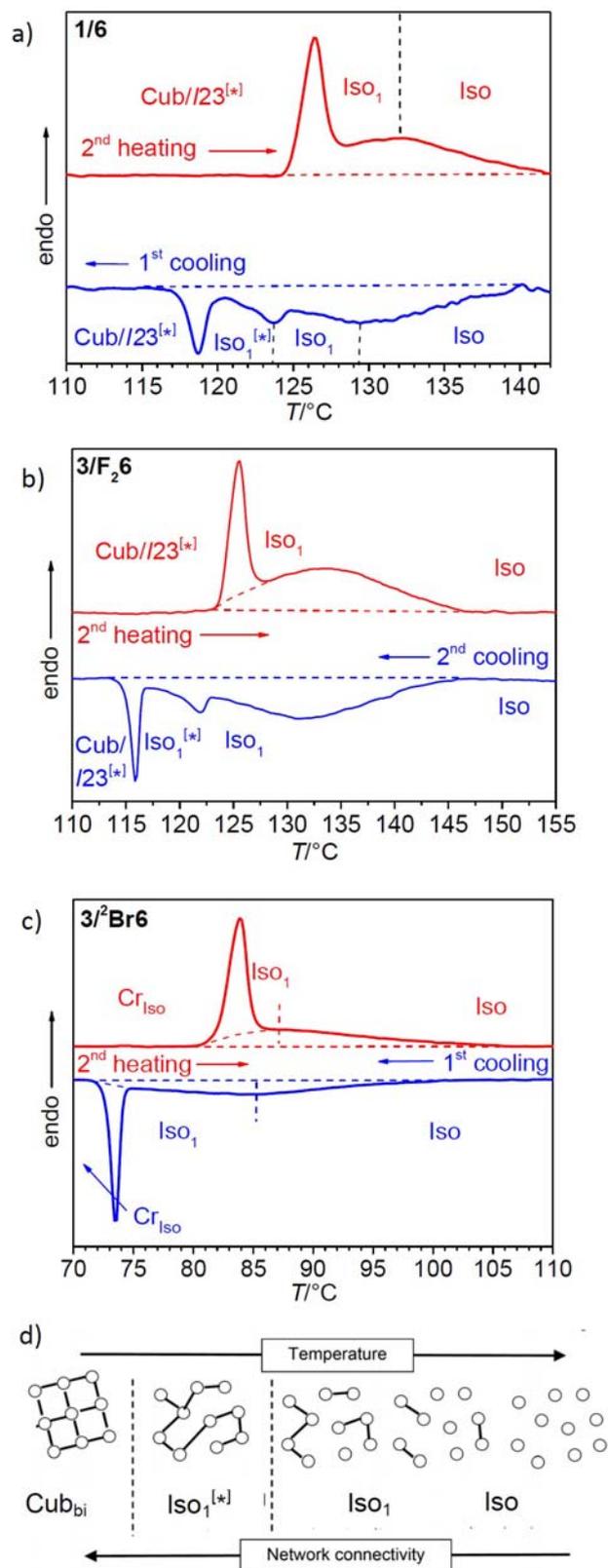
**Table 4.** Comparison of the phase transitions of compounds **3/Y<sub>n</sub>** having additional lateral halogen substituents.<sup>[a]</sup>



Comd.	<i>n</i>	Y <sup>3</sup>	Y <sup>2</sup>	<i>T</i> /°C [ $\Delta H$ kJ mol <sup>-1</sup> ] <sup>[a]</sup>	<i>a</i> <sub>cub</sub> /nm
<b>1/6</b> <sup>[44]</sup>	6	H	H	H: Cr 118 [64.6] ( $\text{Cr}_{\text{Iso}}^{[*]}$ ) 82 [17.3] <b>I23</b> <sup>[*]</sup> 126 [2.2] Iso <sub>1</sub> 134 [5.7] Iso C: Iso 130 [7.1] Iso <sub>1</sub> 123 [0.5] <b>Iso</b> <sub>1</sub> <sup>[*]</sup> 118 [1.1] <b>I23</b> <sup>[*]</sup> 61 [15.3] $\text{Cr}_{\text{Iso}}^{[*]}$	18.1
<b>3<sup>3</sup>F6</b>	6	F	H	H: Cr 93 [54.6] <b>I23</b> <sup>[*]</sup> 116 [0.4] Iso <sub>1</sub> 126 [9.5] Iso C: Iso 123 [7.4] Iso <sub>1</sub> 108 [0.2] <b>Iso</b> <sub>1</sub> <sup>[*]</sup> 103 [0.8] <b>I23</b> <sup>[*]</sup> 78 [17.0] Cr	17.1
<b>3<sup>2</sup>F6</b>	6	H	F	H: Cr 121 <sup>[b]</sup> ( $\text{Cr}_{\text{Iso}}^{[*]}$ ) 96 [24.5] <b>Iso</b> <sub>1</sub> <sup>[*]</sup> 106 [0.2] Iso <sub>1</sub> 114 [3.0] Iso C: Iso 111 [3.1] Iso <sub>1</sub> 104 [0.2] <b>Iso</b> <sub>1</sub> <sup>[*]</sup> 89 [21.5] $\text{Cr}_{\text{Iso}}^{[*]}$	
<b>3<sup>2</sup>F10</b>	10	H	F	H: Cr 103 [45.5] <b>I23</b> <sup>[*]</sup> 113 [1.5] Iso <sub>1</sub> 121 [4.3] Iso C: Iso 120 [4.1] Iso <sub>1</sub> 111 [0.3] <b>Iso</b> <sub>1</sub> <sup>[*]</sup> 101 [0.5] <b>I23</b> <sup>[*]</sup> 82 [31] Cr	18.1
<b>3/F<sub>2</sub>6</b>	6	F	F	H: Cr 93 [16.4] <b>I23</b> <sup>[*]</sup> 126 [2.1] Iso <sub>1</sub> 133 [2.4] Iso C: Iso 131 [2.1] Iso <sub>1</sub> 122 [0.3] <b>Iso</b> <sub>1</sub> <sup>[*]</sup> 117 [0.9] <b>I23</b> <sup>[*]</sup> 80 [17] Cr	17.2
<b>3<sup>2</sup>Cl6</b>	6	H	Cl	H: Cr 109 [67.2] ( $\text{Cr}_{\text{Iso}}$ ) 84 [29.0] Iso <sub>1</sub> 93 [3.0] Iso C: Iso 86 [2.1] Iso <sub>1</sub> 78 [0.2] $Ia\bar{3}d_{(s)}$ 73 [22.3] $\text{Cr}_{\text{Iso}}$	-
<b>3<sup>2</sup>Br6</b>	6	H	Br	H: Cr 77 [21.0] ( $Ia\bar{3}d_{(s)}$ ) <sup>[c]</sup> 80 <sup>[d]</sup> $\text{Cr}_{\text{Iso}}$ 84 [4.2] Iso <sub>1</sub> 90 [3.4] Iso C: Iso 85 [4.5] Iso <sub>1</sub> 73 [2.4] $\text{Cr}_{\text{Iso}}$	-

[a] DSC peak temperatures on heating/cooling (H/C) at 10 K min<sup>-1</sup>; values in brackets give monotropic phase transitions observed in the second heating scan; abbreviations: Cr = birefringent crystalline phase;  $\text{Cr}_{\text{Iso}}$  = optically isotropic crystalline solid,  $\text{Cr}_{\text{Iso}}^{[*]}$  = mirror symmetry broken  $\text{Cr}_{\text{Iso}}$  phase; for

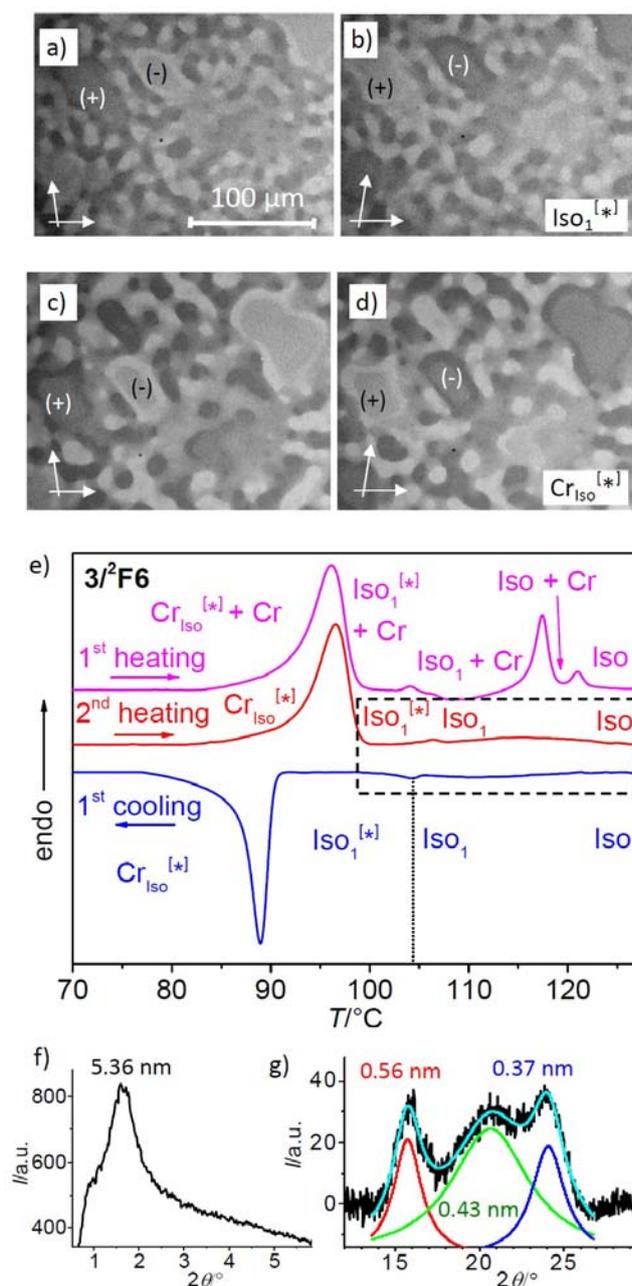
the other abbreviations, see Table 1 and 3; phases shown in bold and with [\*] indicate mirror symmetry broken phases; for DSCs, see Figs. 8, 9e and S1; the maxima of the Iso-Iso<sub>1</sub> transitions are given, the corresponding temperature ranges are shown in Table S1. [b] several crystalline modifications and crystallization processes take place in first heating, only the crystalline phase with highest melting point is given. [c] Due to crystallization no XRD could be performed. [d] The cubic phase can only be observed in the first heating as long as Cr<sub>Iso</sub> is not formed.



**Figure 8.** a-c) Representative DSC heating and cooling traces of a) compound **1/6** and b,c) the laterally core halogenated compounds **3/Y6**,<sup>[44]</sup> a,b) Iso-Iso<sub>1</sub>-Iso<sub>1</sub><sup>[\*]</sup>-Cub<sub>bi</sub>/I23<sup>[\*]</sup> transitions of compounds a) **1/6** and b) **3/F<sub>2</sub>6** and c) Iso-Iso<sub>1</sub>-Cr<sub>Iso</sub> transition of compound **3/<sup>2</sup>Br6**; for full scans and the DSC traces of **3/F<sub>2</sub>6** and **3/<sup>2</sup>Br6**, see Fig. S1o,q. d) Schematic sketch showing the transition from Iso via a cybotactic and a percolated liquid to Cub<sub>bi</sub> by increasing transient network connectivity, the dots represent locally ordered clusters and the lines indicate the connections between them, the vertical dotted lines indicate phase transitions.

Compound **1/6**<sup>[44]</sup> was shown in previous work to form a unique sequence of three mirror symmetry broken phases with conglomerate texture (Fig. 8a). At the transition from the ordinary isotropic liquid (Iso) on cooling a cybotactic Iso<sub>1</sub> phase<sup>[49]</sup> is formed around 130 °C. This is achiral and becomes chiral at the next phase transition at 123 °C which is attributed to a transition to an Iso<sub>1</sub><sup>[\*]</sup> network phase. This turns into the chiral Cub<sub>bi</sub>/I23<sup>[\*]</sup> phase at 118 °C which then on further cooling crystallizes at 61 °C with formation of an optically isotropic crystalline mesophase Cr<sub>Iso</sub><sup>[\*]</sup> composed of a chiral conglomerate (Fig. 8a and Table 4).<sup>[44]</sup> Fluorination in the peripheral 3-position at the less substituted end (compound **3/<sup>3</sup>F6**) retains the fundamental phase sequence, though the Iso<sub>1</sub><sup>[\*]</sup> phase is only observable on cooling and the isotropic Cr<sub>Iso</sub><sup>[\*]</sup> phase is replaced by a birefringent crystalline phase (Cr), see Table 4 and Fig. S1k,l.

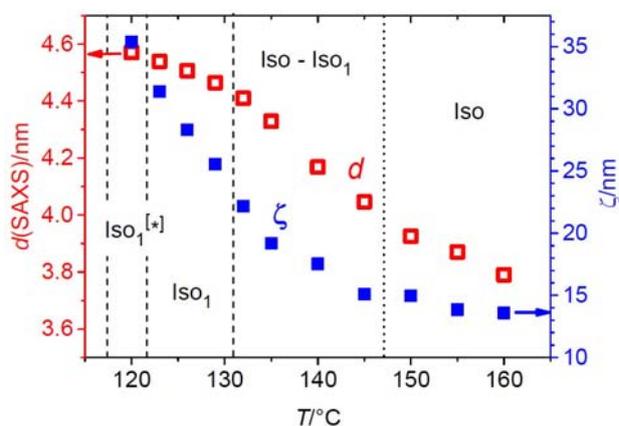
Fluorination at the inside directed 2-position (**3/<sup>2</sup>F6**) retains the mirror symmetry broken Iso<sub>1</sub><sup>[\*]</sup> and Cr<sub>Iso</sub><sup>[\*]</sup> phases, but removes the cubic I23<sup>[\*]</sup> phase of **1/6** completely, i.e. there is a direct transition Iso<sub>1</sub><sup>[\*]</sup> to Cr<sub>Iso</sub><sup>[\*]</sup> (Table 4, Figs. 9 and S1m). There is no observable change of the conglomerate texture at the transition from Iso<sub>1</sub><sup>[\*]</sup> to Cr<sub>Iso</sub><sup>[\*]</sup> (Fig. 9a-d), though it is associated with a significant transition enthalpy of 22-24 kJ mol<sup>-1</sup>.<sup>[57]</sup> As also observed for **1/6**,<sup>44</sup> the XRD pattern of the Cr<sub>Iso</sub><sup>[\*]</sup> phase of **3/<sup>2</sup>F6** is characterized by a relatively broad small angle scattering, with a maximum at  $d = 5.35$  nm, being very similar to the length of intercalated molecular pairs (Fig. 9f). The broadening of the small angle scattering indicates a distorted structure with short correlation length of ~30 nm (Scherrer equation) corresponding to about 5-6 network distances. The multiple wide angle scatterings indicate a crystalline phase (Fig. 9g) and can be attributed to the mean alkyl chain distance (0.43 nm) and the lateral edge-to-edge and face-to-face packings of the aromatics (0.56/0.37 nm), very similar to the Cr<sub>Iso</sub><sup>[\*]</sup> phase reported for **1/6**.<sup>[44]</sup> The unusually low intensity of the wide angle scatterings (see Fig. S6)<sup>[58]</sup> and the optical isotropy are in line with a strongly distorted structure with crystallized polyaromatic cores and alkyl chain segments, with the disordered segments of the chains filling the remaining space.<sup>[59,60]</sup> Additional birefringent crystalline phases with melting points at 117 and 121 °C (magenta curve in Fig. 9e) slowly crystallize from the Iso<sub>1</sub> or Iso phases, meaning that all mesophases of **3/<sup>2</sup>F6** are metastable.



**Figure 9.** Investigation of compound  $3^2F6$ . a, b) optically active domains in the  $Iso_1^{[*]}$  phase at 100 °C and c, d) in the  $Cr_{Iso}^{[*]}$  phase at 60 °C, as observed between slightly uncrossed polarizers after rotation in a), c) anticlockwise and b), d) clockwise direction (contrast enhanced). The different degrees of intermediate brightness result from overlapping with surface films having opposite chirality; the width of the pictures is 200  $\mu m$ ; e) shows the complete DSC heating and cooling traces (the section indicated by the dashed rectangle is shown in Fig. S1m); f) small angle and g) wide angle XRD pattern in the  $Cr_{Iso}^{[*]}$  phase at 25 °C (see also Fig. S5 for the complete scattering pattern).

Either chain elongation ( $3^2F10$ ) or 2,3-difluorination ( $3/F_26$ ) recovers the  $I23^{[*]}$  phase and retains the  $Iso_1^{[*]}$  phase, whereas the  $Cr_{Iso}^{[*]}$  phase is removed and replaced by a birefringent crystalline phase (Table 4). Note that the  $Cub_{bi}$ - $Iso_1$  transition temperature of the difluorinated compound  $3/F_26$  (Figs. 8c, S1o) is almost the same as that observed for the non-fluorinated

compound **1/6**, meaning that the steric mesophase destabilizing effect of 2-substitution is compensated by the additional electron attracting substituent in 3-position, strengthening the intermolecular attraction.



**Figure 10.** Temperature dependence of the  $d$ -value of the small angle scattering and the correlation length (calculated with the Scherrer equation) of the clusters in the Iso phases of compound **3/F<sub>26</sub>**, measured on cooling; for compound **3<sup>3</sup>F<sub>6</sub>**, see Fig. 8b for the DSC traces, the lift-off temperature of the broad DSC feature on cooling is around 147 °C, see Fig. S.5 for the related curve of **3<sup>3</sup>F<sub>6</sub>**.

Investigation of the development of the correlation length  $\zeta$  of the clusters in the isotropic phase range by XRD on cooling was conducted for compound **3/F<sub>26</sub>** as example. The  $\zeta = f(T)$  curve is characterized by an increase of the slope at around 145-150 °C (Fig. 10). This coincides with the onset of the broad DSC feature of the Iso-Iso<sub>1</sub> transition (Fig. 8a). The correlation length increases continuously from 13 nm to 36 nm in the Iso<sub>1</sub><sup>[\*]</sup> phase without any distinct jump at the phase transitions. This is in line with the proposed model. The increase of the  $d$ -value of the small angle scattering is also continuous, which is mainly attributed to the transition from a diffuse scattering, not following the Bragg law, to a more Bragg-like character of this scattering upon approaching the  $d$ -value in the LC phase. Similar observations were made for **3<sup>3</sup>F<sub>6</sub>**, see Fig. S5.

### 3.5 Non-symmetric tetracatenars with other halogens at the less substituted terminal

The effect of replacing fluorine by the larger halogens Cl or Br was investigated for the series **3<sup>2</sup>Y<sub>6</sub>** with the halogen in the 2-position (compounds **3<sup>2</sup>Cl<sub>6</sub>** and **3<sup>2</sup>Br<sub>6</sub>**, see Table 4). The reason for choosing this position is that changes in this position provide a stronger effect on the self-assembly. Whereas for **3<sup>3</sup>F<sub>6</sub>** the fundamental phase sequence of **3/6** is retained, the chiral  $I23^{[*]}$  phase is removed for **3<sup>2</sup>F<sub>6</sub>**. Interestingly, replacing the fluorine of **3<sup>2</sup>F<sub>6</sub>** by chlorine restores the Cub<sub>bi</sub> phase, but the space group is changed to the achiral  $Ia\bar{3}d$  phase,

which occurs adjacent to the achiral  $Iso_1$  phase without additional  $Iso_1^{[*]}$  range. Moreover, the  $Ia\bar{3}d$  phases of  $3^2Cl6$  and  $3^2Br6$  are only monotropic and appear in small temperature ranges, observable only on heating (Tab. 4).<sup>[61]</sup> Though, due to partial crystallization, these  $Cub_{bi}$  phases are not accessible to XRD experiments, they can be investigated by POM. As shown in Fig. S2d-f, in the contact region between the (previously confirmed)  $Cub_{bi}/Ia\bar{3}d_{(S)}$  phase of  $1/14$ <sup>[44]</sup> and the  $Ia\bar{3}d$  phase of compound  $3^2Br6$  no  $I23^{[*]}$  phase with chiral conglomerate texture is observed, meaning that this  $Cub_{bi}$  phase is of the same short pitch  $Ia\bar{3}d_{(S)}$  type. The increasing size of the lateral 2-substituent in the order  $H < F < Cl < Br$  obviously changes the cubic space group from  $I23^{[*]}$  to  $Ia\bar{3}d_{(S)}$ , similar to the effect of alkyl chain elongation in the series  $1/n$ . The crystalline mesophase formed upon further cooling is also optically isotropic as that formed by the fluorinated compound  $3^2F6$ , but in this case it is achiral ( $Cr_{Iso}$ ). It is likely that the network structure in this crystalline mesophase is  $Ia\bar{3}d$ -like, as in the adjacent cubic phase, which is intrinsically achiral (racemic). Also the chirality synchronization in the liquid state is affected by the size of the halogen. Whereas for the non-fluorinated compound  $1/6$  and all three investigated fluorinated compounds  $3^2F6$ ,  $3^2F6$  and  $3^2F6$  chirality synchronization takes place in the temperature range of the percolated liquid phase ( $Iso_1^{[*]}$ , see Fig. 8b,c) it is not observed for  $3^2Cl6$  and  $3^2Br6$ . A possible reason could be that the local network structure in the percolated  $Iso_1$  phase also becomes  $Ia\bar{3}d$ -like by the steric effect of these larger halogens and therefore it is intrinsically achiral.

### 3.6 Local vs. total mirror symmetry breaking

It is noted that the observed conglomerate formation represents only a local mode of mirror symmetry breaking. Total mirror symmetry breaking with stochastic outcome on a macroscopic length scale can be achieved in the  $I23^{[*]}$  phase if seed formation is slow and growth of the cubic phase is fast and it becomes deterministic in the presence of traces of external sources of chirality.<sup>[8,29,38,47a]</sup> Related effects were also observed in the mirror symmetry broken soft crystalline phases formed by mesogenic trimers.<sup>[62]</sup> Tiny chirality sources are also assumed to be responsible for “spontaneous” formation of  $I23^{[*]}$  or  $Iso_1^{[*]}$  phases with uniform chirality, as observed in some cases.<sup>[8]</sup> However, for the benzil based compounds the tendency to form large homogeneous chiral domains is less developed if compared with related 2,2'-bithiophene based polycatenars<sup>[29a,46]</sup> and formation of relatively small chiral domains is dominating in this class of compounds (see Fig. 2a-c and 9a-d). A

possible reason could be a higher viscosity or the bent molecular shape, slowing down the growth processes.

### 3.7 Discussion of the importance of network formation for chirality synchronization

Chirality synchronization of the local helical structure by network formation, suppressing helix reversal defects,<sup>[63]</sup> appears to be the key feature required for mirror symmetry breaking of polycatenar mesogens in the liquid, LC and soft crystalline states. The helical networks, developing in the Iso<sub>1</sub>/Iso<sub>1</sub><sup>[\*]</sup> and Cub<sub>bi</sub>  $Ia\bar{3}d/I23$ <sup>[\*]</sup> phases, can obviously be retained after crystallization of the aromatic cores in the optically isotropic crystalline mesophases of compounds **3**<sup>2</sup>**Yn**, where the polyaromatic cores and crystallized parts of the alkyl chains in the networks assume a crystalline packing and the disordered segments of the alkyl chains fill the remaining space. These crystalline mesophases are in some respect related to gels (“solvent free gels”),<sup>[43,59,60,62,64-66]</sup> though details of their structures require further investigations. A certain degree of net connectivity is in some cases also retained in the isotropic liquid phases, considered as percolated liquids<sup>[67,68]</sup> and representing dynamic networks, which become chiral after crossing the critical network density required for emergence of chirality synchronization.<sup>[47,38]</sup> These percolated liquids can transform into chirality synchronized cubic LC phases after assuming long range periodicity and to disordered crystalline isotropic mesophases by freezing the molecular mobility.

For numerous compounds local clusters and network formation occurs in the liquid state prior to the transition to LC and crystalline phases. Often, these transitions take place already at high temperatures outside the investigated (or accessible) temperature range, or do not show up in the DSC traces, because they take place over extremely broad temperature ranges. However the DSC features of the Iso-Iso<sub>1</sub> transition of the benzil derived polycatenars appear in relatively narrow temperature ranges close to the phase transition to the Cub<sub>bi</sub> phase and therefore become easily detectable. The degree of attractive intermolecular interactions and the strength of segregation of the incompatible units appear to be responsible for the distinct types of behaviour. Polyamorphism in the liquid state appears to be associated with network formation and therefore is observed in the vicinity of Cub<sub>bi</sub> phases. It can also be found if a lamellar or columnar phase separates the Iso<sub>1</sub> and Cub<sub>bi</sub> phase (compounds **2**/**CN** and **2**/**NO<sub>2</sub>**, Fig. 7a). It is however not observed at the transition to non-cubic LC phases which are (with respect to molecular structure or temperature) far away from any Cub<sub>bi</sub> phase range. Depending on the kind of network structure, the resulting liquid, LC or crystalline

mesophases can be optically inactive if a racemic double network ( $Ia\bar{3}d$ ) is formed, or optically active if a homochiral triple network develops ( $I23^{[*]}$ ). As the local structure can change at the phase transitions also phase sequences combining chiral and achiral phases can occasionally be observed (e.g.  $Ia\bar{3}d$ - $Iso_1^{[*]}$ ).

An important point concerns the formation of the  $I23^{[*]}$  structure instead of the usually dominating double gyroid ( $Ia\bar{3}d$ ) structure, which is only observed if rod-like units are involved in the molecules, leading to a helical twist along the networks. Therefore, it can be assumed that this transition is chirality (helicity) induced. One way of thinking considers the matching of the twist at the nodes in the individual nets (intra-network resonance).<sup>[29a]</sup> A second important issue concerns the through-space interaction between the nets, i.e. the interaction between adjacent close packed helix segments. Here a slight change of the twist angle of the molecules along the helices could modify the sign and strength of inter-helix interactions at a given angle and distance between the close packed adjacent helices.<sup>[69]</sup> Preferred heterochiral interactions are obviously compatible with the  $Ia\bar{3}d$  phase structure composed of two enantiomeric networks, leading to chiral extinction (lowest energy racemic state). However, an increasing preference of homochiral helix-helix interaction (lowest energy homochiral state) could destabilize the double gyroid structure and requires a change of the phase structure by retaining the network topology involving exclusively three way junctions. The  $I23^{[*]}$  structure appears to be the best solution for this case, though also non-cubic arrangements of helical networks, as for example in the tetragonal “SmQ phase”,<sup>[40]</sup> could have very similar energy and can compete under certain conditions.

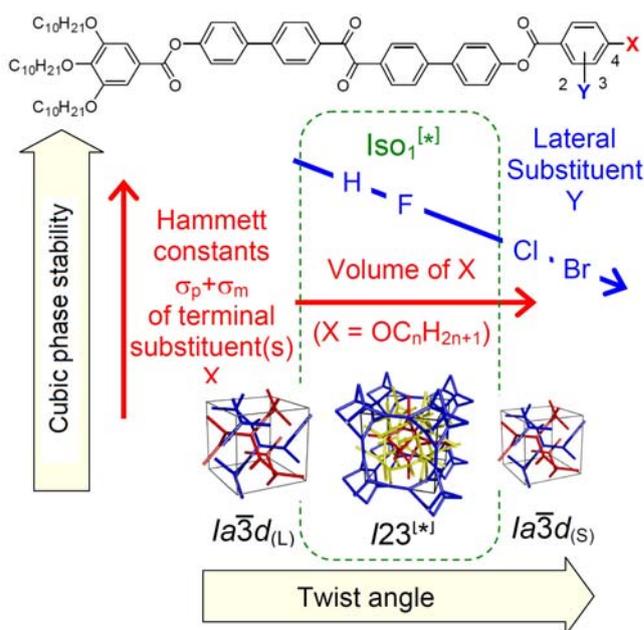
The softening of the helix-helix interactions in the liquid state could change the preferred mode of helix correlation and this could explain the transition between an achiral double gyroid cubic phase and a conglomerate type  $Iso_1^{[*]}$  liquid (with local  $I23$  structure) observed in some cases. Though there is a substantial amount of work concerning the investigation of helix-helix interactions in lipid membranes,<sup>[70]</sup> the general understanding of the helix packing depending on the sign and strength of the interaction parameters, the helical twist, and the angle between the interacting helices needs to be studied and simulated in more detail to support this hypothesis.<sup>[69]</sup>

It is noted that there is a strong relation between the  $Cub_{bi}$ - $Iso^{[*]}$  transitions reported here for achiral molecules with transiently chiral conformations and the BPII-BPIII (BP = blue phase) transition observed for permanently chiral rod-like molecules.<sup>[71,72]</sup> Whereas the cubic BPII has a  $Ia\bar{3}d$  double gyroid structure, the BPIII (blue fog phase) is an isotropic liquid

with dynamic network structure. Even the typical DSC features of this transition resemble those of the  $\text{Cub}_{\text{bi}}\text{-Iso}^{[*]}$  transitions, characterized by a broad diffuse feature in the liquid state.<sup>[49]</sup> The main difference is that in the case of the Blue Phases the networks are chirality induced, whereas for the achiral polycatenar compounds reported here the network structure induces the chirality by destabilizing the achiral/racemic state which then bifurcates into a conglomerate of chiral liquids due to the emergent cooperativity of chirality transfer provided by the network structure.<sup>[8]</sup>

## Conclusions

It is shown that the 4,4'-diphenylbenzil unit is a universal transiently chiral bent building block for the design of mesogens capable of forming network structures in the liquid, the LC and the crystalline state.  $\text{Cub}_{\text{bi}}$  network structures with  $Ia\bar{3}d$  and  $I23^{[*]}$  space groups were obtained for non-symmetric tetracatenars (compounds **1/n**, **4/n** and **3/Yn**) and tricatenars (compounds **2/X**) if the total number of benzene rings incorporated in the core unit is at least five. Polar substituents at the apex (X) were shown to support cubic phase formation, leading to compounds with high transition temperatures and wide cubic ranges. These polar substituents represent strong electron acceptors which reduce the electron density of the  $\pi$ -system of the cores and this strengthens the attractive core-core interactions, thus stabilizing the cubic phases significantly, even against unfavorable steric effects of these substituents (Table 3). The mesophase stabilizing effect grows in the order  $X = \text{F} < \text{OCF}_3 < \text{CN} < \text{NO}_2$ , roughly corresponding to the increasing Hammett constants of these substituents (Fig. 11).<sup>[51]</sup> The cubic phases of all these compounds with polar apex represent long pitch  $Ia\bar{3}d_{(\text{L})}$  phases, thus indicating a relative weak helical twist between the molecules along the networks. Larger twist angles were achieved with the longer alkoxy chains, supporting the formation of the mirror symmetry broken  $I23^{[*]}$  phase. Halogenation of the monoalkylated benzene ring further supports the helical twist, leading to a transition from  $I23^{[*]}$  to the achiral short pitch  $Ia\bar{3}d_{(\text{S})}$  phase for the larger halogens Cl and Br (Fig. 11). Especially strong is this effect in the inside directed 2-position. Besides the effect on the twist, there is also a steric mesophase destabilizing effect of the polar substituents X and Y, becoming more important in the sequence of their positions  $4 < 3 < 2$ . Thus, the steric effects of substituents become more important and override the stabilizing electronic effects, the more they are shifted towards the center of the polyaromatic core.<sup>[73,74]</sup> Figure 11 summarizes the relations between molecular structure and formation of the distinct cubic and accompanying mirror symmetry broken  $\text{Iso}_1^{[*]}$  phases gained herein.



**Figure 11.** Summary of the relations between molecular structure, cubic phase type, cubic phase stability and mirror symmetry breaking in the LC and isotropic liquid state.

Overall, this work contributes to the better understanding of the development of networks and spontaneous mirror symmetry breaking in self-assembled systems, including crystalline helical aggregates,<sup>[43,64-65,75]</sup> gels,<sup>[60,66]</sup> LC phases<sup>[38,59,60,62,76-79]</sup> and the most intriguing case of mirror-symmetry broken isotropic liquids.<sup>[47]</sup> In general, the nano-structures of the liquid phases and their polymorphism (liquid-liquid phase transitions and liquid-liquid phase separations) are still less investigated and represent almost unsolved scientific problems with great importance.<sup>[80]</sup> It appears that transitions in the liquid state with formation of cybotactic clusters or dynamic networks are important features with relevance for the understanding of the special properties of fluids, especially in the context of prebiotic and biological systems.<sup>[8]</sup> It appears that Iso-Iso transitions (polyamorphism) can be found more frequently than commonly thought. Network formation appears to be responsible for many of these transitions, as well as it is a basic prerequisite for development of complexity in any form of matter. Dynamic network formation in liquids obviously provides the basis of the emergence of new features. Among them the bifurcation of achiral and racemic systems into stable homochiral states, thus leading to the transition from achiral to chiral chemical systems, being the first step of the transition from chemical systems to biogenesis.<sup>[8]</sup>

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## TOC:

**Soft helical networks.** Achiral benzil based multi-chained molecules form a series of spontaneously mirror symmetry broken soft matter structures; the steric and electronic effects of polar substituents on helical self-assembly, local and long range network formation as well as through space interhelical interactions are discussed.

